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1

INTRODUCTION TO ORGANIC CHEMISTRY

1.1 DEFINITION OF ORGANIC CHEMISTRY (HISTORICAL BACKGROUND)

A large number of organic compounds* have been discovered and isolated from natural sources by the first quarter of nineteenth century but till then none of the organic compounds could be prepared in laboratory. This led to believe that organic compounds followed laws of formation different from inorganic compounds. **Berzelius** assumed that some **vital force** (life force) was necessary to produce organic compounds and synthesis of these compounds in the laboratory was impossible due to the absence of this vital force which only existed in living organisms.

The vital force theory suffered the first death blow, in 1828, when **Wöhler** synthesised first organic compound, urea, in the laboratory by heating ammonium cyanate (an inorganic compound).

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

Undergo isomeric change, *i.e.*, (molecular rearrangement)

$$[(NH_4)_2SO_4 + 2KCNO \xrightarrow{\text{Heat}} 2NH_4CNO + K_2SO_4]$$

$$[Pb(CNO)_2 + 2NH_4OH \xrightarrow{\text{Heat}} 2NH_4CNO + Pb(OH)_2]$$

$$[NH_4Cl + KCNO \xrightarrow{\text{Heat}} NH_4CNO + KCl]$$

A further blow to vital force theory was given by **Kolbe**, in 1845, when he synthesised acetic acid, the first organic compound, in laboratory from its elements and later by **Berthelot**, in 1856, who synthesised methane.

$$2C + H_2 \xrightarrow[\text{arc}]{\text{Electric}} \underset{\text{Acetylene}}{HC{\equiv}CH} \xrightarrow[HgSO_4]{\text{Dil. } H_2SO_4}$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{\text{Oxidation}} \underset{\text{Acetic acid}}{CH_3COOH}$$

Modern definition of organic chemistry: Since, carbon is an essential constituent of all organic compounds, organic chemistry is defined as the **chemistry of carbon compounds.**

Simplest organic compounds are those which are composed of carbon and hydrogen only and are called **hydrocarbons.** Other organic compounds may be regarded as derivatives of hydrocarbons obtained by replacement of hydrogen by any other element or group. Thus, organic chemistry may also be defined as **the chemistry of hydrocarbons and their derivatives.**

1.2 JUSTIFICATION OF SEPARATE STUDY OF ORGANIC COMPOUNDS

Organic compounds are studied separately because of the following two points:

(i) Large number of organic compounds : Compared with the compounds of other elements, the number of organic compounds is very large. Organic compounds comprise about 90% of all the known compounds.

(ii) Unique chemical and physical properties : Most of the reactions in inorganic chemistry are ionic and occur rapidly while most of the organic reactions involve covalent bonds and are relatively slow. The phenomenon of **isomerism** and tendency of **catenation** are unique properties of organic compounds.

---

*Scheele, in the years 1769–85, isolated tartaric acid from grapes, citric acid from lemons, malic acid from apples, lactic acid from milk and uric acid from urine. Roulle, in 1773, isolated urea from human urine. Liebig, in 1829, isolated hippuric acid from horse urine and Serturner, in 1805 isolated morphine from opium.

Catenation property (long chains of identical atoms) depends upon the value of bond energy which is maximum in the case of carbon.

Bond	C—C	Si—Si	S—S	P—P	N—N	O—O
Bond energy (kcal mol^{-1})	83	54	54	50	39	35

The stability or strength of the bond decreases as the bond energy decreases. Hence, the tendency of catenation decreases in the following manner:

$$C > Si \approx S > P > N > O$$

Carbon has the ability to form strong covalent bonds with many other atoms such as H, O, S, N, Cl, Br, I, etc. The C—C bond energy is approximately equal to the magnitude of bond energies between carbon and various other atoms.

Bond	C—C	C—H	C—O	C—Cl	C—N	C—Br
Bond energy (kcal mol^{-1})	83.0	97.0	86.0	81.0	73.0	68.0

1.3 SOURCES OF ORGANIC COMPOUNDS

There are two major sources of organic compounds:
(i) Natural and (ii) Synthetic.

(i) Natural Sources

(a) Plants : Carbohydrates (glucose, sucrose, starch, cellulose), acids, esters, vegetable oils, vitamins, gums, alkaloids, essential oils, perfumes, alcohol, acetone, etc., are some of the important organic compounds which are obtained from plants.

(b) Animals : Some of the important organic compounds, which are derived from animals, are proteins, hormones, fats and urea.

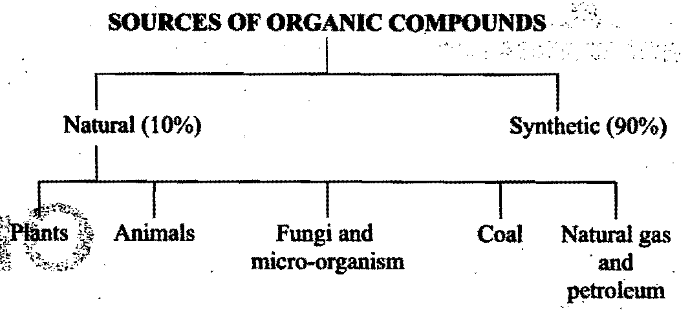
(c) Fungi and micro-organism : This is the source responsible for the production of hosts of useful substances like alcohols, acids, antibiotics (penicillin, streptomycin, tetracycline) and vitamins by using the process of fermentation.

(d) Coal : Coal-tar obtained during destructive distillation of coal is the main source of aromatic hydrocarbons, phenols, heterocyclic compounds, dyes, drugs, perfumes, etc.

(e) Natural gas and petroleum : It is one of the major sources of organic compounds. Gasoline, kerosene, lubricating oil, vaseline, paraffin wax, etc., are few examples which are obtained directly from petroleum by fractional distillation. Hundreds of useful organic compounds are prepared from the wide range of hydrocarbons which serve as starting materials for the synthetic reactions.

(ii) Synthetic Sources

More than 90% of the known organic compounds are synthetic, *i.e.*, prepared by artificial methods. Simple organic compounds derived from petroleum and coal have been converted into useful products by synthetic methods. Now-a-days, many of the natural products such as dyes, fibres, rubber, drugs, vitamins, etc., are prepared by synthetic reactions.



1.4 IMPORTANCE OF ORGANIC COMPOUNDS

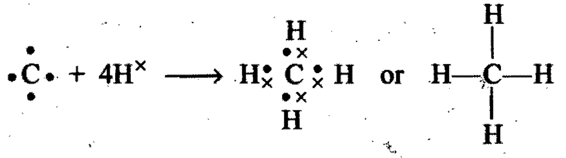
Organic compounds play an important role in our daily activities. The following list clearly illustrates the importance of organic compounds.

1. **Food :** Carbohydrates; Proteins; Fats; Vitamins; Enzymes, etc.
2. **Clothes :** Cotton; Silk; Wool; Nylon; Rayon; Dacron, etc.
3. **Fuels :** Coal; Wood; Natural gas; Petrol, etc.
4. **Medicines :** Penicillin; Streptomycin; Chloromycetin; Sulphadiazine; Sulphathiazole; Morphine; Aspirin; Iodoform; Cocaine; etc.
5. **Explosives :** Nitroglycerine; Nitrocellulose; T.N.B.; T.N.T., etc.
6. **Dyes :** Indigo; Malachite green; Alizarin, etc.
7. **Insecticides :** D.D.T; Gammexane; Malathion, etc.
8. **Household and other common articles :** Soaps; Cosmetics; Perfumes; Detergents; Paper; Rubber; Plastics; Leather; Resins; Inks; Paints; Varnishes; Photographic films; etc.

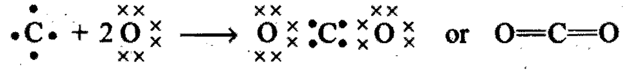
1.5 BONDING IN ORGANIC COMPOUNDS

Organic compounds are essentially covalent compounds or covalent bonding is present in organic compounds.

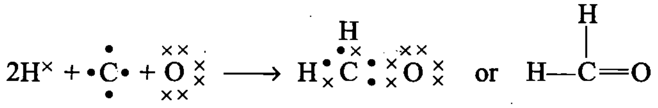
In all organic molecules, carbon atom is tetravalent, *i.e.*, its valency is four. One carbon atom can share its four electrons with four atoms of an univalent element (H), *i.e.*, forming four single covalent bonds,



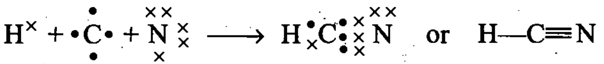
or one carbon atom can share its four electrons with two atoms of a bivalent element (O), *i.e.*, forming two double covalent bonds,



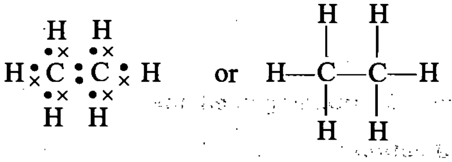
or one carbon atom can share its four electrons with one atom of a bivalent element along with two atoms of an univalent element, *i.e.*, forming one double bond and two single bonds,



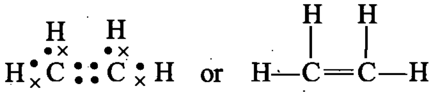
or one carbon atom can share its four electrons with one atom of a trivalent element (N) along with one atom of an univalent element, *i.e.*, forming one triple bond and one single bond,



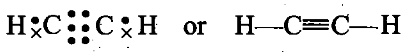
Carbon atom has also the wonderful property of uniting with other carbon atoms through covalent bonds. They can link together by single, double or triple covalent bonds forming long chains or closed structures.



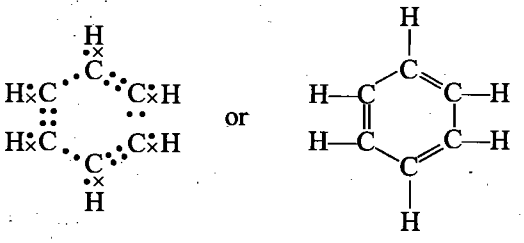
(C — C bond)



(C=C bond)



(C≡C bond)



(C—C and C=C bond)

The four valencies of carbon atom are similar and they are symmetrically arranged around the carbon atom. According to Le Bel and van't Hoff the four valencies of carbon do not lie in one plane. They are directed towards the corners of a regular tetrahedron with carbon atom at the centre and the angle between any two valencies is 109°28′ (or 109.5°).

Modern concept of covalent bonding : According to the modern concept, a covalent bond is formed between two atoms if there is an overlapping of an atomic orbital of one atom with an atomic orbital of another atom. For an effective overlap, it is necessary that two atomic orbitals of the two different atoms must be half filled and approach each other in proper direction. The resultant orbital after overlapping is known as **molecular orbital** and has two electrons with opposite spins. The effective overlapping is possible by two ways:

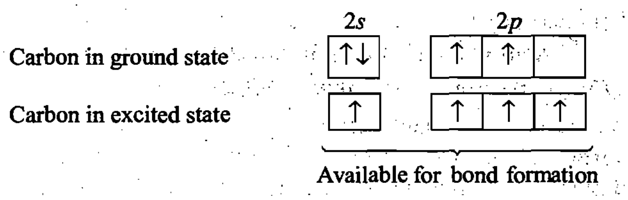
(i) End to end overlapping : This type of overlapping is possible between *s-s*, *s-p* and *p-p* atomic orbitals. The molecular orbital formed by the inphase end to end overlap of atomic orbitals on adjacent atoms is called sigma molecular orbital. Such orbitals are lower in energy than the corresponding atomic orbitals. The bond formed is termed as sigma (σ) bond.

(ii) Sidewise or parallel or lateral overlapping : Such overlapping is possible between *p-p* atomic orbitals. The molecular bond formed is termed as pi (π) bond.

Sigma bond is stronger than π-bond. The electrons in the π-bond are loosely held. The bond is easily broken and is more reactive than sigma bond. The amount of energy released during overlapping indicates the strength of the bond. Greater will be the strength of bond if higher energy is released during overlapping. Energy released during sigma bond formation is always more than π-bond because of greater extent of overlapping in the former. The valency of the atom depends on the number of σ- bonds formed or σ- and π-bonds formed.

Tetravalency of Carbon (Hybridization)

The electronic configuration of carbon in ground state is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$. Two *p*-orbitals are half filled and therefore, carbon is expected to show a valency of two. But in all organic molecules, the carbon atom has a valency of four. It is, therefore, believed that under the conditions of bond formation, the 2*s* paired orbital gets unpaired and one electron is promoted to the vacant $2p_z$-orbital. Thus, in excited state the carbon has the electronic configuration $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$, *i.e.*, it has four half filled orbitals which can be available for overlapping. Under this condition, it can form four bonds with other atoms. This explains the tetravalency of carbon.



On the basis of excited state configuration of carbon atom, it can combine with four hydrogen atoms to form a molecule, CH_4. The three C—H bonds have been formed by the overlap of three 2*p*-orbitals with the 1*s*-orbital of each hydrogen atom. The fourth C—H bond is formed by the overlap of 2*s*-orbital of carbon with 1*s*-orbital of a hydrogen atom. Thus, one bond is different from the other three. But this is not true. The methane molecule possesses the following characteristics:

(i) All the four C—H bonds are identical. This has been shown experimentally as methane forms only one monochloro methane.

$$CH_4 \xrightarrow[+Cl]{-H} CH_3Cl$$

(ii) All the four bonds are not present in the same plane. Actually, there is tetrahedral arrangement, *i.e.*, the bond angle is 109°28′ (or 109.5°).

To have four identical C—H bonds, carbon must contribute a set of four equivalent orbitals. This is possible if one 2*s* and the three 2*p*-orbitals in the excited state mix together to form four equivalent orbitals. **The process of**

mixing atomic orbitals to form a set of new equivalent orbitals is termed as hybridization.

Shapes of simple organic molecules

To explain the structures of organic molecules, the electronic theory of valency and the concept of hybridization was introduced.

There are three types of hybridization encountered in carbon atom. These are sp^3, sp^2 and *sp*-hybridization.

(i) sp^3-hybridization : sp^3-hybridization occurs when one *s*-orbital and three *p*-orbitals mix together to form four equivalent hybrid orbitals directed towards the corners of a regular tetrahedron.

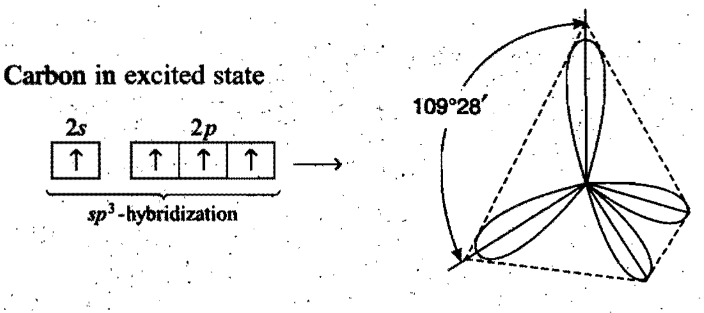


Fig. 1.1 Orientation of four sp^3-hybrid orbitals (tetrahedron)

Each sp^3-hybrid orbital contains one electron. It has 25% *s*-character and 75% *p*-character. All the four hybrid orbitals are identical (same energy and shape) but differ only in their orientation in space with respect to each other. The angle between any two hybrid orbitals is 109°28′ (or 109.5°).

Whenever carbon is bonded to four other atoms or groups, it uses sp^3-hybrid orbitals. The best examples are methane and ethane. In methane, four hybrid orbitals of carbon overlap with 1*s*-orbital of each of the four hydrogen atoms. The bonds formed are sigma bonds. The bond angles in methane are also 109°28′ (or 109.5°) as the C—H bonds are also directed towards the corners of a tetrahedron with carbon at the centre.

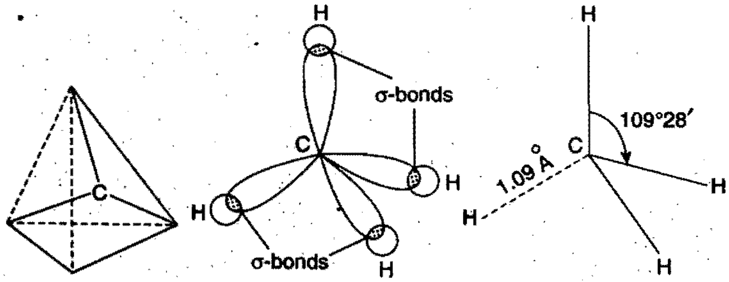


Fig. 1.2 Bonding in methane

In ethane, there are six C—H sigma bonds and one C—C sigma bond. Each C—H bond is formed by the overlap of an sp^3-hybrid orbital of carbon and 1*s*-orbital of hydrogen. The C—C bond results from the overlap of two sp^3-hybrid orbitals, one from each carbon atom. This has been shown in fig. 1.3. The bond angle is again 109°28′ as two tetrahedrons have linked together.

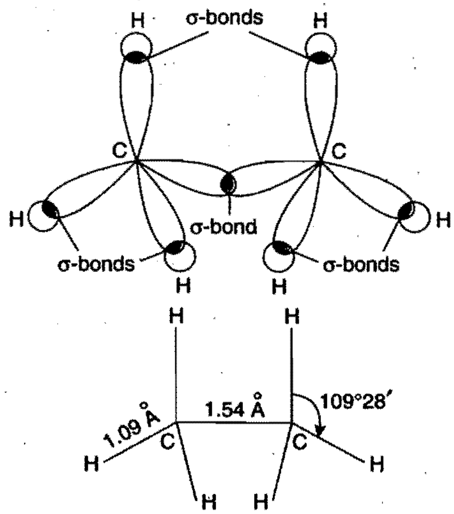


Fig. 1.3 Bonding in ethane

(ii) sp^2-hybridization : sp^2-hybridization occurs when one *s*-orbital and two *p*-orbitals mix together to form three equivalent hybrid orbitals directed towards the corners of an equilateral triangle, *i.e.*, the three hybrid orbitals lie in the same plane. The third $2p_z$-orbital is left unhybridized. This orbital is oriented along an axis perpendicular to the plane of hybrid sp^2-orbitals. Each sp^2-hybrid orbital and $2p_z$-unhybridized orbital contains one electron.

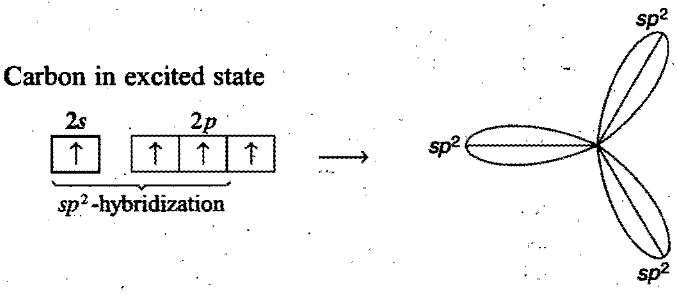


Fig. 1.4 Orientation of three sp^2-hybrid orbitals

Whenever carbon is bonded to three other atoms or groups, it always uses sp^2-hybrid orbitals and a p_z-orbital to form its bonds. The best example is ethylene molecule.

In ethylene molecule, each carbon atom is attached to three other atoms. Each carbon atom is sp^2-hybridized. One sp^2-hybrid orbital of one carbon atom overlaps coaxially with that of another carbon atom to form a sigma bond. The remaining sp^2-hybrid orbitals of two carbon atoms overlap with 1*s*-orbital of different hydrogen atoms and form four sigma bonds. The two carbon atoms and four hydrogen atoms lie in the same plane. The H—C—H bond angle is 120°. The

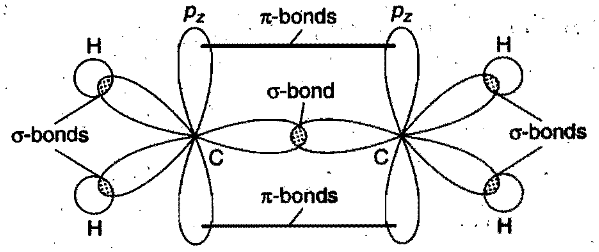


Fig. 1.5 Bonding in ethylene

unhybridized $2p_z$-orbitals of the two carbon atoms overlap laterally to form a π-bond. For the proper sidewise overlap of these $2p$-orbitals, the formation of π-bond restricts the ethylene molecule into a planar shape. Therefore, ethylene is a flat or **trigonal planar** molecule. The double bond between two carbon atoms (C═C), thus, consists of one sigma and one π-bond.

(iii) *sp*-hybridization : *sp*-hybridization occurs when one *s*-orbital and one *p*-orbital mix together to form two equivalent hybrid orbitals. The other two $2p$-orbitals are left unhybridized. Each *sp*-orbital and unhybridized *p*-orbital contain an unpaired electron. Each hybrid orbital possesses same energy and shape. Two *sp*-hybrid orbitals lie in a straight line, *i.e.*, the angle between them is 180°. The unhybridized orbitals are at right angles to the line of *sp*-hybrid orbitals.

Whenever a carbon atom is bonded to two other atoms or groups, it always uses *sp*-hybrid orbitals and two 2*p*-unhybridized orbitals to form its bonds. The best example is the acetylene molecule. One *sp*-hybrid orbital of a carbon atom overlaps coaxially with that of another carbon atom to form a sigma bond. The remaining *sp*-hybrid orbitals of two carbon atoms overlap with 1*s*-orbital of two different hydrogen atoms to form two sigma bonds. The unhybridized *p*-orbitals of two carbon atoms overlap laterally to form two π-bonds. Thus, the triple bond between two carbon atoms (C≡C) consists of one sigma and two π-bonds. Two carbon atoms and two hydrogen atoms of acetylene molecule lie in a straight line.

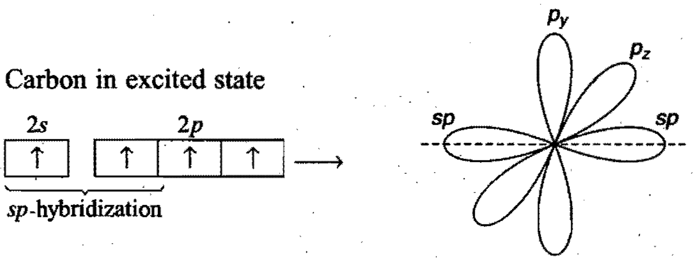


Fig. 1.6 Orientation of two *sp*-hybrid orbitals and unhybridized p_y and p_z-orbitals

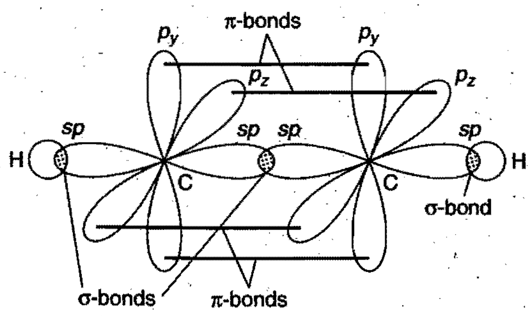


Fig. 1.7 Bonding in acetylene

The three types of hybridization of carbon can, thus, be summarised in the following manner:

Type	Geometry	Bond angle	Number of unhy-bridized *p*-orbitals	Percentage *s*-character	Percentage *p*-character
sp^3	Tetrahedral	109°28′ (109.5°)	0	25.0	75.0
sp^2	Trigonal planar	120°	1	33.3	66.6
sp	Linear	180°	2	50.0	50.0

Relative sizes of sp, sp^2 and sp^3-orbitals : *s*-orbital character in the three hybrid orbitals varies in the following manner:

$$sp > sp^2 > sp^3$$

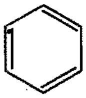
Since, *s*-orbitals are closer to the nucleus than *p*-orbitals, it is, thus, expected that **greater the *s*-character of the hybrid orbital the smaller is its size.** Therefore, the order of the size of the three hybrid orbitals is:

$$sp^3 > sp^2 > sp$$

On the basis of the sizes, *sp*-orbital forms shortest and sp^3-orbital longest bonds with other atoms.

Example 1. *Indicate the number of σ- and π-bonds in the following molecules:*

(*i*) $CH_3—CH═CH_2$ (*ii*) $CH_3—CH_2—CH_2—CH_3$

(*iii*) $CH_3—C≡C—CH_3$ (*iv*) 

Solution : For finding out the number of σ- and π-bonds in a molecule, the following points should be kept in mind:

1. All single bonds are sigma bonds.
2. All double bonds consist of one σ- and one π-bond.
3. All triple bonds consist of one σ- and two π-bonds.

(i) This molecule consists of seven single bonds and one double bond. Thus, number of σ-bonds = 8 and number of π-bond = 1.

(ii) This molecule consists of 13 single bonds.

Thus, number of σ-bonds = 13.

(iii) This molecule consists of 8 single bonds and one triple bond. Thus, number of σ-bonds = 9 and number of π-bonds = 2.

(iv) The molecule of benzene consists of nine single bonds and three double bonds.

Thus, number of σ-bonds = 12 and number of π-bonds = 3.

Example 2. *Indicate the type of hybridization of each carbon atom in the following molecules:*

(*i*) $CH_3—C≡C—CH_3$ (*ii*) $H_2C═C═CH_2$

(*iii*) $CH_3—CH═CH—CH_3$ (*iv*) $CH_3—CH_2—CH_3$

Solution : (i) $\overset{1}{C}H_3—\overset{2}{C}≡\overset{3}{C}—\overset{4}{C}H_3$

Carbon-1 is linked with four atoms = sp^3-hybridization

Carbon-2 is linked with two atoms = sp-hybridization

Carbon-3 is linked with two atoms = *sp*-hybridization
Carbon-4 is linked with four atoms = sp^3-hybridization

(ii) $\overset{1}{H_2C}=\overset{2}{C}=\overset{3}{CH_2}$ $C_1 = sp^2, C_2 = sp$ and $C_3 = sp^2$

(iii) $\overset{1}{CH_3}—\overset{2}{CH}=\overset{3}{CH}—\overset{4}{CH_3}$
$C_1 = sp^3, C_2 = sp^2, C_3 = sp^2$ and $C_4 = sp^3$

(iv) $\overset{1}{CH_3}—\overset{2}{CH_2}—\overset{3}{CH_3}$ $C_1 = sp^3, C_2 = sp^3, C_3 = sp^3$

Bond Length

The average distance between the centres of the nuclei of the two bonded atoms in a molecule is called the **bond length.** The length of a covalent bond between two given atoms depends on whether it is a sigma bond or combination of a sigma and π-bond or π-bonds, *i.e.*, it is a single, double or triple bond. It also depends on the type of hybridization and the resonance. The bond length is :

Single bond > Double bond > Triple bond

The bond length of the sigma bond in different types of hybridization follows the following order :

σ-bond (sp^3) > σ-bond (sp^2) > σ-bond (*sp*)

Bond length between two given atoms is approximately constant in different molecules depending upon the above conditions unless it is not affected by inductive effect and mesomerism. The bond length is expressed in angstrom units (Å) or picometre (pm), (1Å = 10^{-10} m, 1 pm = 10^{-12} m). The bond lengths are measured by X-ray crystallography and by microwave spectroscopy. For most of the bonds the values are 1 to 2 Å. It may be noted that the values of bond lengths are subject to small changes, depending on the structural environment of the bond and the experimental method used to measure it.

The bond lengths of some common covalent bonds are listed below:

Bond	Bond length (Å)	Bond	Bond length (Å)
C—C	1.54	C—N	1.47
C=C	1.34	C—F	1.42
C≡C	1.20	C—Cl	1.77
C—H (sp^3-*s*)	1.112	C—Br	1.91
C—H (sp^2-*s*)	1.103	C—I	2.12
C—H (*sp*-*s*)	1.08	C—S	1.82
C—O	1.40	O—H	0.96
C=O	1.20		

Bond Energies or Bond Strengths

Bond energy or bond strength is defined as **the amount of energy required to break a bond in a molecule.** Each bond has a characteristic value of this energy and is a measure of the strength of the bond. It is generally observed that shorter the bond length, greater is the bond energy, *i.e.*, greater is the strength of the bond. The carbon-carbon bonds, single, double and triple, are not of equal strength, *i.e.*, with the shortening of bond length, bond strength increases. It is in the following order:

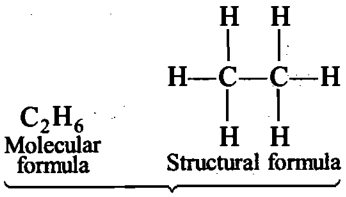
Triple bond > Double bond > Single bond

The value of a bond energy of a particular bond may slightly change in different molecules depending on structural environment of the bond. Bond energies are determined experimentally as heats of chemical reactions (calorimetry) and by spectroscopic methods. The unit of bond energy is kcal/mol. Bond energies of some common bonds are listed below:

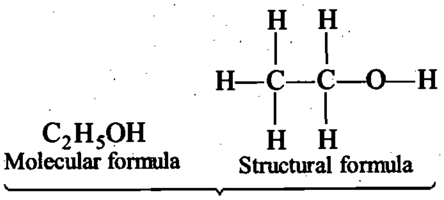
Bond	Bond energy (kcal mol^{-1})	Bond	Bond energy (kcal mol^{-1})
C—C	83	C—Cl	81
C=C	146	C—Br	68
C≡C	192	C—I	51
C—H (sp^3-*s*)	97	H—H	103
C—H (sp^2-*s*)	104	O—H	111
C—H (*sp*-*s*)	120	N—H	93
C—O	86	C—F	107
C=O	179	H—F	136
C≡O	256	H—Cl	103
O—O	35	H—Br	88
O=O	119	H—I	71
N—N	39	F—F	38
N=N	98	Cl—Cl	58
N≡N	226	Br—Br	46
C—N	73	I—I	36

1.6 REPRESENTATION OF ORGANIC MOLECULES

An organic compound can be represented either by molecular formula or structural formula. The structural formula is more informative as it shows the arrangement of various atoms in a molecule. A single covalent bond is shown as a line (—) joining the two atoms. Double line (=) represents a double bond while triple line (≡) a triple bond. Organic molecules possess a three dimensional structure but these are represented in the plane of paper (two-dimensional) and the bond angles between valencies of carbon are shown at right angles in open chain compounds for the sake of convenience. The structural formula written on paper simply indicates the order in which **the various atoms are found and does not give any idea of their disposition in space.** For example, ethane and ethyl alcohol may be written as:

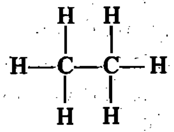
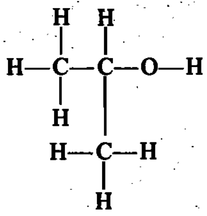
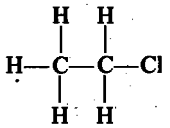
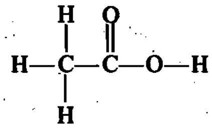
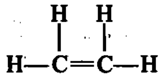
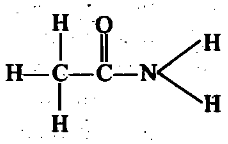
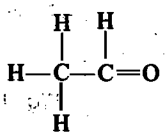
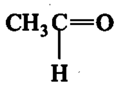
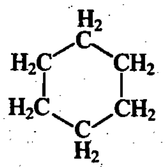
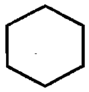
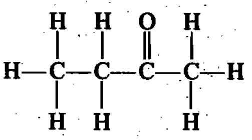
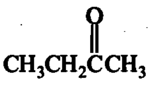
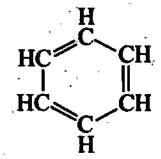


Ethane



Ethyl alcohol

Condensed formula is a short hand method of representing the structural formula. In a condensed formula, all atoms bonded to a carbon atom are written after 'C' in the same line but their bonds are not shown. The atoms or groups other than hydrogen are written after the hydrogen atom. In a condensed structural formula double and triple bonds are shown by double line (=) and triple line (≡) respectively. Some examples are given in the following table:

Compound	Molecular formula	Structural formula	Condensed formula	Compound	Molecular formula	Structural formula	Condensed formula
Ethane	C_2H_6		CH_3CH_3	Isopropyl alcohol	C_3H_8O		$(CH_3)_2CHOH$
Ethyl chloride	C_2H_5Cl		CH_3CH_2Cl	Acetic acid	$C_2H_4O_2$		 $CH_3\overset{O}{\overset{\Vert}{C}}OH$
Ethylene	C_2H_4		$H_2C{=}CH_2$	Acetamide	C_2H_5NO		 $CH_3\overset{O}{\overset{\Vert}{C}}NH_2$
Acetaldehyde	C_2H_4O		 $CH_3\underset{H}{\underset{\vert}{C}}{=}O$	Cyclohexane	C_6H_{12}		
Ethyl methyl ketone	C_4H_8O		 $CH_3CH_2\overset{O}{\overset{\Vert}{C}}CH_3$	Benzene	C_6H_6		

1.7 POLAR AND NON-POLAR BONDS

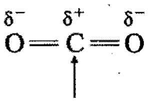
The nature of the covalent bond can be predicted on the basis of the values of electronegativities of the two atoms forming the bond. Electronegativity of an atom is a **measure of its power to attract electrons that it is sharing in a covalent bond.** The decreasing order of electronegativity of some common atoms which are generally encountered in organic chemistry is:

$$F > O > Cl = N > Br > C > H$$

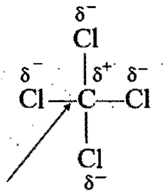
When two identical atoms are joined by a sigma bond, both attract the σ-electrons equally. For example in C—C, H—H and F—F, the electrons involved in the sigma bond are shared equally, *i.e.*, electron density in the molecular orbital binding the two atoms together is same around each atom. There is no development of charge on any of the two atoms. Such a bond is known as **nonpolar bond.**

When two atoms of different electronegativities are bonded by a sigma bond, the electrons involved are not shared equally. The more electronegative atom attracts the bonded electrons more closely than the less electronegative atom, *i.e.*, the electron density in the molecular orbital will be more around the atom with higher electronegativity. As a result the more electronegative atom will acquire a small negative charge, symbolised by δ^- and less electronegative atom a small positive charge, symbolised by δ^+. Such a bond which appears to have a positive and a negative end, is said to be a **polar bond.** The bonds such as C—Cl, C—Br, C—N, C—O, etc., are polar in nature.

The polarity of bonds can lead to polarity of molecules and affect melting point, boiling point and solubility. A molecule is said to be polar if it contains one or more polar bonds and the polar bonds are so directed that there are separate centres of positive and negative charges in the molecule. **A symmetrical molecule is nonpolar even though it contains polar bonds.** For example, molecules like carbon dioxide and carbon tetrachloride possess polar bonds but these are nonpolar molecules as they have symmetrical structures, *i.e.*, the centre of the positive and negative charges is the same in the molecule.



Centre of the positive and negative charge.



Centre of the positive and negative charge

The molecules such as H—F, H_2O, NH_3, CH_3Cl, $CHCl_3$, etc., are polar molecules. Polar molecules behave as small dipoles and possess a dipole moment. The dipole moment (μ) of a bond X—Y is the product of the magnitude of the charges and the distance between the charges. It is roughly equal to the difference in the electronegativities of X and Y in debye.

$$\mu = e \times d$$

Where, μ = dipole moment (in debye unit)

e = magnitude of separated charges (in esu)

d = distance between the centre of charges (in cm)

The dipole moment of an individual bond cannot be measured in polyatomic molecules but it is possible to measure the total moment of the molecule which is a vectorial sum of the individual bond moments. Dipole moment of a molecule does not depend only on the polarity of the bond but also depends on the directions of the bond, *i.e.*, the shape of the molecule.

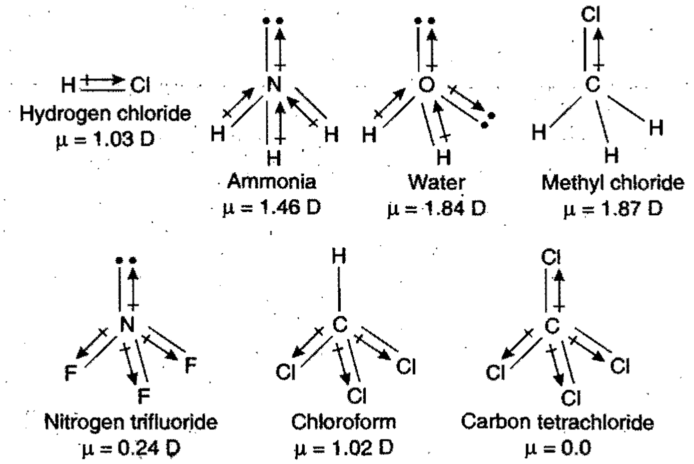


Fig. 1.8

(i) Dipole moment of symmetrical compound is always zero ($\mu = 0$).

For example $H_2, O_2, N_2, Cl_2, Br_2, CH_4, CCl_4, BH_3, BF_3, CO_2, CS_2, H_2C{=}CH_2$ and $HC{\equiv}CH$, etc.

(ii) Dipole moment of unsymmetrical compound is always greater than zero.

For example $H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}$, $H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{S}}$, HCl, $CHCl_3$, CH_3Cl, NH_3 and HF, etc.

(iii) Dipole moment increases with increase of electronegativity. Thus, the dipole moment of

$$HF > HCl > HBr > HI \text{ and}$$
$$CHF_3 > CHCl_3 > CHBr_3 > CHI_3$$

(iv) Dipole moment of *cis* is greater than *trans* in geometrical isomers and dipole moment of *trans* derivative of the compound C (a) (b) = C (a) (b) will only be zero if both (a) and (b) will be in the form of atom (or groups having linear moment). For example

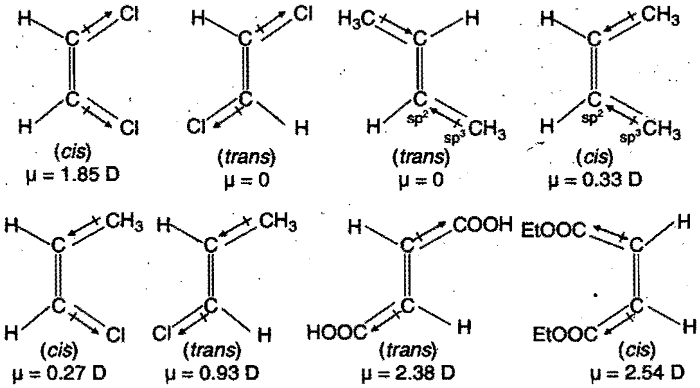


Fig. 1.9

(v) Dipole moment of disubstituted benzene

(a) When both groups X and Y are electron donating or both groups are electron withdrawing then

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

where, μ_1 = dipole moment of bond C—X

μ_2 = dipole moment of bond C—Y

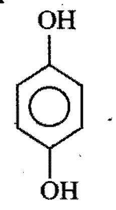
θ = angle between X and Y

dipole moment of *ortho*-di > *meta*-di > *para*-di ($\mu = 0$)

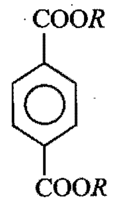
For example, Dimethyl benzenes: *o*- > *m*- > *p*- ($\mu = 0$)

Dichloro benzenes: *o*- > *m*- > *p*- ($\mu = 0$)

Some exceptions are:



($\mu \neq 0$, but $\mu = 0.83$ D)



($\mu \neq 0$, but $\mu = 0.27$ D)

(b) When one group is electron withdrawing and the other group is electron donating then

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 - 2\mu_1\mu_2 \cos\theta}$$

Hence, dipole moment is as follows:

p-disubstituted > *m*-disubstituted > *o*-disubstituted

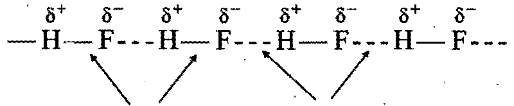
For example, chlorotoluenes: *p*- > *m*- > *o*-

1.8 HYDROGEN BONDING IN ORGANIC COMPOUNDS

In 1920 **Latimer and Rodebush** introduced the idea of **"hydrogen bond"** to explain the nature of association in liquid state of substances like water, hydrogen fluoride, ammonia and formic acid, etc. In a hydrogen compound, when a hydrogen atom lies between two atoms having high electronegativities, it shows a unique property of forming a bond or a bridge between them, holding one of the atoms by a covalent bond and other by purely electrostatic forces (dipole-dipole attraction). This chemical combination between highly electronegative atoms of small atomic radius, such as F, O and N through a hydrogen bond is referred to as **Hydrogen bond** or **Hydrogen bridge.**

For example, hydrogen fluoride has a great tendency to polymerise at temperature below 90°C, hence it occurs as H_2F_2 molecule. In H—F, the hydrogen is attached to a strongly electronegative element, fluorine. As a result, the fluorine acquires a partial negative charge and hydrogen acquires a partial positive charge $[H^{\delta+} — F^{\delta-}]$.

The positive charge on hydrogen in a molecule of hydrogen fluoride will be attracted electrostatically by a negative charge on the fluorine atom in another molecule of hydrogen fluoride. This electrostatic attraction (dipole-dipole attraction) between different molecules of hydrogen fluoride continues resulting in the formation of large molecular aggregate.



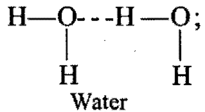
(Covalent bond) (Hydrogen bond)

So, the linkage between hydrogen and the other fluorine is simply due to electrostatic forces of attraction, which results a weak bond, commonly known as **Hydrogen bond** and represented by dotted lines (- - -).

Thus, hydrogen bond is defined as **"an electrostatic attractive force between the covalent bonded hydrogen atom of one molecule and an electronegative atom (such as F, O, N) of the other molecule"**. The resultant bond (hydrogen bond) is weaker (strength about 2–10 kcal/mol or 8.4–42 kJ/mol) as compare to a covalent bond (strength about 50–100 kcal/mol or 209–418.4 kJ/mol). Liquids in which molecules are held together by hydrogen bonds are said to be **associated.** Such liquids have high boiling points due to the greater energy required to break the hydrogen bonds present in them. Examples of H-bonding in between the two molecules of same compounds are:

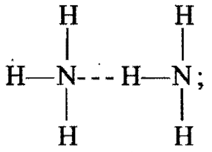
H—F---H—F;

Hydrogen fluoride
(associated)



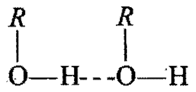
$$\mathrm{H{-}\underset{\underset{H}{|}}{O}\cdots H{-}\underset{\underset{H}{|}}{O}};$$

Water
(associated)



$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}\cdots H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}};$$

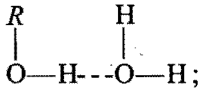
Ammonia
(associated)



$$\overset{\overset{R}{|}}{\mathrm{O}}\mathrm{{-}H\cdots}\overset{\overset{R}{|}}{\mathrm{O}}\mathrm{{-}H}$$

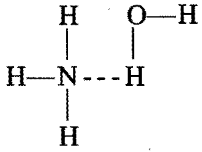
Alcohol
(associated)

Examples of H-bonding in between the two moles of different compounds are:



$$\overset{\overset{R}{|}}{\mathrm{O}}\mathrm{{-}H\cdots}\overset{\overset{H}{|}}{\mathrm{O}}\mathrm{{-}H};$$

Alcohol and water



$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}\cdots \overset{\overset{O-H}{|}}{H}}$$

Ammonia and water

Conditions for Hydrogen Bonding

(i) Hydrogen atom should be linked to a highly electronegative atoms such as F, O or N.

(ii) The size of electronegative atom should be small.

Further larger the electronegativity and smaller the size of the atom (F, O, N), the strongest is the hydrogen bond which is evident from the relative order of energies of hydrogen bonds in the three elements. For example, electronegativities decrease as F > O > N. Consequently, strength of hydrogen bond decreases as:

H—F---H	>	H—O---H	>	H—N---H
10 kcal/mol		7 kcal/mol		2 kcal/mol

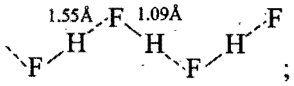
Although Cl has the same electronegativity as nitrogen but no hydrogen bonds are formed in case of H—Cl because of the larger size of Cl atom. Similarly, sulphur forms a very weak hydrogen bond due to its low electronegativity, although oxygen present in the same group forms a strong hydrogen bond.

Types of Hydrogen Bonding

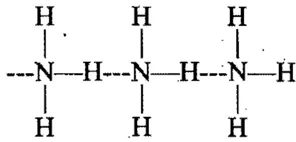
Generally speaking, the hydrogen bonds can be classified into two categories:

1. Intermolecular hydrogen bonding : This type of bonding is between two or more same or different molecules when combine together to form a dimer or polymer respectively and leads to a phenomenon called **association.**

Examples are:

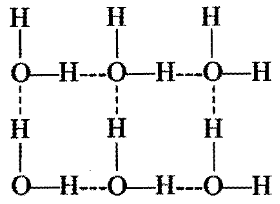


Hydrofluoric acid

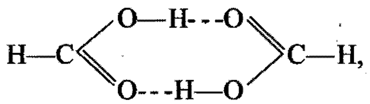


$$\mathrm{\cdots\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}{-}H\cdots\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}{-}H\cdots\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}{-}H\cdots}$$

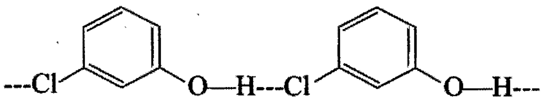
Ammonia molecule



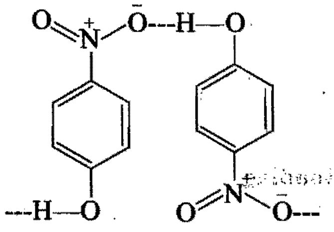
Water molecule



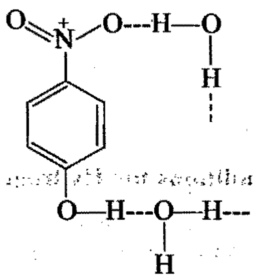
Formic acid (Dimer)



m-Chlorophenol



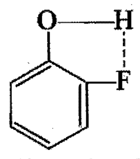
p-Nitrophenol



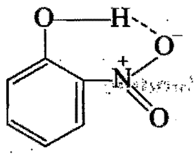
p-Nitrophenol and water

This type of hydrogen bonding increases the boiling point of the compound and also its solubility in water. The increase in boiling point is due to association of several molecules of the compound.

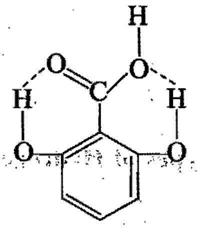
2. Intramolecular hydrogen bonding : This type of bonding occurs within two atoms of the same molecule and leads to a phenomenon called **chelation.** This type of hydrogen bonding frequently occurs in organic compounds and results in the cyclisation (six or five membered ring) of the molecule. Examples are:



o-Fluorophenol



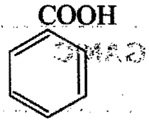
o-Nitrophenol

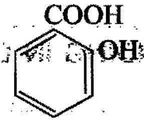


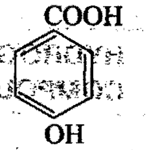
2,6-Dihydroxy benzoic acid

This type of hydrogen bonding decreases the boiling point of the compound and also its solubility in water. The chelation between the *ortho* substituted groups restricts the possibility of intermolecular hydrogen bonding and thus prevents association of the molecules which would have raised the melting point or boiling point. In *m*- and *p*-isomers chelation does not take place because the two groups (atoms) are far away from each other and hence in such cases intermolecular hydrogen bonding occurs. Thus, we can explain the low melting and boiling points of the *ortho* isomers of hydroxy, nitro, carbonyl compounds than their corresponding *m*- and *p*-isomers.

Intramolecular hydrogen bonds are also considered to influence the acidity of certain acids. Thus, *o*-hydroxy benzoic acid is about 18 times more acidic than benzoic acid, whereas *p*-hydroxy benzoic acid is half as acidic as benzoic acid, *i.e.,*







	Benzoic acid	Salicylic acid	*p*-hydroxy benzoic acid
K_a	6.2×10^{-5}	105×10^{-5}	2.9×10^{-5}

The large acidity is due to the intramolecular hydrogen bonding which is capable of stabilizing the salicylate ion.

Thus, intramolecular H-bonding is weaker than intermolecular H-bonding.

Nature and Importance of Hydrogen Bonding

(i) Hydrogen bond is merely an electrostatic force rather than a chemical bond.

(ii) Hydrogen bond never involves more than two atoms.

(iii) Bond energy of hydrogen bond is in the range of 3 to 10 kcal/mol or 10 to 40 kJ/mol, *i.e.*, about 1/10th the energy of a covalent bond.

(iv) With the increase of electronegativity of the atom to which hydrogen is covalently linked, the strength of the hydrogen bond increases.

(v) All the three atoms in X—H- - -X lie in a straight line.

Effects of Hydrogen Bonding on Physical Properties

Almost all physico-chemical properties (such as boiling and melting points, solubility, spectra, acidic strength and basic strength of amines, etc.) are affected by hydrogen bonding. Some of them are discussed below.

(a) Boiling point and melting point : The boiling point of a liquid is the temperature where its kinetic energy is sufficient to overcome the intermolecular attractive forces. Thus, heavier the molecule and stronger the intermolecular forces, higher will be the boiling point of the compound and so the boiling and melting points generally increase with increase in number of carbon atoms in most of the homologues series. Examples are:

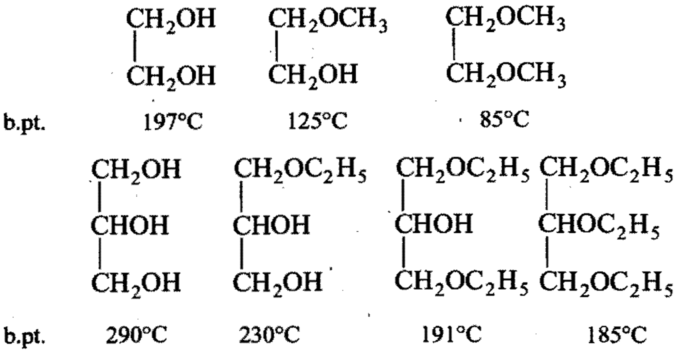
(i) **Water :** The boiling point of covalent compounds increases with increase in molecular weight and thus H_2O (mol. wt. = 18) should have low boiling point than H_2S (mol. wt. = 34). But H_2O is liquid (high boiling point) and H_2S is gas. Because in water molecule, hydrogen bonding is present and so become more compact and requires more energy to get them separated during evaporation, while sulphur is less electronegative nature than oxygen and give S—H bond, a smaller ionic character than the O—H bond and thus H_2S forms very weak hydrogen bond. Hence, it is the H-bonding which leads for the facts that:

(ii) Boiling point of HF (liquid) is greater than boiling point of HCl (gas).

(iii) NH_3 has high boiling point than PH_3.

(iv) **Alcohols :** (R—OH) have high boiling point than those of corresponding thioalcohols (R—SH, mercaptans) and ethers (R—O—R). But the b.pt. of water (100°C) is higher than ethyl alcohol (78°C) because greater number of water molecules are associated (through H-bonding) than the ethyl alcohol.

(v) Polyhydric alcohols have higher boiling points than their ethers, inspite of increase in the molecular masses of ethers. For example:



$$\begin{array}{cccc} & CH_2OH & CH_2OCH_3 & CH_2OCH_3 \\ & | & | & | \\ & CH_2OH & CH_2OH & CH_2OCH_3 \\ \text{b.pt.} & 197°C & 125°C & 85°C \end{array}$$

$$\begin{array}{ccccc} & CH_2OH & CH_2OC_2H_5 & CH_2OC_2H_5 & CH_2OC_2H_5 \\ & | & | & | & | \\ & CHOH & CHOH & CHOH & CHOC_2H_5 \\ & | & | & | & | \\ & CH_2OH & CH_2OH & CH_2OC_2H_5 & CH_2OC_2H_5 \\ \text{b.pt.} & 290°C & 230°C & 191°C & 185°C \end{array}$$

Glycerol ($CH_2OH — CHOH — CH_2OH$) having three —OH groups per molecule (b.pt. 290°C) can form more hydrogen bonds per molecule than that of water. So, glycerol is more viscous than alcohol because of more binding sites available for H-bonding.

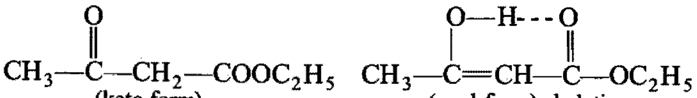
(vi) Boiling points of aldehydes and ketones are lower than alcohols.

(vii) **Amines :** The boiling points of primary (R—NH_2) and secondary amines (R_2NH) are higher than the isomeric tertiary amines (R_3N) because like water and alcohols, the primary and secondary amines are capable of forming intermolecular hydrogen bonding but tertiary amine does not.

Hence, in general the boiling point is increased due to intermolecular hydrogen bonding but there are certain cases where the boiling point is decreased due to intramolecular hydrogen bonding. For example, the *ortho* isomers of hydroxy -nitro, -carbonyl, -carboxylic or -chloro compounds have lower melting and boiling points than the respective *meta* or *para* isomers. Example (given in the table):

Compound	***ortho*-isomer** m.pt.	***para*-isomer** m.pt.
Nitrophenol	44°C	114°C
Nitrobenzaldehyde	44°C	106°C
Nitrobenzoic acid	144°C	241°C

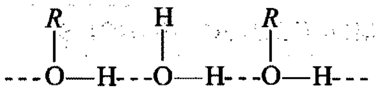
So, intermolecular H-bonding is more stronger than intramolecular H-bonding. That is why m- or p-nitrophenol has high boiling point than o-nitrophenol (which is steam volatile) and o- substituted compound leads to chelation which decreases boiling point. Chelation also explains the low boiling point of enolic form of acetoacetic ester than the ketonic form of the same.



$$CH_3—\overset{\overset{O}{\|}}{C}—CH_2—COOC_2H_5 \qquad CH_3—\overset{\overset{O—H---O}{|\qquad\quad \|}}{C=CH—C}—OC_2H_5$$

(keto form) (enol form) chelation

(b) Solubility in water : A hydrogen-bonded organic compound is usually soluble in another hydrogen-bonded substance. So, compounds whose molecule can form H-bonds with water molecule are soluble in water. Because of this reason lower members of alcohols, acids, primary and secondary amines, phenols and carbonyl compounds are more soluble in water, whereas alkanes, ethers and thiols are insoluble in water.



$$\begin{array}{ccc} R & H & R \\ | & | & | \\ ---O—H--- & O—H--- & O—H--- \end{array}$$

However, as the hydrocarbon chain (R—) in organic compounds increases, the hydrophobic character of alkyl chain predominates over H-bonding with the result the solubility of alcohols in water decreases with increase in molecular mass and alcohols become almost insoluble when alkyl groups of more than seven carbon atoms are present, while methyl, ethyl and propyl alcohols are very much soluble in water.

When the compound has a large ratio of —OH groups to hydrocarbon groups, the compound will have a significant solubility in water. For example sugars, certain starches and polyvinyl alcohols are fairly soluble in water.

It is important to note that while the **intermolecular hydrogen bonding increases solubility of the compound in water, the intramolecular hydrogen bonding decreases** and therefore the solubility of o-nitrophenol is lower (because of chelation) than m- and p-nitrophenols.

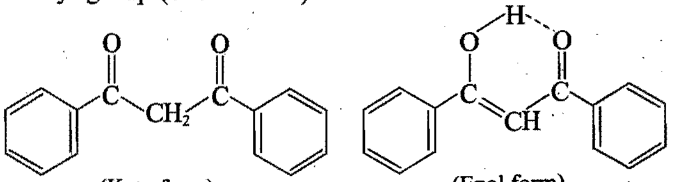
(c) Stereo isomerism : Intramolecular H-bonding have a strong influence on the spatial configuration of a molecule and inhibits isomerisation of one form to another. For example, the *trans*-isomer of indigo is so stabilised by H-bonding that it resists photochemical isomerisation to the *cis*-isomer.

(d) Adsorption : Intermolecular H-bonding plays a very important role in the process of dyeing of textiles.

(e) Miscellaneous effects : Besides these many other properties such as colour, dipole moments, heat of mixing, heat of vaporisation, viscosity and refractive index, etc., are also affected by H-bonding.

In fact, H-bonding is likely to affect most of the physical properties.

(f) Effect of hydrogen bonding on chemical properties: The presence of H-bonding also affects the chemical property of certain compounds. For example, the dibenzoyl methane does not give the normal reactions of carbonyl group, *i.e.*, it does not add HCN or $NaHSO_3$, etc. This is due to the formation of H-bonding which ties up the carbonyl group (enolic form).



(Keto form) (Enol form)

Dibenzoyl methane

Moreover the —OH group formed is also not free and is neither acetylated by acetic anhydride nor does it give methane with methyl magnesium iodide. Similarly *o*- hydroxy azo-compounds unlike *p*-isomers, do not give the normal reactions of hydroxyl group.

(g) Hydrogen bonding in biological systems : H-bonding in biological systems also plays an important role and stabilizes usual structure of proteins and nucleic acids.

1.9 INTERMOLECULAR FORCES

In non-ionic compounds such as organic compounds, the structural units are molecules. The forces holding these molecules together are generally very weak and are of three types:

(i) Dipole-dipole attraction : In polar molecules, the positive end of one molecule is attracted by the negative end of another molecule. As a result of this dipole-dipole attraction, polar molecules are held to each other.

(ii) Hydrogen bonding : Intermolecular hydrogen bonding brings association of the molecules and thus, increases the melting and boiling points of the compound.

(iii) van der Waals' forces : In non-polar compounds, there is a very weak intermolecular attraction due to electrostatic attraction between the nuclei of one molecule and the electrons of the other. This attraction is largely compensated by the repulsion between the electrons of neighbouring molecules as well as the repulsion between the nuclei of neighbouring molecules. The van der Waals' forces are very weak and are significant only when the molecules are very close to each other. van der Waals' forces are stronger in the compounds of high molecular masses.

The relative order of these intermolecular forces is:

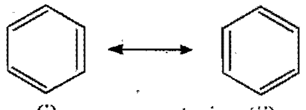
Hydrogen bond > dipole-dipole attraction > van der Waals' attraction

1.10 RESONANCE

An organic molecule is generally represented by an electronic structure and it is expected that this structure satisfactorily explains all the observed properties of the compound. But very often single electronic structure cannot explain all the observed properties. For example, benzene is ordinarily represented as inside figure.

This structure has two types of carbon-carbon bonds. Three carbon-carbon bonds are single bonds and three carbon-carbon bonds are double bonds. However, it has been observed experimentally that all carbon-carbon bonds are identical and have the same bond length (1.39 Å). The normal carbon-carbon single bond length is 1.54 Å and normal carbon-carbon double bond length is 1.34 Å. Actually benzene can be represented by the given two alternative structures but none is able to explain fully all the observed properties of benzene. These two structures differ only in the position of electrons.

The actual structure of benzene, which can explain all the observed properties, lies somewhere in between these two structures.

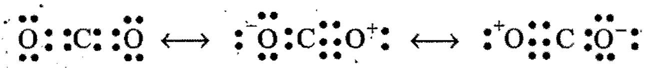


(i) (ii)

So, it was found in certain compounds, that no structural formula (electronic picture) could satisfactorily explain all the properties. For example, the electronic structure of carbon dioxide may be represented by at least three electronic arrangements given as follows:

$$O{=}C{=}O \longleftrightarrow {}^{-}O{-}C{\equiv}O^{+} \longleftrightarrow {}^{+}O{\equiv}C{-}O^{-}$$

or



$$\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}:\,:C:\,:\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}} \longleftrightarrow\ :\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}{}^{-}:C\underset{\bullet\bullet}{\overset{\bullet\bullet}{::}}O^{+}: \longleftrightarrow\ :{}^{+}O\underset{\bullet\bullet}{\overset{\bullet\bullet}{::}}C:\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}{}^{-}:$$

This led to the idea that such compounds exist in a state which is some combination of two or more structures and each one of which makes some contribution to its structure, but none of them describes all the properties of the molecule or an ion. **Ingold,** (1933) called this phenomenon as **mesomerism** (between the parts, *i.e.*, an intermediate structure).

This phenomenon in which two or more structures can be written for a compound, but none of them represents it accurately, is referred to as **resonance.** The actual structure of the compound is said to be a resonance hybrid of various possible alternative structures which themselves are known as resonating structures or canonical structures. In canonical structures, there is only delocalization of electrons (π-electrons and unshared electrons) without shifting any atom. The resonance hybrid is a definite form which cannot be represented. It does not oscillate between various structures or it is not the mixture of various canonical forms. Its properties are fixed and these are the properties of the actual hybrid structure. Thus, resonance is hybridization of resonating structures and takes place in conjugated compounds (containing alternate single bond and multiple bond).

Conditions of Resonance

(i) Structures contributing towards the hybrid must conform to real Lewis structures.

(ii) The arrangement of atoms must be identical or almost the same in every contributing structure, *i.e.*, canonical form.

(iii) Resonance involves delocalization of only π-electrons.

(iv) All canonical forms must have same number of unpaired electrons.

(v) The energy contents of all the canonical forms must be nearly the same.

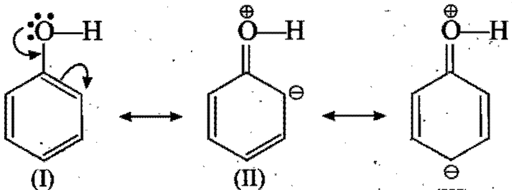
(vi) All resonance structures (canonical forms) do not contribute equally to the hybrid. Structures with more covalent bonds are more stable than those with lesser number of covalent bonds. The non-polar form of butadiene (I) is most stable of all its canonical forms (II and III).

$$\underset{(I)}{CH_2=CH-CH=CH_2} \longleftrightarrow \underset{(II)}{\overset{+}{C}H_2-CH=CH-\overset{-}{C}H_2}$$

$$\longleftrightarrow \underset{(III)}{\overset{-}{C}H_2-CH=CH-\overset{+}{C}H_2}$$

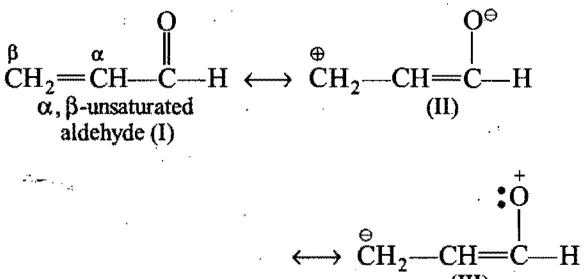
(vii) Resonance structures having like charges on adjacent atoms contribute very little towards resonance hybrid as these structures possess high energy and thus are less stable.

(viii) Structures with isolated unlike charges have less contribution than those in which they are close to each other. Thus, structure (II) of phenol has more contribution than structure (III) to its resonance hybrid.



(I) (II) (III)

(ix) Structures with negative formal charge on the most electronegative atom and positive charge on the least electronegative atom have significant contribution. Structures with negative formal charge on the electropositive atom and positive charge on the electronegative atom have least contribution to the resonance hybrid. The structure (II) is more contributing than structure (III) to the resonance hybrid of acrolein [acrylic aldehyde, an α, β-unsaturated aldehyde (I)].



$$\overset{\beta}{C}H_2=\overset{\alpha}{C}H-\overset{\overset{O}{\|}}{C}-H \longleftrightarrow \overset{\oplus}{C}H_2-CH=\overset{\overset{O^{\ominus}}{|}}{C}-H$$

α, β-unsaturated aldehyde (I) (II)

$$\longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\overset{:\overset{+}{O}}{|}}{C}-H$$

(III)

(x) Structures with electron deficient atom (*i.e.*, possessing less than eight electrons in its outermost shell) have high energy, *i.e.*, low stability, hence they contribute less than those structures in which octet rule is not violated. Thus, structure (I) contributes more than structure (II) to the resonance hybrid of diazomethane (CH_2N_2).

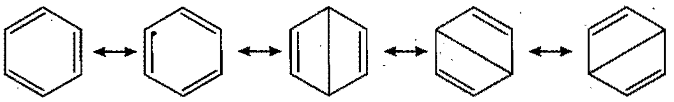
$$\underset{(I)}{CH_2=\overset{\oplus}{N}=\underset{\bullet\bullet}{\overset{\ominus}{\overset{\bullet\bullet}{N}}}} \longleftrightarrow \underset{(II)}{CH_2=\overset{\bullet\bullet}{N}-\underset{\bullet\bullet}{\overset{\bullet\bullet}{N}}}$$

(xi) Resonating structures are more important in conjugated system than those in isolated system.

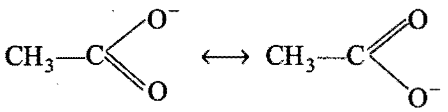
(xii) Resonating structures must be planar.

Examples of Some Molecules or Ions Showing Resonance

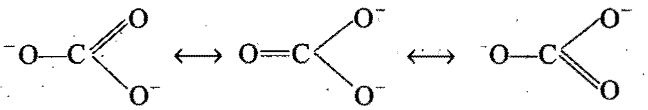
(i) Benzene, C_6H_6



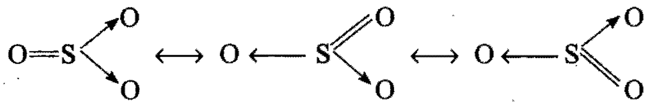
(ii) Acetate, CH_3COO^-



(iii) Carbonate ion, CO_3^{2-}



(iv) Sulphur trioxide, SO_3



(v) Diazo methane, CH_2N_2

$$H_2C=\overset{+}{N}=\overset{-}{\overset{\bullet\bullet}{N}}: \longleftrightarrow H_2\overset{-}{\overset{\bullet\bullet}{C}}-\overset{+}{N}\equiv N:$$

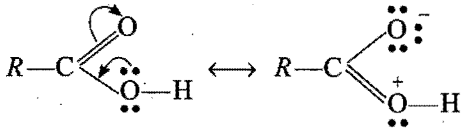
(vi) Vinyl chloride, $H_2C=CHCl$

$$\underset{(a)}{H_2C=CH-\underset{\bullet\bullet}{\overset{\bullet\bullet}{Cl}}:} \longleftrightarrow \underset{(b)}{H_2\overset{-}{\overset{\bullet\bullet}{C}}-CH=\underset{\bullet\bullet}{\overset{+}{Cl}}:} \longleftrightarrow$$

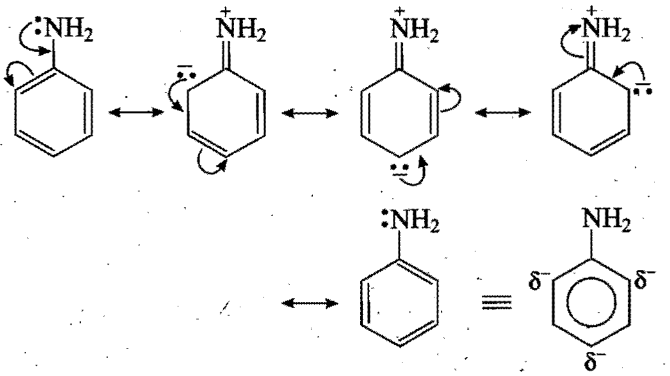
$$\underset{(c)}{H_2\overset{+}{C}-CH=\underset{\bullet\bullet}{\overset{\bullet\bullet}{Cl^-}}:}$$

(The order of stability (a) > (b) > (c), *i.e.*, structure (a) is more stable because it has no formal charge and (c) is least stable having an electron deficient carbon.)

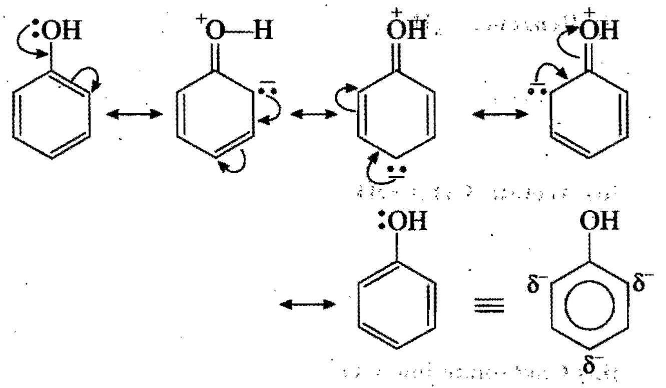
(vii) Carboxylic acid, *R*—COOH



(viii) Aniline, $C_6H_5NH_2$



(ix) Phenol, C_6H_5OH



Effects of Resonance

(i) Resonance is responsible for the greater stability of the molecule.

(ii) In a resonance hybrid, the bond length is smaller than in canonical forms.

(iii) Heat of formation of a resonance hybrid is abnormal in comparison to canonical forms.

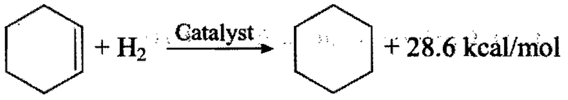
(iv) On account of greater stability of the resonance hybrid, the reactivity of the molecule decreases.

Resonance Energy

One of the most important effect of resonance is that resonance hybrid (the real molecule) has much lower energy than the energy calculated for any of the canonical forms. The difference between the actual energy of the molecule (the energy of resonance hybrid) and the energy calculated for the most stable of the canonical form, *i.e.*, having the lowest energy among the canonical forms is called the **resonance energy.**

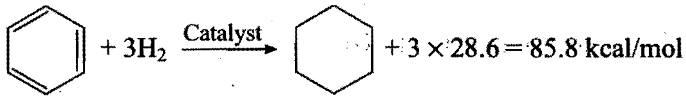
[Experimental heat of formation (observed) – Theoretical heat of formation (calculated)]

The resonance energy is calculated from the difference between the theoretical and experimental heats of hydrogenation of the compound. For example, it is possible to determine the resonance energy of benzene from the following data:



Cyclohexene Cyclohexane

Accordingly,



Cyclohexatriene (hypothetical) Cyclohexane

But, however, the experimental value of heat of hydrogenation of benzene is 49.8 kcal/mol.

Therefore, benzene is having 36 kcal/mol (85.8 – 49.8) less energy than expected for a typical compound which is having three double bonds. Hence, resonance energy of benzene molecule is 36 kcal/mol by which the benzene molecule gets stabilized. The greater the resonance energy, the greater is the stability of the molecule. The resonance hybrid is represented by a double headed arrow (⟷).

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Which of the following has maximum bond energy?

(a) Cl_2 (b) F_2

(c) Br_2 (d) I_2

[**Ans.** (a)]

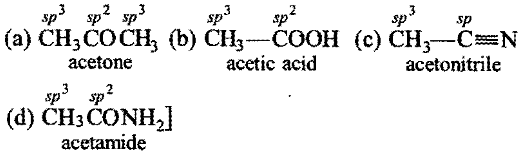
2. Which one of the following does not have sp^2-hybridized carbon?

(a) CH_3COCH_3 (b) CH_3COOH

(c) $CH_3—C{\equiv}N$ (d) CH_3CONH_2

[**Ans.** (c)]

[**Hint :**



(a) $\overset{sp^3}{CH_3}\overset{sp^2}{CO}\overset{sp^3}{CH_3}$ acetone (b) $\overset{sp^3}{CH_3}—\overset{sp^2}{COOH}$ acetic acid (c) $\overset{sp^3}{CH_3}—\overset{sp}{C}{\equiv}N$ acetonitrile

(d) $\overset{sp^3}{CH_3}\overset{sp^2}{CONH_2}$ acetamide]

3. Which bond is not polar?

(a) O—F (b) C—Cl

(c) C—F (d) C—N

[**Ans.** (a)]

[**Hint :** O—F bond is non-polar due to very much less difference in electronegativities of oxygen and fluorine.]

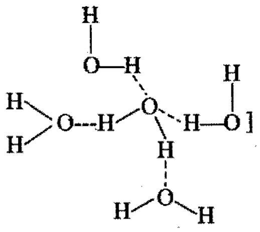
4. Number of H-bonds formed by a water molecule is:

(a) 2 (b) 8

(c) 1 (d) 4

[**Ans.** (d)]

[**Hint:**



]

5. The electronegativity follows the order :

(a) F > Cl > Br > O (b) F > O > Cl > Br

(c) O > F > Cl > Br (d) Cl > F > O > Br

[**Ans.** (b)]

[**Hint:** Electronegativity decreases from F to I and O is next to F in order of decreasing electronegativity.]

6. In which of the following compounds, delocalized bonding is not possible?

(a) 1,3-Butadiene (b) 1,4-Pentadiene

(c) 1,3,5-Hexatriene (d) Benzene

[**Ans.** (b)]

[**Hint:** (b) is not a conjugated system.]

7. The carbonyl group has following resonating structures,

(i) $>C=O$ (ii) $>\overset{-}{C}—\overset{+}{O}$ (iii) $>C^+—O^-$

The correct order of stability of these structures is:

(a) (i) > (ii) > (iii) (b) (iii) > (i) > (ii)

(c) (i) > (iii) > (ii) (d) (iii) > (ii) > (i)

[**Ans.** (c)]

[**Hint:** The resonating structure with minimum or no charge is more stable. Thus, the stability of structure (i) is maximum. As the negative charge is present on more electronegative oxygen atom {as in structure (iii)}. (iii) is more stable than structure (ii).]

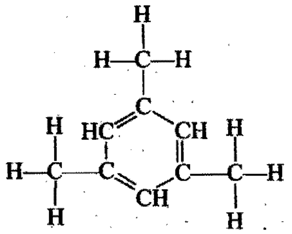
8. The ratio of σ and π-bonds in mesitylene is:

(a) 3 (b) 5

(c) 6 (d) 7

[**Ans.** (d)]

[**Hint:** The structure of mesitylene is



Total number of σ-bonds = 21

Total number of π-bonds = 3

So, ratio of σ and π-bonds is 7 : 1]

1.11 PURIFICATION OF ORGANIC COMPOUNDS

The organic compounds derived from natural sources or prepared in the laboratory are seldom pure. They are usually contaminated with other substances. **Purification means the removal of undesirable impurities associated with a particular organic compound, *i.e.*, to obtain the organic compound in pure state.** The methods commonly used for the separation and purification of organic compounds are:

- (i) Crystallisation:
  - (a) Simple crystallisation
  - (b) Fractional crystallisation
- (ii) Sublimation
- (iii) Distillation:
  - (a) Simple distillation
  - (b) Fractional distillation
  - (c) Vacuum distillation
  - (d) Steam distillation
- (iv) Solvent extraction
- (v) Chromatography.

Methods Employed for Purification of Solids

(a) Simple crystallisation : It involves the preparation of saturated solution of the impure organic compound in a suitable solvent at a higher temperature, *i.e.*, near its boiling point. The solution so formed is filtered while hot to remove insoluble impurities. The clear solution is cooled when the solid organic compound separates out in the form of fine crystals. The solid is filtered and dried.

Examples : (i) Sugar mixed with common salt can be purified with ethanol.

(ii) Phthalic acid mixed with naphthalene can be purified with hot-water.

(b) Fractional crystallisation : The method is used for the separation of a mixture of two compounds which are soluble in the same solvent but their solubilities are different. The hot saturated solution of the mixture is allowed to cool when the less soluble component crystallises out earlier than the more soluble component. The various fractions are separated from time to time. These fractions are now separately put to crystallisation. A series of repeated crystallisations separate the two compounds in pure form.

(ii) Sublimation : Certain organic substances pass directly from solid to vapour state on heating and *vice-versa* on cooling. This is called **sublimation** and the process is very useful for separation of substances which sublime on heating from non-volatile impurities. The organic compounds such as benzoic acid, naphthalene, anthracene, camphor, indigo, anthraquinone, etc., are purified by this process.

$$\text{Solid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Vapours}$$

The process of sublimation requires no solvent and is completed in a short time but it can be applied to only a limited number of organic substances which possess high vapour pressure at normal atmospheric pressure.

Methods Employed for Purification of Liquids

(i) Distillation : Distillation is the most important method for purifying the organic liquids. Several methods of distillation, such as simple distillation, fractional distillation, vacuum distillation, steam distillation, etc., are used. The type of distillation depends mainly on the nature of impurities present in the organic compound.

Distillation is a process which involves two steps:

1. Vaporisation : Liquid is converted into vapours.

2. Condensation : Vapours are condensed again into liquid.

(a) Simple distillation : Simple distillation is applied only for volatile liquids which boil without decomposition at atmospheric pressure and contains non-volatile impurities.

This method can also be used for separating liquids having sufficient difference in their boiling points. For example,

(i) benzene (b.pt. 80°C) and aniline (b.pt. 184°C)

(ii) chloroform (b.pt. 61°C) and aniline (b.pt. 184°C)

(iii) ether (b.pt. 35°C) and toluene (b.pt. 110°C)

Nitrobenzene prepared in the laboratory can also be purified by distillation.

(b) Fractional distillation : This method is used for the separation and purification of organic liquids from non-volatile impurities or for separating two or more volatile liquids from a liquid mixture which have boiling points close to each other.

Since, in this process, the distillate is collected in fractions under different temperatures, it is known as fractional distillation.

Liquids forming constant boiling mixture (azeotropic mixture) cannot be separated by this method. Fractional distillation is used these days in industry, especially, in the distillation of petroleum, coal-tar and crude alcohol. A mixture of methanol (b.pt. 65°C) and propanone (b.pt. 57°C) or a mixture of benzene and toluene may be separated by fractional distillation.

(c) Distillation under reduced pressure (Vacuum distillation) : The compounds, which decompose at a temperature below their normal boiling points, cannot be purified by distillation under ordinary atmospheric pressure. Glycerine is one such compound which decomposes at its boiling point.

The pressure is reduced by suction pump and the distillation is carried out at lower temperature as glycerine can be distilled at 180°C (normal b.pt. 290°C) under a pressure of 10–12 mm. Cane juice can also be concentrated by this method. This technique can be used to separate glycerol from spent lye in soap industry.

Distillation under reduced pressure is not only useful in avoiding decomposition but also serves to economise fuel for industrial concerns.

(d) Steam distillation : This type of distillation is essentially a co-distillation with water and is carried out when a solid or liquid, practically insoluble in water, is volatile with steam, possesses a vapour pressure of about 10-15 mm of mercury but the impurities are non-volatile.

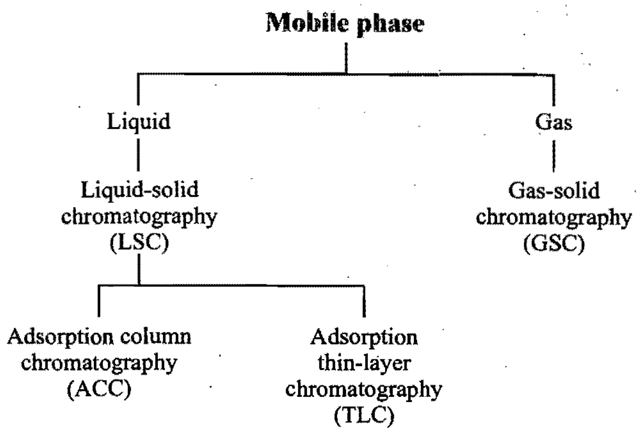
This process is used in the purification of compounds such as chlorotoluenes, aniline and nitrobenzene. It is also employed in the isolation of essential oils from flowers.

(ii) Solvent extraction : The process of separation of an organic compound from its aqueous solution by shaking with a suitable organic solvent is termed **solvent extraction.** The solvent should be immiscible with water and the organic compound to be separated (by using separating funnel) should be highly soluble in it.

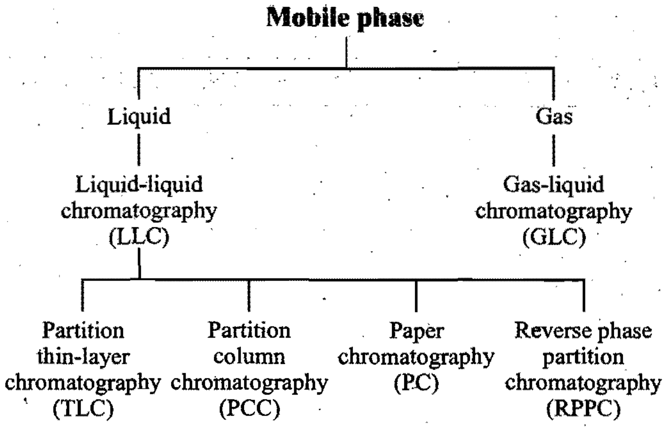
(iii) Chromatography : It is a recent and most efficient technique which was first used by **Tswett**, a botanist, in 1906 for the separation of coloured substances into individual components. The name chromatography (Greek word, *chroma* = colour and *graphy* = writing) means colour writing. The name is no longer accurate as the technique has undergone tremendous modifications and is now used to separate almost any given mixture, whether coloured or colourless, into its constituents and to test the purity of these constituents. This technique is even applicable to micro quantities (even less than 50 mg or 1 mL).

Chromatography is based on selective distribution of the various constituents of a mixture between two phases, a stationary phase and a moving (mobile) phase. Different constituents migrate, at different rates, through the stationary phase. The stationary phase can be a solid or a liquid, while the mobile (moving) phase is a liquid or a gas. Based on the nature of the stationary phase and the mobile phase, different types of chromatographic techniques have been developed.

(a) When stationary phase is solid, the chromatography is known as **adsorption or column chromatography.** Depending upon the nature of mobile phase, adsorption chromatography is further classified as follows:



(b) When stationary phase is liquid, the chromatography is known as **partition chromatography.** Depending upon the nature of mobile phase, partition chromatography is further classified as follows:



The most common ones are:

(i) Column chromatography or adsorption chromatography,
(ii) Thin layer chromatography (TLC),
(iii) Paper chromatography,
(iv) Gas chromatography,
(v) Ion-exchange chromatography.

The first three techniques have been described as:

Column (Adsorption) chromatography : This is based on adsorption (or surface) phenomenon. The extent of adsorption of various constituents present in a mixture liquid (mobile phase) varies with a given adsorbent (stationary phase). The common adsorbents used are magnesium oxide, alumina, cellulose powder, silica gel, active animal charcoal, etc.

Column chromatography involves the

(i) preparation of adsorbent column,
(ii) adsorption and
(iii) elution of components and recovery.

Thin layer chromatography (TLC) : It is a special technique of adsorption chromatography in which thin layers of adsorbents such as silica gel are spread on glass plates. A slurry of the adsorbent in an organic solvent is prepared. The slurry is then coated on the glass plate with the help of a device called applicator. A spot of the solution of the mixture to be separated is kept at a distance of 2 cm from one side of the glass plate with the help of capillary. The size of the spot should be as small as possible. The plate is then dried. The glass plate is now placed vertically in a developing chamber (close jar) containing a suitable solvent or solvent mixture at the bottom (about 1 cm deep). The end which has the sample spot is dipped in the solvent. The chamber is closed and the solvent is allowed to ascend. The solvent consequently resolves the original spot of mixture into a series of spots, each corresponding to a single component. The relative adsorption of each component of the mixture is expressed in terms of its retardation factor, *i.e.*, R_f **value.**

$$R_f = \frac{\text{Distance moved by the substance from base line}}{\text{Distance moved by the solvent from base}}$$

The plate is taken off and dried. Each spot is now eluted separately.

Paper chromatography: It is a type of **partition chromatography.** The process is similar to thin layer chromatography, except that a strip of paper acts as the adsorbent. Paper chromatography is based on a mechanism which is partly partition and partly adsorption. The paper consists of cellulose fibres having molecules of water strongly adsorbed on them. This serves as the **stationary phase** while a suitable organic solvent is used as a **mobile phase.** A drop of the solution of a mixture to be separated is placed on a strip of chromatographic paper and the solvent is allowed to travel along the strip. When the eluting solvent moves upwards, it is termed **ascending paper chromatography** and when the eluting solvent moves downwards, it is termed **descending paper chromatography.**

Finally, the paper strip is taken out and dried in air. The position of various components, on the paper, is determined by spraying some suitable reagent which makes the spots (components) visible. In the separation and identification of amino acids, ninhydrin is used for developing the coloured spots.

1.12 CRITERIA OF PURITY OF ORGANIC COMPOUNDS

Melting point: A pure organic solid has a definite and sharp (sudden, rapid and complete) melting point, while an impure substance has a lower and indefinite melting point. The melting point of a solid may be defined as the temperature at which the solid and liquid states of the compound are in equilibrium with each other at an external pressure of 1 atmosphere.

Mixed melting point: The melting point of two thoroughly mixed substances is called mixed melting point. This can also be used for ascertaining the purity of a compound.

The substance, whose purity is to be tested, is mixed with a pure sample of the same compound. The melting point of the mixture is determined. If the melting point of the mixture is sharp and comes out to be the same as that of pure compound, it is sure that the compound under test is pure. On the other hand, if the melting point of the mixture is less than the melting point of the pure compound, the compound in question is not pure.

Boiling point*: The boiling point of a liquid is defined as the temperature at which the vapour pressure of a liquid is equal to external pressure. Boiling points are also normally quoted for standard atmospheric pressure. A pure organic liquid boils at a fixed temperature which is characteristic of that substance.

If enough liquid is available, it can be distilled in a distillation apparatus and the constant temperature recorded by the thermometer is the boiling point.

When the amount of the liquid is small, Siwoloff's method (capillary tube method) is used.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

9. Suggest a method to purify benzene containing non-volatile impurities:
   (a) steam distillation
   (b) distillation under reduced pressure
   (c) simple distillation
   (d) sublimation
   [**Ans.** (c)]

10. A substance has boiling point 563 K, but it starts decomposing near this temperature. Which type of distillation process is suitable for its purification?
   (a) Distillation
   (b) Fractional distillation
   (c) Steam distillation
   (d) Distillation under reduced pressure
   [**Ans.** (d)]

11. Petroleum refining involves:
   (a) vacuum distillation
   (b) fractional distillation
   (c) steam distillation
   (d) passing over activated charcoal
   [**Ans.** (b)]
   [**Hint:** Crude petroleum is subjected for fractional distillation to get different products.]

12. In steam distillation of toluene, the pressure of toluene vapour is:
   (a) equal to the pressure of barometer
   (b) less than the pressure of barometer
   (c) equal to vapour pressure of toluene in simple distillation
   (d) more than the vapour pressure of toluene in simple distillation
   [**Ans.** (b)]

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*Boiling point is not as reliable a test of purity as is the melting point for the solids. There are many liquids which are miscible with other liquids and mixtures have fixed boiling points (azeotrope). Thus, other physical properties are being used for deciding the purity.

IMPORTANT POINTS TO REMEMBER (SUMMARY)

- All organic compounds contain **carbon** and **hydrogen** as essential constituents.
- Carbon has the maximum tendency of **catenation** as it can combine with other carbon atoms by single, double or triple covalent bonds. The bonding can be extended to form long open chains (straight or branched) or closed one. This leads to a large number of organic compounds.
- Organic compounds being **covalent** are generally insoluble in water and other polar solvents but soluble in non-polar solvents.
- The nature of the covalent bonding in organic compounds can be described in terms of **orbitals hybridization** concept, according to which carbon can have sp^3, sp^2 and sp-hybridized orbitals. The tetrahedral shape of methane, planar shape of ethene and linear shape of ethyne can be understood on the basis of this concept.
- A sp^3-hybrid orbital can overlap with 1s-orbital of hydrogen to give a carbon hydrogen (C—H) **single bond (sigma, σ bond).** The bond angle is 109°28′ (or 109.5°). Overlap of a sp^2-hybrid orbital of one carbon atom coaxially with that of another carbon atom to form a (C—C) sigma bond. The unhybridized $2p_z$-orbitals on two adjacent carbon atoms overlap laterally (side-by-side) to form a **pi (π) bond.** The H—C—H bond angle is 120°. Similarly the triple bond between two carbon atoms (C≡C) consists of one sigma and two pi-bonds (sp-hybridization) and the bond angle is 180°.
- Greater the *s*-character of the hybrid orbital, the smaller is its size. So, the order of the size of the three hybrid orbitals is:

$$sp^3 > sp^2 > sp.$$

- The distance between the nuclei of the two atoms joined by the bond is called **Bond Length** (Single bond > Double bond > Triple bond). The amount of energy required to break a bond in a molecule is called **Bond Energy** or **Bond Strength.** It is in the following order:

  (Triple bond > Double bond > Single bond).
- An electrostatic attractive force between the covalent bonded hydrogen atom of one molecule and highly electronegative atom of small atomic radius (such as F, O, N) of the other molecule is referred to as **Hydrogen bond**. The strength of hydrogen bond decreases as:

$$\mathrm{H\cdots F > H\cdots O > H\cdots N}$$

- **Resonance:** If a molecule or an ion can be shown by two or more structures, differing only in the distribution of electrons, but none of them truly explain all the properties of the molecule or an ion, these structures are called **resonating** or **contributing** or **canonical** structures and this phenomenon is called **Resonance.**
- Benzene can be shown by two or more resonating structures and each one makes some contribution to its structure, but none of them describe all the properties of benzene molecule and actual structure lies some where in between, called **resonance hybrid.**
- It has been proved experimentally that all C—C bonds are identical and have the same bond length (1.39 Å). The normal C—C single bond length is 1.54 Å and normal C—C double bond length is 1.34 Å.

Types of Resonance:

(i) Isovalent: The different contributing structures having same number of covalent bonds is called **Isovalent resonance.** For example, benzene have isovalent resonating structures similarly in carboxylate anion, there is same number of bonds.

(ii) Heterovalent: The different contributing structures having different number of bonds is called **Heterovalent resonance.** For example,

$$\underset{\text{(I)}}{\mathrm{H_2C{=}CH{-}CH{=}CH_2}} \longleftrightarrow \underset{\text{(II)}}{\mathrm{H_2\overset{+}{C}{-}CH{=}CH{-}\overset{-}{C}H_2}}$$

$$\longleftrightarrow \underset{\text{(III)}}{\mathrm{H_2\overset{-}{C}{-}CH{=}\overset{+}{C}H{-}CH_2}}$$

In buta-1,3-diene, there are eleven bonds in structure (I) while ten bonds in structures (II) and (III) respectively.

Conditions of Resonance:

- All contributing structures must have same number of paired or unpaired electrons, same or nearly the same energy contents, same atomic skeleton a planar structure and involves delocalization of only π-electrons.
- Resonating structures with more covalent bonds are more stable. They are more important in conjugated system than those in isolated system and non-polar structures are more stable than the polar structures.

Effects of Resonance:

- Resonance is responsible for the greater stability of the molecule.
- The bond lengths of hybrid form are different from any of the resonating structures.
- The heat of hydrogenation determined experimentally and that calculated theoretically for the most stable structure are different. This difference is called **Resonance energy.**
- Purification, Qualitative and Quantitative analysis of organic compounds are carried out for determining their structures.
- **Purification** means the removal of undesirable impurities associated with a particular organic compound, *i.e.*, to obtain the organic compound in pure state. The methods employed for **purification of solids** are as follows:
- **Crystallisation** is used to purify organic solids by dissolving them in suitable solvent followed by filtration of the hot solution and crystallisation.
- **Fractional crystallisation** is used to separate two or more organic solids with different solubilities in the same solvent.
- **Sublimation** is used for separation of certain organic substances which sublime (passes directly from solid to vapour state on heating and *vice-versa*) on heating from non-volatile impurities. Examples are camphor, benzoic acid, naphthalene and anthracene, etc.

- ☐ The methods employed for **purification of liquids** are as follows:
- ☐ **Simple distillation** is applied only for volatile liquids which boil without decomposition at atmospheric pressure and contains non-volatile impurities or liquid mixture in which the components differ in boiling points by at least 30–50 K.
- ☐ **Fractional distillation** is applied for separating two or more volatile liquids from a liquid mixture in which the components differ in boiling points close to each other by 10 to 20 K.
- ☐ **Vacuum distillation** is applied for liquids which decompose at a temperature below their normal boiling points.
- ☐ **Steam distillation** is applied for separation and purification of liquids which is appreciably volatile in steam, practically immiscible with water but the impurities are non-volatile.
- ☐ **Solvent extraction** method is used to separate a given organic compound from its aqueous solution by shaking with a suitable organic solvent in which the compound is more soluble than water.
- ☐ **Chromatography** is a useful technique of separation, identification and purification of compounds even if available in very small amount.
- ☐ **Adsorption (column) chromatography** is based on the differences in rates at which the components of a mixture liquid (moving phase) are adsorbed on an adsorbent (stationary phase).
- ☐ **Partition chromatography** involves continuous partitioning of the components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography.
- ☐ **Criteria of purity** of an organic compound is best determined by mixed melting point.

(i) Resonance decreases the stability of the molecule and increases its reactivity.
(j) With the shortening of bond length, bond strength increases.
(k) A symmetrical molecule is non-polar even though it contains polar bonds.
(l) CCl_4 has high value of dipole moment.
(m) Resonance involves movement of σ- and π-electrons.
(n) The greater the resonance energy, the lower is the stability of the molecule.
(o) More is the number of canonical forms for a molecule, more is the resonance energy of molecule.
(p) A carbon-carbon double bond is stronger than a carbon-carbon single bond.
(q) A polar bond results when the atoms have same electronegativity.
(r) Acetylene is a linear molecule.
(s) The criterion of purity of a solid organic compound is its molecular mass.
(t) Chromatography is a method to separate and purify compounds when present in small amounts.
(u) Naphthalene can be separated from ammonium chloride by sublimation.
(v) Aniline is purified by steam distillation.
(w) Benzene and toluene can be separated by fractional distillation.
(x) In organic compounds, carbon is always sp^3- hybridized.
(y) All bond length values in ethane are same.
(z) A triple bond consists one sigma and two pi bonds.

4. Match the following:

(a)

(A) Vital force theory	(i) Bond angle 120°
(B) sp^3-hybridization	(ii) Kolbe
(C) Hydrogen bonding	(iii) Wöhler
(D) Resonance	(iv) One sigma two pi bonds
(E) sp^2-hybridization	(v) Sublimation
(F) Urea	(vi) Vacuum distillation
(G) Acetic acid	(vii) CH_4
(H) Naphthalene	(viii) Berzelius
(I) Triple bond	(ix) C_6H_6
(J) Glycerol	(x) C_2H_5OH

(b)

(A) Sublimation	(i) Benzene + Toluene
(B) Chromatography	(ii) Tswett
(C) Steam distillation	(iii) Camphor
(D) Fractional distillation	(iv) Aniline

5. In each case, select the property which is typical of organic rather than inorganic compounds:
A. (i) Water soluble
 (ii) Water insoluble
B. (i) Low melting point
 (ii) High melting point
C. (i) Flammable
 (ii) Non-flammable
D. (i) Ionic bonding
 (ii) Covalent bonding
E. (i) Chemical reactions are slow
 (ii) Chemical reactions are fast

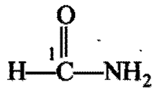
6. Classify the following into polar and non-polar molecules :
(i) CO_2, (ii) $CHCl_3$, (iii) CCl_4, (iv) CH_3OCH_3, (v) C_2H_5OH, (vi) C_2H_6, (vii) CH_2Cl_2, (viii) NH_3, (ix) H_2O, (x) CH_3Cl.

7. Indicate the type of hybridization of each carbon atom in the following molecules:

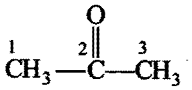
(i) $\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$ (ii) $H-\overset{1}{C}\equiv\overset{2}{C}-\overset{3}{C}\equiv\overset{4}{C}-H$

(iii) $\overset{1}{C}H_3-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_3$ (iv) $\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_3$

(v) $\overset{1}{C}H_3-\overset{2}{C}\equiv N$

(vi) 
$H-\overset{O}{\overset{\|}{\overset{1}{C}}}-NH_2$

(vii) $\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}\equiv N$

(viii) 
$\overset{1}{C}H_3-\overset{O}{\overset{\|}{\overset{2}{C}}}-\overset{3}{C}H_3$

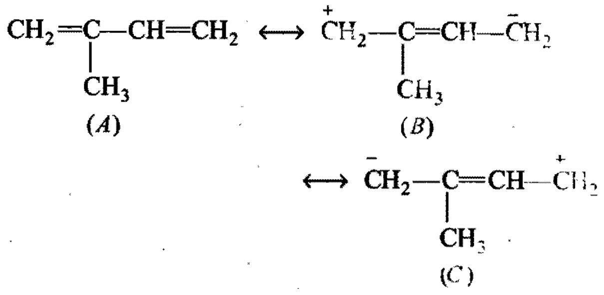
(ix) $H_2C=C=O$ (x) $CH_3\overset{+}{C}H_2$

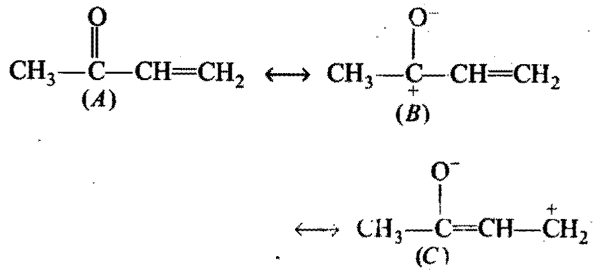
(xi) $CH_3\overset{-}{C}H_2$ (xii) $CH_3\overset{\bullet}{C}H_2$

8. Indicate the number of σ- and π-bonds in the following molecules:
(i) $CH_3-C\equiv C-H$ (ii) $CH_3-CH=CH_2$
(iii) $H_2C=C=CH_2$ (iv) $CH_3-CH_2-CH_3$
(v) $H_2C=C=CH-CH_3$
(vi) $HC\equiv C-CH=CHCH_3$
(vii) $H_2C=CH-C\equiv N$ (viii) CH_3OH
(ix) $CH_3-C\equiv N$ (x) CH_3NO_2
(xi) CH_2Cl_2 (xii) C_6H_{12} (Hexene)

9. (a) How do bond length and bond strength vary in the following cases?
$C-C$, $C=C$, $C\equiv C$
(b) Arrange the sp, sp^2- and sp^3-hybridization in increasing order of:
(i) bond length (ii) bond angle (iii) bond energy
(iv) size of orbitals (v) s-character

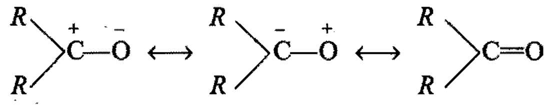
10. Which resonance form in each of the following sets is the major contributor to the real structure?

(i) 

(ii) 

(iii) $\underset{(A)}{CH_2{=}CH{-}CH{=}CH_2} \longleftrightarrow \underset{(B)}{\overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{C}H_2}$

$\longleftrightarrow \underset{(C)}{\overset{-}{C}H_2{-}CH{=}CH{-}\overset{+}{C}H_2}$

(iv)

(A) (B) (C)

11. Answer of the following:
    (i) The type of hybridization which carbon atoms undergo in the formation of ethane molecule is.
    (ii) The type of hybridization which carbon atoms undergo in the formation of ethene molecule ($H_2C{=}CH_2$) is.
    (iii) The type of hybridization which carbon atoms undergo in the formation of ethyne molecule ($HC{\equiv}CH$) is.
    (iv) Carbon-carbon bond distance in benzene is intermediate between the C—C bond distances in ethene and ethane.
    (v) Alcohols have higher boiling points than the corresponding isomeric ethers.
    (vi) CH_3OH has higher boiling point than CH_3SH.
    (vii) The *o*- and *p*-chlorophenols have different boiling points.
    (viii) The three carbon-oxygen bonds are equal in carbonate ion.
    (ix) Carbon-oxygen bond lengths in formic acid are 1.23 Å and 1.36 Å and both the carbon-oxygen bonds in sodium formate have same value, *i.e.*, 1.27 Å.
    (x) A mixture of plant pigments is separated by which method?
    (xi) The purity of an organic solid is tested by which physical property?
    (xii) C—C bond lengths in ethane, ethylene and acetylene are.
    (xiii) What are the bond angles in sp^3-sp^2- and *sp*-hybrid orbitals?
    (xiv) Chloral hydrate, $CCl_3CH(OH)_2$ is stable although it has two hydroxyl groups attached to the same carbon atom.
    (xv) C=C bond length is shorter than the C—C bond length.
    (xvi) Why *o*-hydroxy benzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid?

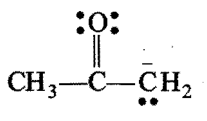
12. Arrange the followings in increasing order of a dipole moment.
    (a) HF, HCl, HBr, HI
    (b) CH_3Cl, CH_3Br, CH_3I, CH_3F
    (c) CHF_3, CHI_3, $CHBr_3$, $CHCl_3$
    (d) CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$
    (e) NH_3, SbH_3, AsH_3, PH_3
    (f) SO_3, SiO_2, P_2O_5, Cl_2O_7
    (g) *o*-chlorotoluene, *m*-chlorotoluene, *p*-chlorotoluene
    (h) *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol
    (i) *o*-dichlorobenzene, *m*-dichlorobenzene, *p*-dichlorobenzene

➤ SHORT ANSWER TYPE

13. Explain the following:
    (i) Why is ethylene a planar molecule and acetylene a linear molecule?
    (ii) Why does bond length decrease in the order?
    $C{-}C > C{=}C > C{\equiv}C$
    (iii) The boiling point of methanol is 66°C and that of methyl mercaptan is 6°C, whereas the boiling points of diethyl ether and diethyl sulphide are 35°C and 92°C respectively.
    (iv) Ethanol boils at higher temperature than ethylamine inspite of the fact that both have nearly same molecular masses.
    (v) What effect should the following resonance of vinyl chloride have on its dipole moment?
    $CH_2{=}CH{-}Cl \longleftrightarrow \overset{-}{C}H_2{-}CH{=}\overset{+}{Cl}$
    (vi) The central carbon-carbon bond in 1,3-butadiene is shorter than that of *n*-butane.
    (vii) What property of carbon accounts for the occurrence of large number of its compounds?
    (viii) The C—Cl bond is polar while CCl_4 is non-polar.
    (ix) Explain the factor on which polarity of bond depends?
    (x) The Cl atom has same electronegativity as nitrogen but it does not form effective hydrogen bonding.

14. Explain how the following mixtures may be separated:
    (i) A mixture of two miscible liquids.
    (ii) A mixture of benzoic acid and sodium chloride (solid mixture).
    (iii) A mixture of plant pigments.
    (iv) Ether and water.
    (v) Benzoic acid-water mixture.

15. (i) Discuss orbital structure of methane.
    (ii) Discuss orbital structure of ethylene.
    (iii) Discuss orbital structure of acetylene.
    (iv) Discuss the hybridization of carbon atoms in allene (C_3H_4) and show the π-orbital overlaps.

16. (A) Write the resonance structures of the following species:
    (i) $:\overset{-}{C}H_2{-}C{\equiv}N:$
    (ii) $CH_3CH{=}CH{-}\overset{+}{C}H{-}CH_3$
    (iii) $\overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{C}H_2$
    (iv)

$CH_3{-}\overset{\overset{:O:}{\|}}{C}{-}\overset{-}{\underset{\bullet\bullet}{C}}H_2$

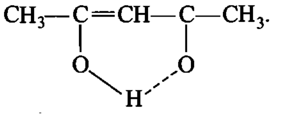
    (B) Write resonance structures for the intermediate carbocation in the aromatic chlorination of benzene.
    (C) Write the main resonance structures of the conjugate base of a 1,3-diketone.
    (D) Write the resonance structures of $CH_2{=}CH{-}CHO$. Indicate relative stability of the contributing structures.

17. Write short notes on the following:
    (i) Vital force theory.

(ii) General characteristics of organic compounds.
(iii) Hybridization.
(iv) Polar and non-polar bonds.
(v) Hydrogen bonding.
(vi) Resonance.
(vii) Fractional crystallisation.
(viii) Vacuum distillation.
(ix) Mixed melting point.
(x) Purity of an organic compound.

ANSWERS

1. (a) hydrocarbons; (b) catenation; (c) Berzelius; (d) ammonium cyanate; (e) acetic acid; (f) covalent, molecular, slow; (g) carbon dioxide; (h) synthetic; (i) three; (j) sp^3; (k) sp^2; (l) sp^3; (m) sigma, two pi; (n) sp^3, 109°28′; (o) smallest, longest; (p) 146; (q) higher; (r) 1.20 Å; (s) sp; (t) sp^2; (u) hydrogen; (v) lower, less; (w) more; (x) three; (y) non-polar; (z)



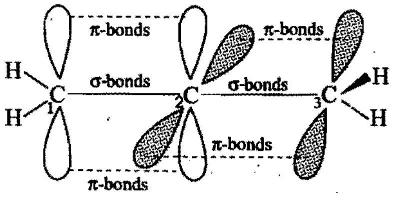
$CH_3-C=CH-C-CH_3$.

2. (i) vacuum distillation; (ii) fractional distillation; (iii) sublimation; (iv) steam volatile, sparingly soluble; (v) alumina or silica gel; (vi) rapidly; (vii) crystallisation from solution in ethanol; (viii) melting point; (ix) boiling point; (x) less; (xi) steam distillation; (xii) elution; (xiii) sublimation; (xiv) steam distillation; (xv) vacuum distillation; (xvi) fractional distillation; (xvii) steam distillation; (xviii) fractional distillation; (xix) separating funnel; (xx) vacuum distillation.
3. (a) True; (b) False—organic compounds have low melting and boiling points. These are bad conductors and insoluble in water; (c) True; (d) True; (e) False—More than 90% of organic compounds have been prepared by synthetic methods; (f) False—*s*-character 33%, *p*-character 66%; (g) True; (h) True; (i) False—Resonance increases the stability of a molecule and decreases its reactivity; (j) True; (k) True; (l) False—CCl_4 being symmetrical has zero dipole moment; (m) False—resonance involves only π-electrons; (n) False—The greater the resonance energy, the greater is the stability of the molecule; (o) True; (p) True; (q) False—Polar bond results when atoms have different electronegativity; (r) True; (s) False—criterion of purity of a solid organic compound is its melting point; (t) True; (u) False—With the help of water; (v) True; (w) True; (x) False—Carbon undergoes sp^3-sp^2- or sp-hybridization; (y) False—All bond lengths are same except between carbon and carbon atoms; (z) True.
4. **(a)** (A—viii); (B—vii); (C—x); (D—ix); (E—i); (F—iii); (G—ii); (H—v); (I—iv); (J—vi).
   (b) (A—iii); (B—ii); (C—iv); (D—i).
5. A. (ii); B. (i); C. (i); D. (ii); E. (i).
6. CO_2, CCl_4, C_2H_6 are non-polar molecules while rest are polar molecules.
7. (i) $C_1 = sp^3,\quad C_2 = sp^2,\quad C_3 = sp^2,\quad C_4 = sp^3$
   (ii) $C_1 = sp,\quad C_2 = sp,\quad C_3 = sp,\quad C_4 = sp$
   (iii) $C_1 = sp^3,\quad C_2 = sp,\quad C_3 = sp,\quad C_4 = sp^3$
   (iv) All carbon atoms are sp^3-hybridized.
   (v) $C_1 = sp^3,\quad C_2 = sp$
   (vi) $C_1 = sp^2$
   (vii) $C_1 = sp^3,\quad C_2 = sp^2,\quad C_3 = sp^2,\quad C_4 = sp$
   (viii) $C_1 = sp^3,\quad C_2 = sp^2,\quad C_3 = sp^3$
   (ix) sp^2, sp (x) sp^3, sp^2
   (xi) sp^3, sp^3 (xii) sp^3, sp^3
8. (i) σ-bonds = 6, π-bonds = 2
   (ii) σ-bonds = 8, π-bond = 1
   (iii) σ-bonds = 6, π-bonds = 2
   (iv) σ-bonds = 10
   (v) σ-bonds = 9, π-bonds = 2
   (vi) σ-bonds = 10, π-bonds = 3
   (vii) σ-bonds = 6, π-bonds = 3
   (viii) σ-bonds = 5, π-bonds = Nil
   (ix) σ-bonds = 5, π-bonds = 2
   (x) σ-bonds = 6, π-bond = 1
   (xi) σ-bonds = 4
   (xii) σ-bonds = 17, π-bond = 1
9. (a) Bond length order $C-C > C=C > C\equiv C$
   Bond strength order $C\equiv C > C=C > C-C$
   (b) (i) $sp-s < sp^2-s < sp^3-s$ (ii) $sp^3 < sp^2 < sp$
   (iii) $sp^3 < sp^2 < sp$ (iv) $sp < sp^2 < sp^3$
   (v) $sp^3 < sp^2 < sp$
10. Form *A* in (i), (ii), (iii) and form *C* in (iv) is the major contributor because in these structures each atom has octet and no formal charge is present.
11. (i) sp^3; (ii) sp^2; (iii) sp; (iv) resonance in benzene molecule; (v) hydrogen bonding is present in alcohols; (vi) oxygen is more electronegative than sulphur. Thus, hydrogen bonding is present in CH_3OH; (vii) *o*-chlorophenol involves intramolecular hydrogen bonding while *p*-chlorophenol involves intermolecular hydrogen bonding; (viii) due to resonance; (ix) no resonance is present in formic acid molecule but in formate ion resonance exists; (x) chromatography; (xi) melting point; (xii) C—C . . . 1.54 Å, C=C... 1.34 Å, C≡C...1.20 Å; (xiii) sp^3...109°28′, sp^2... 120°, sp... 180°; (xiv) Chloral hydrate is stable due to intramolecular hydrogen bonding between hydrogen and chlorine atom; (xv) With increase in *s*-character, the size of hybridized orbital decreases which leads to more overlapping and shortening of bond length in C=C; (xvi) *o*-hydroxy benzaldehyde has **intramolecular** H-bonding (so low melting point and is a liquid at room temperature), while *p*-hydroxy benzaldehyde have **intermolecular** H-bonding (so high melting point).
12. (a) $HI < HBr < HCl < HF$
    (b) $CH_3I < CH_3Br < CH_3Cl < CH_3F$
    (c) $CHI_3 < CHBr_3 < CHCl_3 < CHF_3$
    (d) $CH_4 < CH_3Cl < CH_2Cl_2 < CHCl_3$
    (e) $SbH_3 < AsH_3 < PH_3 < NH_3$
    (f) $Cl_2O_7 < SO_3 < P_2O_5 < SiO_2$
    (g) *o*-chlorotoluene < *m*-chlorotoluene < *p*-chlorotoluene
    (h) *p*-nitrophenol < *m*-nitrophenol < *o*-nitrophenol
    (i) *p*-dichlorobenzene < *m*-dichlorobenzene < *o*-dichlorobenzene
13. (i) In ethylene each carbon atom undergoes sp^2-hybridization while in acetylene each carbon undergoes sp-hybridization; (ii) As the *s*-character increases in the hybridized orbitals, greater overlapping occurs with the shortening of bond length; (iii) CH_3OH has higher boiling point than CH_3SH due to hydrogen bonding. Diethyl sulphide has higher boiling point than diethyl ether due to larger molecular mass; (iv) Oxygen being more electronegative than nitrogen forms stronger hydrogen bond than

the latter; (v) Resonance decreases the dipole moment of vinyl chloride as the positive charge on chlorine and a negative charge on carbon oppose each other; (vi) 1,3-butadiene has sp^2-sp^2 C—C bond length, while *n*-butane has sp^3-sp^3 C—C bond length. More is '*s*' character in hybridization, lesser is bond length; (vii) (a) catenation, (b) carbon can link with other carbon atom with single, double and triple bonds. It can form bonds with other atoms also, (c) isomerism; (viii) The dipole moment of CCl_4 is zero inspite of four similar polar (C—Cl) bonds on account of symmetrical structure; (ix) The polarity of bond depends upon electronegativity difference of two atoms involved in covalence; (x) The size of Cl atom is large as compared to nitrogen and so it pulls the shared pair of electron from hydrogen atom less effectively and thus it does not possess appreciable partial charge to show hydrogen bonding.

14. (i) By fractional distillation; (ii) By sublimation; (iii) By chromatography; (iv) By simple distillation; (v) By distilling of water.

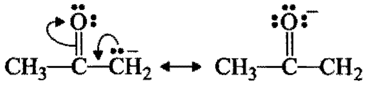
15. (iv) Allene are cummulative dienes, $\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H_2$ (Propa-1,2-diene). In allene C_1 and C_3 are sp^2-hybridized and C_2 is *sp*-hybridized. The two π-bonds are present in the central carbon, one each from p_y- and p_z-orbitals thus, overlapping planes in C_1 and C_3 are also different.



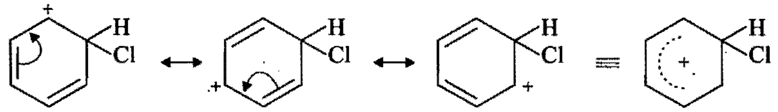
16. (A) (i) $:CH_2-C\equiv N \longleftrightarrow CH_2=C=\ddot{N}:$

(ii) $CH_3-CH=CH-\overset{+}{C}H-CH_3 \longleftrightarrow CH_3=\overset{+}{C}H-CH=CH-CH_3$

(iii) $\overset{+}{C}H_2-CH=CH-\overset{-}{C}H \longleftrightarrow \overset{-}{C}H_2-CH=CH-\overset{+}{C}H_2 \longleftrightarrow CH_2=CH-CH=CH_2$

(iv)


$CH_3-\overset{\ddot{O}:}{\overset{\|}{C}}-\ddot{C}H_2^- \longleftrightarrow CH_3-\overset{:\ddot{O}:^-}{\overset{\|}{C}}-CH_2$

(B)


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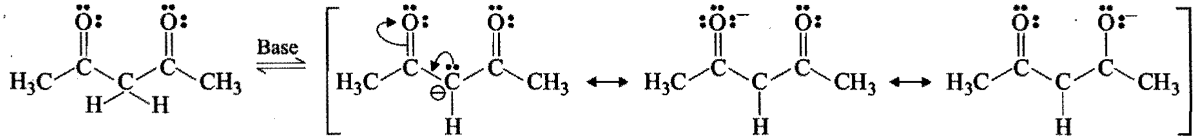

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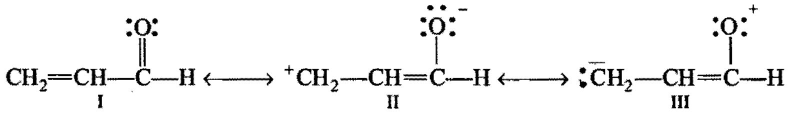


$$\underset{\text{I}}{CH_2=CH-\overset{:O:}{\overset{\|}{C}}-H} \longleftrightarrow \underset{\text{II}}{{}^+CH_2-CH=\overset{:\ddot{O}:^-}{\overset{|}{C}}-H} \longleftrightarrow \underset{\text{III}}{\bar{:}CH_2-CH=\overset{:O:^+}{\overset{|}{C}}-H}$$

Stability I > II > III

Structure I: More stable, because it has more number of covalent bonds and have no formal charge. Each carbon and oxygen atom has an Octet.

Structure II: Less stable, because it has negative charge on more electronegative atom and positive charge on more electropositive atom.

Structure III: Least stable, because it does not contribute as oxygen has positive charge and carbon has negative charge.

OBJECTIVE QUESTIONS

SET I : This set contains questions with single correct answer.

1. The property of catenation is strongest in carbon because:
(a) its ionisation potential is low ☐
(b) its electronegativity is low ☐
(c) the C—C bond energy is high ☐
(d) its atomic radius is small ☐

2. The main source of organic compounds is:
(a) vegetable kingdom ☐ (b) synthetic reactions ☐
(c) animal kingdom ☐ (d) petroleum ☐

3. The first organic compound prepared from inorganic compounds was:
(a) acetic acid ☐ (b) methane ☐
(c) urea ☐ (d) ethyl alcohol ☐

4. The first organic compound synthesised in the laboratory from its elements:
(a) urea ☐ (b) methane ☐
(c) ethylene ☐ (d) acetic acid ☐

5. The bond between carbon atom (1) and carbon atom (2) in compound $N\equiv\overset{1}{C}-\overset{2}{C}H=CH_2$, involves hybridization:
(a) sp^2 and sp^2 ☐ (b) sp^3 and sp ☐
(c) sp and sp^2 ☐ (d) sp and sp ☐

6. The C—H bond distance is the longest in: **[UGET (Med.) 2006]**
(a) C_2H_2 ☐ (b) C_2H_4 ☐
(c) C_2H_6 ☐ (d) $C_2H_2Br_2$ ☐

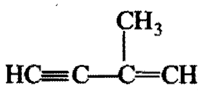
7. The enolic form of acetone contains:
(a) 9 sigma bonds, 1 pi bond and 2 lone pairs of electrons ☐
(b) 8 sigma bonds, 2 pi bonds and 2 lone pairs of electrons ☐
(c) 10 sigma bonds, 1 pi bond and 1 lone pair of electrons ☐
(d) 9 sigma bonds, 2 pi bonds and 1 lone pair of electrons ☐

8. The number of sigma and pi bonds in but-1-ene-3-yne are:
(a) 5 sigma and 5 pi ☐ (b) 7 sigma and 3 pi ☐
(c) 8 sigma and 2 pi ☐ (d) 6 sigma and 4 pi ☐

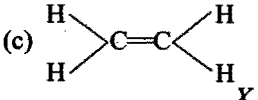
9. How many sigma and pi bonds are there in tetracyano ethylene molecule? **[BHU (Mains) 2008]**
(a) 9σ and 9π ☐ (b) 9σ and 7π ☐
(c) 5σ and 9π ☐ (d) 5σ and 7π ☐

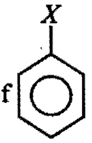
10. In benzene molecule, there are 3 pi bonds and:
(a) 3 sigma bonds ☐ (b) 6 sigma bonds ☐
(c) 10 sigma bonds ☐ (d) 12 sigma bonds ☐

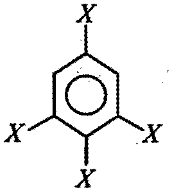
11. The compound buta-1,2-diene has: **[UGET (Med.) 2006]**
(a) only sp-hybridized carbon atom ☐
(b) only sp^2-hybridized carbon atom ☐
(c) both sp-and sp^2-hybridized carbon atoms ☐
(d) sp, sp^2-and sp^3-hybridized carbon atoms ☐
[**Hint :** The structure of buta-1,2-diene is $H_3C-HC=C=CH_2$]

12. In the compound  $HC\equiv C-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$, the hybridization of C_2 and C_3 carbons are respectively: **[JEE (WB) 2009]**
(a) sp^3 and sp^2 ☐ (b) sp^2 and sp^3 ☐
(c) sp^3 and sp ☐ (d) sp^2 and sp ☐

13. The Cl—C—Cl angle in 1,1,2,2-tetrachloroethene and tetrachloromethane will be about:
(a) 90° and 109.5° ☐ (b) 109.5° and 90° ☐
(c) 109.5° and 120° ☐ (d) 120° and 109.5° ☐

14. Which of the following molecules does not have net dipole moment ? **[AMU (Engg. 2010)]**
(a) CH_3-Br ☐ (b) CH_2Cl_2 ☐
(c)  ☐ (d) HCOOH ☐

15. Dipole moment of  is 1.5 D. The dipole moment of

 is : **[JEE (WB) 2010]**

(a) 1 D ☐ (b) 1.5 D ☐
(c) 2.25 D ☐ (d) 3 D ☐

16. The shape of acetylene molecule is:
(a) linear ☐ (b) planar ☐
(c) pyramidal ☐ (d) tetrahedral ☐

17. The compound in which carbon uses only its sp^3-hybrid orbitals for bond formation is:
(a) HCOOH ☐ (b) $(CH_3)_3COH$ ☐
(c) NH_2CONH_2 ☐ (d) $(CH_3)_3C-CHO$ ☐

18. The bond energy (in k cal mol^{-1}) of a C—C single bond is approximately : **[IIT 2010]**
(a) 1000 ☐ (b) 100 ☐
(c) 10 ☐ (d) 1 ☐

19. Which of the following bonds is strongest?
(a) $>C-C<$ ☐ (b) $>C=C<$ ☐
(c) $-C\equiv C-$ ☐ (d) None of these ☐

20. In which case, the carbon-carbon bond length is same?
(a) 2-butene ☐ (b) benzene ☐
(c) 1-butene ☐ (d) 1-propyne ☐

21. All carbon atoms are sp^2-hybridised in : **[PET (Kerala) 2010]**
(a) $HC\equiv C-C\equiv CH$ ☐ (b) $H_2C=C=CH_2$ ☐
(c) 2-butene ☐ (d) 1,3-butadine ☐
(e) cyclohexane ☐

22. Resonance is due to:
(a) delocalisation of sigma-electrons ☐
(b) delocalisation of pi-electrons ☐
(c) migration of H-atoms ☐
(d) migration of protons ☐

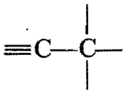
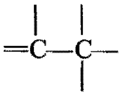
23. Resonance structures of a molecule do not have:
(a) identical arrangement of atoms ☐
(b) nearly the same energy content ☐
(c) the same number of paired electrons ☐
(d) identical bonding ☐

24. Which of the following statements is false about resonance?
(a) It increases stability of the molecule ☐
(b) It leads to similar type of bonding ☐
(c) It increases reactivity of the molecule ☐
(d) It decreases reactivity of the molecule ☐

25. How many sigma and pi-bonds are there in the molecule of dicyanoethene ($CN-CH=CH-CN$)?
(a) 3 sigma and 3 pi ☐ (b) 5 sigma and 2 pi ☐
(c) 7 sigma and 5 pi ☐ (d) 2 sigma and 3 pi ☐

26. Which of the following compounds shows evidence of the strongest hydrogen bonding ? **[JEE (WB) 2010]**
(a) Propane-1,2,3-triol ☐ (b) Propane-1,2-diol ☐
(c) Propan-1-ol ☐ (d) Propan-2-ol ☐

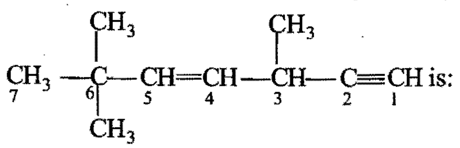
27. The hydrogen bond is strongest in which one of the following? **[DPMT 2006; AIEEE 2007]**
(a) $F-H---F$ ☐ (b) $O-H---O$ ☐
(c) $S-H---F$ ☐ (d) $F-H---O$ ☐

28. C—C bond length would be minimum in:
(a) 
$\equiv C-\overset{|}{\underset{|}{C}}-$ ☐
(b) 
$=\overset{|}{C}-\overset{|}{\underset{|}{C}}-$ ☐
(c) 
$=\underset{|}{C}-\underset{|}{C}=$ ☐
(d) $\equiv C-C\equiv$ ☐

29. C—H bond energy in ethane, ethene and ethyne is:
(a) equal in all the three compounds ☐
(b) maximum in ethane ☐
(c) maximum in ethene ☐
(d) maximum in ethyne ☐

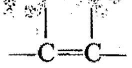
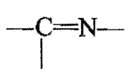
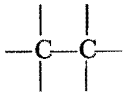
30. Hybridized carbon atoms used in the formation of the compound, $CH_3-CH=CH-CH_2-CH_3$ are:
(a) sp and sp^3 ☐ (b) sp and sp^2 ☐
(c) only sp ☐ (d) sp^2 and sp^3 ☐

31. The state of hybridization of C_2, C_3, C_5 and C_6 of the hydrocarbon, **[CBSE (Med.) 2009]**



$\underset{7}{CH_3}-\overset{CH_3}{\underset{CH_3}{\underset{6}{C}}}-\underset{5}{CH}=\underset{4}{CH}-\overset{CH_3}{\underset{3}{CH}}-\underset{2}{C}\equiv\underset{1}{CH}$ is:

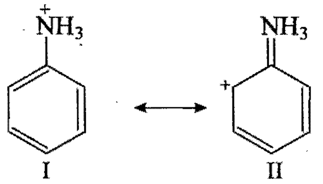
(a) sp, sp^3, sp^2 and sp^3 ☐ (b) sp, sp^2, sp^2 and sp^3 ☐
(c) sp, sp^2, sp^3 and sp^2 ☐ (d) sp^3, sp^2, sp^2 and sp ☐

32. Which bond is the smallest?
(a) 
$-\overset{|}{C}=\overset{|}{C}-$ ☐
(b) $>C=O$ ☐
(c) 
$-\underset{|}{C}=N-$ ☐
(d) 
$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$ ☐

33. Maximum hydrogen bonding would be observed in the compound:
(a) methanol ☐ (b) glycol ☐
(c) diethylamine ☐ (d) diethyl ether ☐

34. ...... bond is the most polar.
(a) $C-O$ ☐ (b) $C-Br$ ☐
(c) $C-S$ ☐ (d) $C-F$ ☐

35. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below.



(a) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions ☐
(b) II is not an acceptable canonical structure because it is non-aromatic ☐
(c) II is not an acceptable canonical structure because nitrogen has 10 valence electrons ☐
(d) II is acceptable canonical structure ☐

36. s-character of sp-sp^2-and sp^3-hybrid orbitals follows the decreasing order:
(a) $sp^3 > sp^2 > sp$ ☐ (b) $sp > sp^2 > sp^3$ ☐
(c) $sp^2 > sp^3 > sp$ ☐ (d) $sp^2 > sp > sp^3$ ☐

37. A straight chain hydrocarbon has the molecular formula, C_8H_{10}. The hybridization for the carbon atoms from one end of the chain to the other are sp^3, sp^2, sp^2, sp^3, sp^2, sp^2, sp and sp respectively. The structural formula of the hydrocarbon would be:
(a) $CH_3-C\equiv C-CH_2-CH=CH-CH=CH_2$ ☐
(b) $CH_3-CH=CH-CH_2-CH=CH-C\equiv CH$ ☐
(c) $CH_3-CH=CH-CH_2-C\equiv C-CH=CH_2$ ☐
(d) $CH_3-C\equiv C-CH_2-C\equiv C-CH=CH_2$ ☐

38. Which one of the following does not have sp^2-hybridized carbon? **[JCECE (Med.) 2008]**
(a) Acetone ☐ (b) Acetic acid ☐
(c) Acetonitrile ☐ (d) Acetamide ☐

39. Number of pi bonds in $H_2C=CH-CH=CH-C\equiv CH$ is:
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 5 ☐

40. Number of pi-electrons present in naphthalene is:
(a) 4 ☐ (b) 6 ☐
(c) 10 ☐ (d) 14 ☐

41. In a resonance hybrid, the bond length:
(a) is smaller than in canonical structure ☐
(b) is greater than in canonical structure ☐
(c) is the same as in canonical structure ☐
(d) none of the above ☐

42. Resonance energy of benzene is about so much kcal/mol:
(a) 35 ☐ (b) 58 ☐
(c) 100 ☐ (d) 109 ☐

43. Resonance in a molecule results in:
(a) destabilisation ☐
(b) stabilisation ☐
(c) increase in bond length ☐
(d) none of the above ☐

44. In which of the compounds below is there more than one kind of hybridization (sp, sp^2, sp^3) for carbon?
(i) $CH_3CH_2CH_2CH_3$ (ii) $CH_3—CH{=}CH—CH_3$
(iii) $H_2C{=}CH—CH{=}CH_2$ (iv) $H—C{\equiv}C—H$
(a) (i) and (iv) ☐ (b) (ii) and (iii) ☐
(c) (ii) ☐ (d) (iii) and (iv) ☐

45. Which of the following has a bond formed by overlap of sp^3-sp-hybrid orbitals?
(a) $CH_3—C{\equiv}C—CH_3$ ☐
(b) $CH_3—CH{=}CH—CH_3$ ☐
(c) $CH_2{=}CH—CH{=}CH_2$ ☐
(d) $HC{\equiv}CH$ ☐

46. Maximum amount of hydrogen bonding occurs in case of:
(a) HOH ☐ (b) HF ☐
(c) C_2H_5OH ☐ (d) NH_3 ☐

47. Intramolecular hydrogen bonding is exhibited by:
(a) *o*-nitrophenol ☐ (b) catechol ☐
(c) salicylic acid ☐ (d) all of these ☐

48. The maximum possible number of hydrogen bonds, a water molecule can form is: **[CET (Karnataka) 2008]**
(a) 4 ☐ (b) 3 ☐
(c) 2 ☐ (d) 1 ☐

49. Which of the following explanations accounts for *o*-nitrophenol to be more volatile than *p*-nitrophenol?
(a) Intermolecular hydrogen bonding ☐
(b) Resonance ☐
(c) Intramolecular hydrogen bonding ☐
(d) Inductive effect ☐

50. Bond energy is maximum in:
(a) O—O ☐ (b) C≡C ☐
(c) C≡N ☐ (d) N≡N ☐

51. The bond energy of C—C bond in kcal/mol is:
(a) 58 ☐ (b) 83 ☐
(c) 145 ☐ (d) 192 ☐

52. The maximum bond energy is present in:
(a) C—H ☐ (b) C—C ☐
(c) C—N ☐ (d) C—O ☐

53. Among the C—*X* bonds, the correct bond energy order is:
(a) C—Cl > C—Br > C—I ☐
(b) C—I > C—Cl > C—Br ☐
(c) C—Br > C—Cl > C—I ☐
(d) C—I > C—Br > C—Cl ☐

54. Arrange the following compounds in order of increasing dipole moment:
(i) toluene (ii) *m*-dichloro benzene
(iii) *o*-dichloro benzene (iv) *p*-dichloro benzene
(a) (i) < (iv) < (ii) < (iii) ☐
(b) (iv) < (i) < (ii) < (iii) ☐
(c) (iv) < (i) < (iii) < (ii) ☐
(d) (iv) < (ii) < (i) < (iii) ☐

55. Sublimation is a process in which a solid:
(a) changes into another allotropic form ☐
(b) changes into liquid form ☐
(c) changes into vapour form ☐
(d) none of the above ☐

56. Naphthalene is a volatile solid. It is best purified by:
(a) crystallisation ☐ (b) distillation ☐
(c) steam distillation ☐ (d) sublimation ☐

57. Methanol and acetone can be separated by:
(a) fractional distillation ☐ (b) distillation ☐
(c) steam distillation ☐ (d) vacuum distillation ☐

58. Separation of two substances by fractional crystallisation depends upon their differences in:
(a) densities ☐ (b) volatility ☐
(c) solubility ☐ (d) crystalline shape ☐

59. Aniline is separated from a mixture by:
(a) fractional crystallisation ☐
(b) fractional distillation ☐
(c) vacuum distillation ☐
(d) steam distillation ☐

60. Glycerol is purified by: **[PMT (Kerala) 2010]**
(a) steam distillation ☐ (b) vacuum distillation ☐
(c) sublimation ☐ (d) simple distillation ☐

61. Two immiscible liquids are separated by:
(a) separating funnel ☐ (b) fractional distillation ☐
(c) chromatography ☐ (d) sublimation ☐

62. Latest technique for purification, isolation and separation of organic compounds is: **[PMT (Kerala) 2007; Punjab CET (Engg.) 2008]**
(a) chromatography ☐ (b) steam distillation ☐
(c) crystallisation ☐ (d) vacuum distillation ☐

63. Steam distillation is applied to those organic compounds which are steam volatile and:
(a) soluble in water ☐
(b) insoluble in water ☐
(c) sparingly soluble in water ☐
(d) insoluble in all solvents ☐

64. There are several criteria for purity of organic compounds. Out of these which one is considered best?
(a) Melting point ☐
(b) Microscopic examination ☐
(c) Mixed melting point ☐
(d) Colour ☐

65. Two volatile and miscible liquids can be separated by fractional distillation into pure components under the conditions when:
(a) they have low boiling points ☐
(b) the difference in their boiling points is large ☐
(c) the boiling points of the liquids are close to each other ☐
(d) they do not form azeotropic mixture ☐

66. The boiling points of two miscible liquids, which do not form azeotropic mixture, are close to each other. Their separation is best carried out by:
(a) vacuum distillation ☐ (b) fractional distillation ☐
(c) steam distillation ☐ (d) redistillation ☐

67. In paper chromatography:
(a) the moving phase is a liquid and stationary phase is a solid ☐
(b) the moving phase is a solid and stationary phase is a liquid ☐
(c) both the phases are liquids ☐
(d) both the phases are solids ☐

68. Oils are purified by:
(a) fractional distillation ☐ (b) steam distillation ☐
(c) vacuum distillation ☐ (d) simple distillation ☐

69. Chromatography technique is used for the separation of:
(a) small samples of mixtures ☐
(b) plant pigments ☐
(c) dye stuffs ☐
(d) all of the above ☐

70. A mixture of naphthalene and benzoic acid can be separated by: **[JIPMER 2007]**
(a) chromatography ☐
(b) sublimation ☐
(c) fractional crystallisation ☐
(d) distillation ☐

71. In column chromatography, the moving phase is:
(a) the substances which are to be separated ☐
(b) eluent ☐
(c) adsorbent ☐
(d) mixture of eluent and substances to be separated ☐

72. Azeotropic mixtures:
(a) boil at different temperatures ☐
(b) are mixtures of solids ☐
(c) are constant boiling mixtures ☐
(d) none of the above ☐

73. Which is useful for the separating benzoic acid from methyl benzoate?
(a) Aq. $NaHCO_3$ ☐ (b) Dil. HCl ☐
(c) Aq. $NaHSO_3$ ☐ (d) Dil. H_2SO_4 ☐

74. A mixture of camphor and benzoic acid can be easily separated by: **[BHU 2005]**
(a) sublimation ☐
(b) fractional distillation ☐
(c) chemical method ☐
(d) extraction with solvents ☐

75. Anthracene is purified by:
(a) filtration ☐ (b) distillation ☐
(c) crystallisation ☐ (d) sublimation ☐

76. Which of the following is useful for making pure water from a solution of salt in water?
(a) Filtration ☐ (b) Simple distillation ☐
(c) Steam distillation ☐ (d) Chromatography ☐

77. Water and alcohol can be separated from a mixture by:
(a) fractional distillation ☐ (b) sublimation ☐
(c) decantation ☐ (d) evaporation ☐

78. A mixture of water and NaCl can be separated by:
(a) sublimation ☐ (b) evaporation ☐
(c) decantation ☐ (d) filtration ☐

79. In laboratory, solvent can be separated from solute by the process:
(a) decantation ☐ (b) sedimentation ☐
(c) distillation ☐ (d) filtration ☐

80. In simple distillation of liquids, it involves simultaneously:
(a) vaporisation and condensation ☐
(b) heating and sublimation ☐
(c) vaporisation and sublimation ☐
(d) boiling and filtration ☐

81. Distillation under reduced pressure is used to purify liquids which:
(a) are highly volatile ☐
(b) have high boiling points ☐
(c) are explosives ☐
(d) decomposes below their boiling points ☐

82. Which one of the following reagents is useful for separating aniline from nitrobenzene?
(a) Aq. $NaHCO_3$ ☐ (b) Aq. $NaHSO_3$ ☐
(c) Aq. HCl ☐ (d) Dilute H_2SO_4 ☐

83. A mixture of phenol and benzoic acid will completely dissolve in an aqueous solution of:
(a) HCl ☐ (b) NaCl ☐
(c) $NaHCO_3$ ☐ (d) NaOH ☐

84. Silica gel is used for keeping away the moisture because it:
(a) adsorbs water molecule ☐
(b) absorbs water molecule ☐
(c) reacts with water ☐
(d) none of the above ☐

85. Anhydrous $CaCl_2$ is used as drying agent, because it:
(a) adsorbs water molecule ☐
(b) absorbs water molecule ☐
(c) both adsorbs and absorbs water molecule ☐
(d) none of the above ☐

86. The function of fractionating column is:
(a) to separate the two components ☐
(b) to provide greater cooling surface to the vapours ☐
(c) to kept the vapour pressure constant ☐
(d) to avoid mixing of the vapours of two components ☐

87. One having high vapour pressure at temperature below its melting point is:
(a) benzoic acid ☐ (b) salicylic acid ☐
(c) citric acid ☐ (d) all of these ☐

88. Osazone formation is used to separate and identify:
(a) alcohols ☐ (b) carboxylic acids ☐
(c) carbohydrates ☐ (d) starch ☐

89. Fractional distillation is used to separate liquids which differ in their boiling points by:
(a) 0–10° C ☐ (b) 10–20° C ☐
(c) 20–40° C ☐ (d) 40–80° C ☐

90. Which of the substance is purified by sublimation? **[DCE (Engg.) 2007]**
(a) Naphthalene ☐ (b) Benzoic acid ☐
(c) Camphor ☐ (d) All of these ☐

91. A mixture of oil and water is separated by:
(a) filtration ☐
(b) using separating funnel ☐
(c) sublimation ☐
(d) fractional distillation ☐

92. Styrene can be purified by: **[JIPMER 2008]**
(a) simple distillation ☐ (b) fractional distillation ☐
(c) vacuum distillation ☐ (d) steam distillation ☐

93. (*A*) is a higher phenol and (*B*) is an aromatic carboxylic acid. Separation of a mixture of (*A*) and (*B*) can be carried out easily by using a solution of:
(a) NaOH ☐ (b) lime ☐
(c) $NaHCO_3$ ☐ (d) Na_2CO_3 ☐

94. Which is correct statement about azeotropic mixture?
(a) It boils at constant temperature ☐
(b) It does not obey Raoult's law ☐
(c) It cannot be separated by fractional distillation ☐
(d) All of the above ☐

95. Separation of organic compounds by column chromatography is due to:
(a) selective absorption ☐
(b) selective adsorption ☐
(c) both absorption and adsorption ☐
(d) solubilities ☐

96. The technique of gas liquid chromatography is suitable for compounds which are:
(a) soluble in water ☐
(b) highly volatile ☐
(c) vaporise without decomposition ☐
(d) liquids ☐

97. Two substances when separated out on the basis of their extent of adsorption, by one material, the phenomenon is called:
(a) chromatography ☐ (b) paper chromatography ☐
(c) steam distillation ☐ (d) sublimation ☐

98. When a hybridization state of carbon atom changes from sp^3 to sp^2 and finally to *sp*, the angle between the hybridized orbitals:
(a) is not affected ☐
(b) increases progressively ☐
(c) decreases gradually ☐
(d) decreases considerably ☐

99. Allyl isocyanide has:
(a) 9 sigma and 4 pi bonds ☐
(b) 8 sigma and 5 pi bonds ☐
(c) 8 sigma, 3 pi and 4 non-bonded electrons ☐
(d) 9 sigma, 3 pi and 2 non-bonded electrons ☐

100. In the compound $CH_2{=}CH{-}CH_2{-}CH_2{-}C{\equiv}CH$, the $C_2{-}C_3$ bond is of the type:
(a) $sp\text{-}sp^2$ ☐ (b) $sp^3\text{-}sp^3$ ☐
(c) $sp\text{-}sp^3$ ☐ (d) $sp^2\text{-}sp^3$ ☐

101. *p*-nitrophenol and *o*-nitrophenol are separated by: **[DPMT 2003; PMET (Punjab) 2008]**
(a) crystallisation ☐ (b) fractional distillation ☐
(c) distillation ☐ (d) steam distillation ☐

102. Intermolecular hydrogen bonding is strongest in: **[AIIMS 2003]**
(a) methylamine ☐ (b) phenol ☐
(c) formaldehyde ☐ (d) methanol ☐

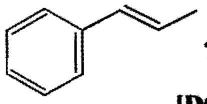
103. In the compound $H_2\overset{1}{C}{=}\overset{2}{C}{=}\overset{3}{C}H{-}\overset{4}{C}H_3$, the hybridization of 1st and 2nd carbon atom is: **[BHU 2003]**
(a) $sp^3\text{-}sp$ ☐ (b) $sp^2\text{-}sp^3$ ☐
(c) $sp^2\text{-}sp$ ☐ (d) $sp^2\text{-}sp^2$ ☐

104. Camphor is often used in molecular mass determination because: **[CBSE (Med.) 2004]**
(a) it is readily available ☐
(b) it has very high cryoscopic constant ☐
(c) it is volatile ☐
(d) it is a solvent for organic substances ☐

105. How will you separate a solution (miscible) of benzene + $CHCl_3$? **[AFMC 2005]**
(a) Distillation ☐ (b) Sublimation ☐
(c) Filtration ☐ (d) Crystallisation ☐

106. Allyl cyanide contains σ and π-bonds: **[PMT (MP) 2004]**
(a) $5\sigma, 7\pi$ ☐ (b) $9\sigma, 3\pi$ ☐
(c) $3\sigma, 4\pi$ ☐ (d) $9\sigma, 9\pi$ ☐

107. Which of the following gives correct arrangement of compounds involved based on their bond strength? **[BHU 2005]**
(a) HF > HCl > HBr > HI ☐ (b) HI > HBr > HCl > HF ☐
(c) HF > HBr > HCl > HI ☐ (d) HCl > HF > HBr > HI ☐

108. How many bonds are there in  ? **[DCE 2005]**
(a) $14\sigma, 8\pi$ ☐ (b) $18\sigma, 8\pi$ ☐
(c) $19\sigma, 4\pi$ ☐ (d) $14\sigma, 2\pi$ ☐

109. The correct order regarding the electronegativity of hybrid orbitals of carbon is: **[CBSE (Med.) 2006]**
(a) $sp < sp^2 > sp^3$ ☐ (b) $sp < sp^2 < sp^3$ ☐
(c) $sp > sp^2 < sp^3$ ☐ (d) $sp > sp^2 > sp^3$ ☐

110. Among the following mixtures, dipole-dipole as the major interaction is present in: **[AIEEE 2006]**
(a) benzene and ethanol ☐
(b) acetonitrile and acetone ☐
(c) KCl and water ☐
(d) benzene and carbon tetrachloride ☐

111. Consider the following compounds:

(A) chloroethene (B) benzene
(C) buta-1,3-diene (D) 1,3,5-hexatriene

All the carbon atoms are sp^2-hybridized in:
[PET (Kerala) 2006]

(a) A, C, D only ☐ (b) A, B only ☐
(c) B, C, D only ☐ (d) C, D only ☐
(e) A, B, C, D ☐

112. The decreasing order of bond dissociation energies of C—C, C—H and H—H bonds is:
[EAMCET (Engg.) 2007]

(a) H—H > —C—H > —C—C— ☐
(b) —C—C— > —C—H > H—H ☐
(c) —C—H > —C—C— > H—H ☐
(d) —C—C— > H—H > —C—H ☐

113. Number of σ and π-bonds in C_6H_5COOH is:
[DPMT 2007]

(a) 13σ, 4π ☐ (b) 14σ, 4π ☐
(c) 15σ, 4π ☐ (d) 16σ, 4π ☐

114. Compare List I and List II and choose the correct matching codes from the choices given:

List I	List II
(A) Glycerol	(i) Sublimation
(B) *o*-nitrophenol	(ii) Beilstein's test
(C) Anthracene	(iii) Victor-Meyer's method
(D) Halogens	(iv) Steam distillation
(E) Molecular weight	(v) Vacuum distillation
	(vi) Eudiometry

Codes: **[PET (Kerala) 2007]**

(a) (A—v), (B—iv), (C—i), (D—ii), (E—iii) ☐
(b) (A—iv), (B—v), (C—i), (D—vi), (E—ii) ☐
(c) (A—vi), (B—iv), (C—i), (D—iii), (E—ii) ☐
(d) (A—v), (B—iv), (C—vi), (D—ii), (E—iii) ☐
(e) (A—iv), (B—vi), (C—ii), (D—iii), (E—v) ☐

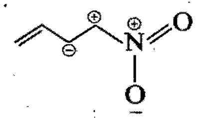
115. Which one of the following can be purified by sublimation?
[MHCET (Med.) 2007]

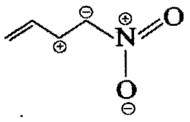
(a) F_2 ☐ (b) Cl_2 ☐
(c) Br_2 ☐ (d) I_2 ☐

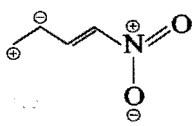
116. What is the percentage of *p*-character of hybrid orbits of carbon in methane, ethene and ethyne respectively?
[SCRA (Med.) 2007]

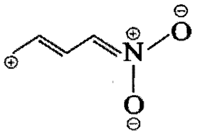
(a) 75, 66, 50 ☐ (b) 50, 66, 75 ☐
(c) 25, 33, 50 ☐ (d) 50, 33, 25 ☐

117. In the following the least stable resonance structure is:
[IIT 2007]

(a)


(b)


(c)


(d)


118. Which one of the following arrangements does not give the correct picture of the trends indicated against is?
[CPMT (Med.) 2008]

(a) $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy ☐
(b) $F_2 > Cl_2 > Br_2 > I_2$: Electronegativity ☐
(c) $F_2 > Cl_2 > Br_2 > I_2$: Oxidising power ☐
(d) $F_2 > Cl_2 > Br_2 > I_2$: Electron gain enthalpy ☐

119. In the hydrocarbon,

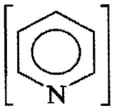
$$\underset{6}{H_3C}—\underset{5}{CH}=\underset{4}{CH}—\underset{3}{CH_2}—\underset{2}{C}\equiv\underset{1}{CH}$$

The state of hybridization of carbons 1,3,5 are in the following sequence: **[CPMT (Med.) 2008]**

(a) sp, sp^2, sp^3 ☐ (b) sp^3, sp^2, sp ☐
(c) sp^2, sp, sp^3 ☐ (d) sp, sp^3, sp^2 ☐

120. The enolic form of butanone contains:
[PMT (Kerala) 2008]

(a) 12σ bonds, 1π bond and 2 lone pairs of electrons ☐
(b) 11σ bonds, 1π bond and 2 lone pairs of electrons ☐
(c) 12σ bonds, 1π bond and 1 lone pair of electrons ☐
(d) 10σ bonds, 2π bonds and 2 lone pairs of electrons ☐
(e) 13σ bonds, 1π bond and 2 lone pairs of electrons ☐

121. Hybridization of nitrogen atom in pyridine

is:
[BHU (Mains) 2008]

(a) sp^3 ☐ (b) sp^2 ☐
(c) sp ☐ (d) sp^3d ☐

122. The number of π-bonds in the following compound $O_2N—C\equiv C—NO_2$ is: **[DPMT 2008]**

(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 1 ☐

123. The compound in which underlined carbon uses only its sp^3-hybrid orbitals for bond formation is:
[BCECE (Med.) 2008]

(a) $CH_3\underline{C}OOH$ ☐ (b) $CH_3\underline{C}ONH_2$ ☐
(c) $CH_3\underline{C}H_2OH$ ☐ (d) $CH_3\underline{C}H=CH_2$ ☐

124. Match the following:

(A) Simple distillation	(i) to separate the liquids which are steam volatile, insoluble in water and contains non-volatile impurities
(B) Fractional distillation	(ii) to separate liquids which decomposes at a temperature below their normal boiling points
(C) Vacuum distillation	(iii) to separate two or more liquids which have boiling points close to each other.
(D) Steam distillation	(iv) to separate liquid from non-volatile impurities

	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iv)	(iii)	(ii)	(i)
(c)	(iii)	(i)	(iv)	(ii)
(d)	(ii)	(iv)	(i)	(iii)

125. Match the following:

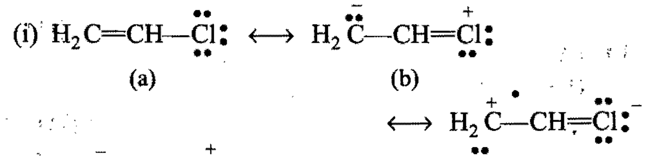
(A) Sublimation	(i) Ether + toluene
(B) Distillation	(ii) *o*-Nitrophenol + *p*-nitrophenol

(C) Vacuum distillation (iii) Benzoic acid + benzaldehyde
(D) Steam distillation (iv) Glycerol from spent lye

	A	B	C	D
(a)	(iv)	(iii)	(ii)	(i)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(iii)	(i)	(iv)	(ii)
(d)	(ii)	(iv)	(i)	(iii)

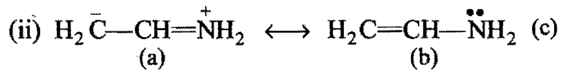
SET II : This set contains the questions having one or more correct answers.

126. Which resonance form in each of the following sets is the major contributor to the real structure?



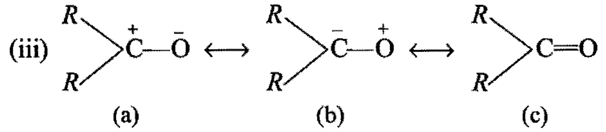
(i) $H_2C=CH-\overset{..}{\underset{..}{Cl}}: \longleftrightarrow H_2\overset{-}{\ddot{C}}-CH=\overset{+}{\underset{..}{Cl}}: \longleftrightarrow H_2\overset{+\,\bullet}{C}-CH=\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}:^{-}$

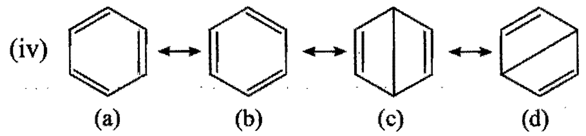
(a) (b)

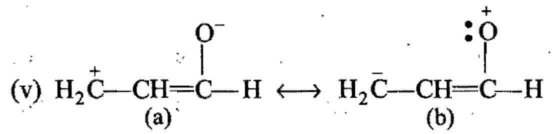


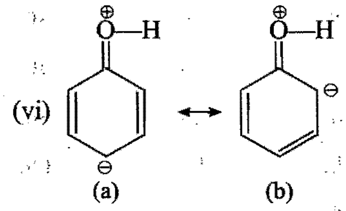
(ii) $H_2\overset{-}{C}-CH=\overset{+}{N}H_2 \longleftrightarrow H_2C=CH-\ddot{N}H_2$ (c)

(a) (b)









127. Chromatography technique is used in the separation of:
(a) volatile liquids ☐ (b) amino acids ☐
(c) plant pigments ☐ (d) sugars ☐

128. Mixed melting point is determined to check:
(a) the purity of organic compound ☐
(b) whether the two compounds are same ☐
(c) whether the two compounds are different ☐
(d) whether the two compounds can be separated by fractional crystallisation method ☐

129. Which of the following compounds can be purified by vacuum distillation?
(a) Glycerine ☐ (b) Glycerol ☐
(c) Propane-1,2,3-triol ☐ (d) Ethanol ☐

130. Which of the following compounds can be purified by steam distillation?
(a) Salicylaldehyde ☐
(b) Bromobenzene ☐
(c) *p*-Hydroxy benzaldehyde ☐
(d) Nitrobenzene ☐

131. Mixture of benzene and aniline can be separated by:
(a) distillation ☐ (b) steam distillation ☐
(c) dil. HCl ☐ (d) dil. NaOH ☐

132. Absolute alcohol can be prepared from rectified spirit by:
(a) azeotropic distillation with benzene ☐
(b) fractional distillation ☐
(c) keeping over fresh CaO for few hours and then distilling ☐
(d) distillation under reduced pressure ☐

133. Select the wrong statements about chromatography.
(a) Moving phase is liquid and stationary phase is solid ☐
(b) Moving phase is liquid and stationary phase is liquid ☐
(c) Moving phase is solid and stationary phase is solid ☐
(d) Moving phase is solid and stationary phase is liquid ☐

134. A substance which decomposes at or below its boiling point cannot be purified by:
(a) steam distillation ☐
(b) simple distillation ☐
(c) fractional distillation ☐
(d) distillation under reduced pressure ☐

135. Refining of petroleum does not involve :
(a) simple distillation ☐
(b) steam distillation ☐
(c) fractional distillation ☐
(d) distillation under reduced pressure ☐

ASSERTION-REASON TYPE QUESTIONS

Instructions: Each question contains **statement-1** (Assertion, **A**) and **statement-2** (Reason, **R**). Of these statements mark correct choice if

(a) Statement-1 **(A)** and statement-2 **(R)** are true and statement-2 **(R)** is the correct explanation for statement-1 **(A)**.
(b) Statement-1 **(A)** and statement-2 **(R)** are true and statement-2 **(R)** is not the correct explanation for statement-1 **(A)**.
(c) Statement-1 **(A)** is true, statement-2 **(R)** is false.
(d) Statement-1 **(A)** is false, statement-2 **(R)** is true.

1. (A) Oils are purified by steam distillation.
(R) The compounds which decompose at their boiling points can be purified by steam distillation.
[AIIMS 2008]

2. (A) Mixture of glucose and *m*-dinitrobenzene can be separated by shaking it with ether.

(R) Glucose is soluble in water.

3. (A) Thiophene present in benzene as impurity can be removed by shaking the mixture with cold conc. H_2SO_4.
   (R) Thiophene is a heterocyclic aromatic compound.
4. (A) A mixture of camphor and benzoic acid cannot be separated by sublimation.
   (R) Camphor on heating sublimes but benzoic acid does not.
5. (A) A mixture of *o*-nitrophenol and *p*-nitrophenol can be separated by steam distillation.
   (R) *o*-nitrophenol is steam volatile but *p*-nitrophenol is not though both are water soluble.
6. (A) Acetone (b.pt. 329K) and methyl alcohol (b.pt. 338 K) are separated by fractional distillation.
   (R) Fractional distillation helps in separating two liquids from their mixture when their boiling points differ by 10°C.
7. (A) Aniline has odd molecular mass, *i.e.*, 93.
   (R) All nitrogenous compounds containing odd no. of nitrogen has odd molecular mass.
8. (A) Molecular nitrogen is less reactive than molecular oxygen.
   (R) The bond length of N_2 is shorter than that of oxygen.
9. (A) *p*-hydroxy benzoic acid has a lower boiling point than *o*-hydroxy benzoic acid.
   (R) *o*-hydroxy benzoic acid has intramolecular hydrogen bonding. **[IIT 2007]**
10. (A) Chlorine has higher electron affinity than fluorine.
    (R) Chlorine is a poor oxidising agent than fluorine. **[AIIMS 2007]**

ANSWERS

OBJECTIVE QUESTIONS

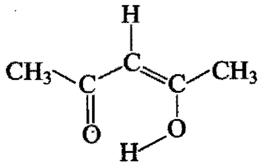
1. (c)	**2.** (b)	**3.** (c)	**4.** (d)	**5.** (c)	**6.** (c)	**7.** (a)	**8.** (b)	**9.** (a)	**10.** (d)
11. (d)	**12.** (d)	**13.** (d)	**14.** (c)	**15.** (b)	**16.** (a)	**17.** (b)	**18.** (b)	**19.** (c)	**20.** (b)
21. (d)	**22.** (b)	**23.** (d)	**24.** (c)	**25.** (c)	**26.** (a)	**27.** (a)	**28.** (d)	**29.** (d)	**30.** (d)
31. (a)	**32.** (b)	**33.** (a)	**34.** (d)	**35.** (c)	**36.** (b)	**37.** (b)	**38.** (c)	**39.** (c)	**40.** (c)
41. (a)	**42.** (a)	**43.** (b)	**44.** (c)	**45.** (a)	**46.** (b)	**47.** (d)	**48.** (a)	**49.** (c)	**50.** (d)
51. (b)	**52.** (a)	**53.** (a)	**54.** (b)	**55.** (c)	**56.** (d)	**57.** (a)	**58.** (c)	**59.** (d)	**60.** (b)
61. (a)	**62.** (a)	**63.** (b)	**64.** (c)	**65.** (d)	**66.** (b)	**67.** (c)	**68.** (b)	**69.** (d)	**70.** (a)
71. (d)	**72.** (c)	**73.** (a)	**74.** (c)	**75.** (d)	**76.** (b)	**77.** (a)	**78.** (b)	**79.** (c)	**80.** (a)
81. (d)	**82.** (c)	**83.** (d)	**84.** (a)	**85.** (b)	**86.** (b)	**87.** (a)	**88.** (c)	**89.** (a)	**90.** (d)
91. (b)	**92.** (d)	**93.** (c)	**94.** (d)	**95.** (b)	**96.** (c)	**97.** (a)	**98.** (b)	**99.** (d)	**100.** (d)
101. (d)	**102.** (d)	**103.** (c)	**104.** (c)	**105.** (a)	**106.** (b)	**107.** (a)	**108.** (c)	**109.** (d)	**110.** (b)
111. (e)	**112.** (a)	**113.** (c)	**114.** (a)	**115.** (d)	**116.** (a)	**117.** (a)	**118.** (a)	**119.** (d)	**120.** (a)
121. (b)	**122.** (c)	**123.** (c)	**124.** (b)	**125.** (c)	**126.** (i) (a) (ii) (b) (iii) (c) (iv) (a,b) (v) (a) (vi) (b)				
127. (b,c,d)	**128.** (a,b,c)	**129.** (a,b,c)	**130.** (a,b,d)	**131.** (a,c)	**132.** (a,c)	**133.** (a,c,d)	**134.** (a,b,c)	**135.** (a,c,d)	

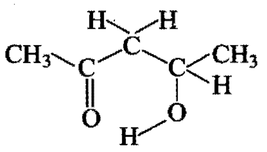
ASSERTION-REASON TYPE QUESTIONS

1. (c)	**2.** (b)	**3.** (b)	**4.** (c)	**5.** (a)	**6.** (a)	**7.** (a)	**8.** (a)	**9.** (d)	**10.** (c)

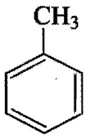
BRAIN STORMING PROBLEMS

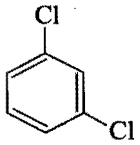
1.  , This hydrocarbon has hybridization on C-atoms:
   (a) sp, sp^2, sp^3 ☐ (b) sp, sp^2 ☐
   (c) sp^2, sp^3 ☐ (d) sp, sp^3 ☐
2. 1°, 2°, 3° and 4° carbon atoms are present in:
   (a) 2,2,3-trimethyl pentane ☐
   (b) 2,3,4-trimethyl pentane ☐
   (c) both (a) and (b) ☐
   (d) none of the above ☐
3. Two molecules indicated below are capable to intra-molecular H-bonding. Which is likely to form more stable hydrogen bonds?

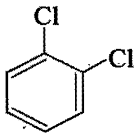

(I)

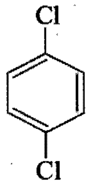

(II)

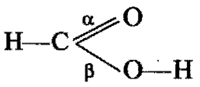
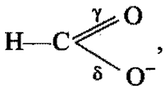
   (a) I ☐
   (b) II ☐
   (c) Both are equally capable ☐
   (d) Cannot be predicted ☐
4. Which one of the underlined carbons is sp^3-hybridized?
   (a) $CH_3\underline{C}H{=}CH_2$ ☐ (b) $CH_3\underline{C}H_2NH_2$ ☐
   (c) $CH_3\underline{C}ONH_2$ ☐ (d) $CH_3CH_2\underline{C}N$ ☐
5. The hybridization of iodine in iodosobenzene is :
   (a) sp ☐ (b) sp^2 ☐
   (c) sp^3 ☐ (d) sp^3d ☐
6. Carboxylic acids do not give the characteristic reactions of $>C{=}O$ group because of :
   (a) polar nature ☐ (b) resonance ☐
   (c) symmetrical structure ☐ (d) attached alkyl group ☐
7. Which among the following has highest boiling point?
   (a) $CH_3CH_2CH_2CH_2Cl$ ☐
   (b) $(CH_3)_2CHCH_2Cl$ ☐
   (c) $(CH_3)_3C{-}Cl$ ☐
   (d) None of the above ☐
8. Which among the following has highest melting point?
   (a) $(CH_3CO)_2O$ ☐ (b) CH_3CN ☐
   (c) CH_3CONH_2 ☐ (d) CH_3COCl ☐
   [**Hint :** (c) Amide has highest melting point due to formation of intermolecular hydrogen bonding.]
9. Order of arrangement of the following compounds with increasing dipole moment is :

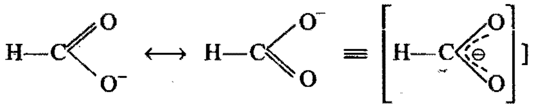
(i) 

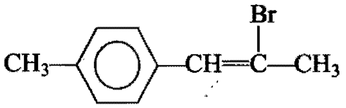
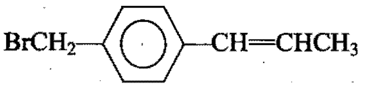
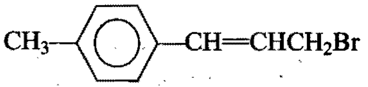
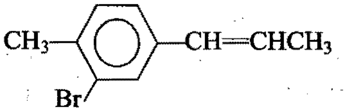
(ii) 

(iii) 

(iv) 

   (a) (i) < (iv) < (ii) < (iii) ☐ (b) (iv) < (i) < (ii) < (iii) ☐
   (c) (iv) < (i) < (iii) < (ii) ☐ (d) (iv) < (ii) < (i) < (iii) ☐
10.   , C—O bond lengths designated by α, β, γ and δ are in order:
   (a) $\alpha = \gamma < \beta = \delta$ ☐ (b) $\alpha < \beta < \gamma = \delta$ ☐
   (c) $\alpha < \gamma = \delta < \beta$ ☐ (d) all are equal ☐
   [**Hint :** Length of γ and δ will be same due to the resonance.



11. Which one of the following compounds is an allylic halide?
   (a)  ☐
   (b)  ☐
   (c)  ☐
   (d)  ☐
   [**Hint :** (a) is vinylic (b) is benzylic
   (c) is allylic (d) is arylic]
12. The compound in which all carbon atoms use only sp^3-hybrid orbitals for bond formation is:
   (a) CH_3CHO ☐ (b) CH_3COCH_3 ☐
   (c) $(CH_3)_3COH$ ☐ (d) $HCOOH$ ☐
13. Which of the following is unacceptable resonating structure of buta-1,2,3-triene?
   (a) $\ddot{\bar{C}}H_2{-}C{\equiv}C{-}\overset{\oplus}{C}H_2$ ☐ (b) $CH_2{=}C{=}C{=}CH_2$ ☐
   (c) $\overset{\oplus}{C}H_2{-}C{\equiv}C{-}\ddot{\bar{C}}H_2$ ☐ (d) $\dot{C}H_2{-}C{\equiv}C{-}\dot{C}H_2$ ☐

14. The resonating structures of cyanate ion are,

$$\underset{\text{(i)}}{O{=}C{=}N^-} \longleftrightarrow \underset{\text{(ii)}}{{}^-O{-}C{\equiv}N} \longleftrightarrow \underset{\text{(iii)}}{{}^+O{\equiv}C{-}N^{2-}}$$

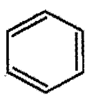
The correct set of oxidation states of O, C, and N respectively with the most stable structure out of the above is:

(a) (i) $-3, +4, -2$ ☐ (b) (ii) $-2, +4, -3$ ☐

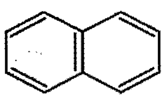
(c) (iii) $-1, +4, -3$ ☐ (d) (i) $0, +4, -5$ ☐

15. Arrange the following molecules in increasing order of σ to π bond ratio:

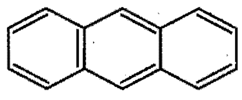
(1)



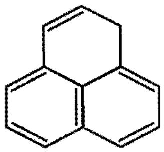
(2)



(3)



(4)



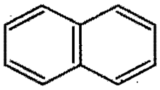
(a) $2<3<4<1$ ☐ (b) $2<4<3<1$ ☐

(c) $3<2<1<4$ ☐ (d) $2<3<1<4$ ☐

[**Hint:**

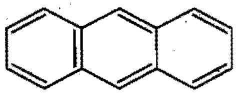
12σ, 3π

$\frac{\sigma}{\pi} = \frac{4}{1} = 4$



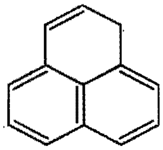
19σ, 5π

$\frac{\sigma}{\pi} = \frac{19}{5} = 3.8$



26σ, 7π

$\frac{\sigma}{\pi} = \frac{26}{7} = 3.71$



25σ, 6π

$\frac{\sigma}{\pi} = \frac{25}{6} = 4.166$]

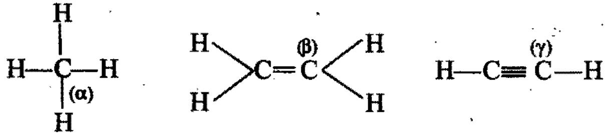
16. Which one of the following ions is the most resonance stabilized ? **[PMT (Kerala) 2010]**

(a) Ethoxide ☐ (b) *iso*-Propoxide ☐

(c) *n*-Butoxide ☐ (d) *tert.* Butoxide ☐

(e) Phenoxide ☐

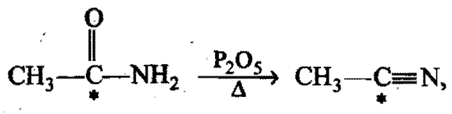
17. Arrange the following C—H bonds (α, β, γ) in decreasing order of bond energy :



(a) $\alpha>\beta>\gamma$ ☐ (b) $\gamma>\beta>\alpha$ ☐

(c) $\beta>\alpha>\gamma$ ☐ (d) $\gamma>\alpha>\beta$ ☐

18. In the reaction,



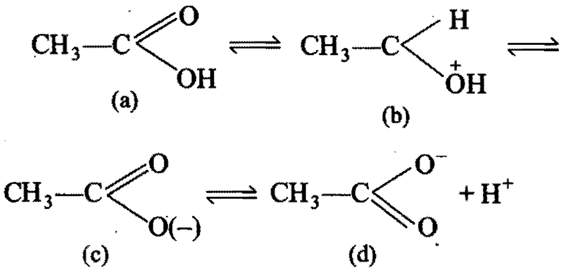
$$CH_3-\underset{*}{\overset{O}{\overset{\|}{C}}}-NH_2 \xrightarrow[\Delta]{P_2O_5} CH_3-\underset{*}{C}{\equiv}N,$$

the hybridization state of marked carbon atom changes from:

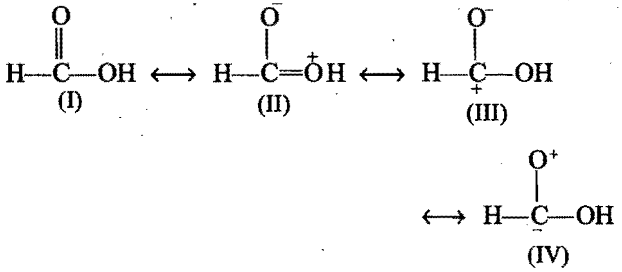
(a) sp^2 to sp ☐ (b) sp^3 to sp ☐

(c) sp^3 to sp^2 ☐ (d) sp^2 to sp^3 ☐

19. Which of the following structures have resonance stability?



20. Arrange the following resonating structures of formic acid in order of decreasing stability :



$$\underset{\text{(I)}}{H-\overset{O}{\overset{\|}{C}}-OH} \longleftrightarrow \underset{\text{(II)}}{H-\overset{O^-}{\overset{|}{C}}=\overset{+}{O}H} \longleftrightarrow \underset{\text{(III)}}{H-\overset{O^-}{\overset{|}{\underset{+}{C}}}-OH} \longleftrightarrow \underset{\text{(IV)}}{H-\overset{O^+}{\overset{|}{C}}-OH}$$

(a) II > I > III > IV ☐ (b) I > III > II > IV ☐

(c) III > II > IV > I ☐ (d) IV > III > I > II ☐

21. Arrange the following resonating structures of vinyl chloride in order of decreasing stability :

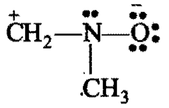
$$\underset{\text{(I)}}{CH_2{=}CH{-}Cl} \longleftrightarrow \underset{\text{(II)}}{\overset{-}{C}H_2{-}CH{=}\overset{+}{Cl}} \longleftrightarrow \underset{\text{(III)}}{\overset{+}{C}H_2{-}CH{=}\overline{Cl}}$$

(a) I > II > III ☐ (b) III > II > I ☐

(c) II > I > III ☐ (d) I > II ≡ III ☐

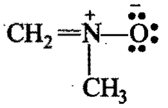
22. Among the following four structures, one is not a permissible resonance form. Identify the wrong structure.

(a)



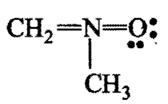
$\overset{+}{C}H_2-\underset{CH_3}{\underset{|}{\ddot{N}}}-\ddot{\underset{..}{O}}\!:$ ☐

(b)



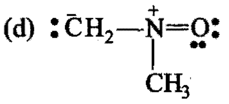
$CH_2=\underset{CH_3}{\underset{|}{\overset{+}{N}}}-\ddot{\underset{..}{O}}\!:$ ☐

(c)



$CH_2=\underset{CH_3}{\underset{|}{N}}=\underset{..}{O}\!:$ ☐

(d)



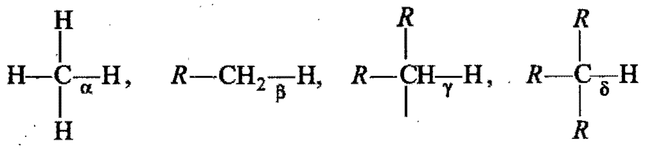
$:\overset{-}{C}H_2-\underset{CH_3}{\underset{|}{\overset{+}{N}}}=\underset{..}{O}\!:$ ☐

23. Which of the following compounds has (have) *sp*-hybridized carbon atom?

(a) $CH_2{=}C{=}O$ ☐ (b) $CH_2{=}CH{-}CN$ ☐

(c) $CH_3{-}CH{=}CH_2$ ☐ (d) $H_2C{=}O$ ☐

24. Identify the weakest C—H bond among the following :

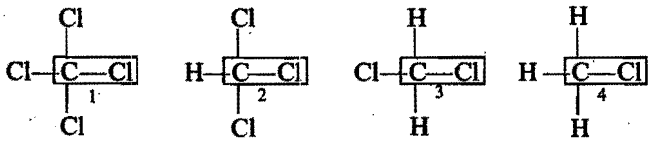


$$H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}\underset{\alpha}{-}H,\quad R-CH_2\underset{\beta}{-}H,\quad R-\underset{|}{\overset{R}{\overset{|}{C}H}}\underset{\gamma}{-}H,\quad R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}\underset{\delta}{-}H$$

(a) α ☐ (b) β ☐
(c) γ ☐ (d) δ ☐

25. Which of the following is the correct sequence of the bond length?
(a) S—H > C—H > N—H > O—H ☐
(b) C—H > S—H > O—H > N—H ☐
(c) O—H > N—H > C—H > S—H ☐
(d) S—H > O—H > N—H > C—H ☐

26. Arrange the following bonds in decreasing order of bond length:



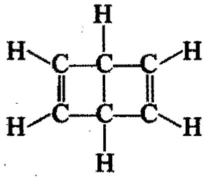
(a) 1 > 2 > 3 > 4 ☐ (b) 4 > 3 > 2 > 1 ☐
(c) 2 > 3 > 1 > 4 ☐ (d) 4 > 1 > 2 > 3 ☐

27. Which of the following compounds has weakest C—*X* bond?
(a) CH_3F ☐ (b) CH_3Cl ☐
(c) CH_3Br ☐ (d) CH_3I ☐

28. How many electrons are present in the *p*-orbitals of a methyl cation?
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) None of these ☐

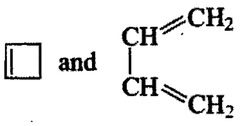
29. In which of the following, delocalisation of π-electrons is/are possible?
(a) $CH_2{=}CH_2$ ☐
(b) $CH_3—CH_2—CH{=}CH_2$ ☐
(c) $CH_2{=}CH—CH{=}CH_2$ ☐
(d) $CH_2{=}CH—CH_2—CH{=}CH_2$ ☐

30.

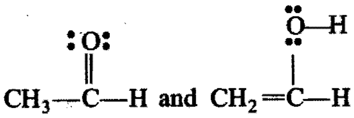


In the given Dewar structure of benzene, which of the following statement(s) is/are correct?
(a) All the carbons are in sp^2-hybrid state ☐
(b) All the carbons are in sp^3-hybrid state ☐
(c) Four carbons are in sp^2 and two in sp^3-hybrid state ☐
(d) Four carbons are in sp^3 and two in sp^2-hybrid state ☐

31. The pair of structures that are resonance hybrid is :
(a) $H\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}—\overset{+}{C}HCH_3$ and $H\overset{+}{\underset{\bullet\bullet}{O}}{=}CHCH_3$ ☐
(b)



☐
(c)

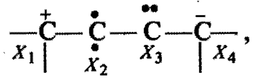


☐
(d) $CH_3\overset{+}{C}H_2$ and $\overset{+}{C}H_2CH_3$ ☐

32. The correct decreasing order of stability of I, II and III carbocations is:
(I) $CH_3—\overset{+}{C}H—CH_3$ (II) $CH_3—\overset{+}{C}H—COCH_3$
(III) $CH_3—\overset{+}{C}H—OCH_3$
(a) I > II > III ☐ (b) II > III > I ☐
(c) III > I > II ☐ (d) II > I > III ☐

33. The hybrid states of carbon atoms in $(\overset{B}{C}N)_4\overset{A}{C}_2$ are *A* and *B* and number of π bonds in compound is *C*. Then :
(a) $A = sp, B = sp^2$ and $C = 9$ ☐
(b) $A = sp^2, B = sp,$ and $C = 9$ ☐
(c) $A = sp^3, B = sp$ and $C = 9$ ☐
(d) $A = sp^2, B = sp^2$ and $C = 9$ ☐

34.



$—\underset{X_1|}{\overset{+}{C}}—\underset{\underset{X_2}{\bullet}}{\overset{\bullet}{C}}—\underset{X_3}{\overset{\bullet\bullet}{C}}—\underset{|X_4}{\overset{-}{C}}—$, Select the correct state of hybridization at X_1, X_2, X_3 and X_4.

	X_1	X_2	X_3	X_4	
(a)	sp^2	sp	sp^2	sp^3	☐
(b)	sp^3	sp^2	sp	sp	☐
(c)	sp^2	sp^2	sp^2	sp^3	☐
(d)	sp^3	sp^2	sp^2	sp	☐

35. Resonating structures of a molecule have :
(a) identical bonding ☐
(b) different bonding ☐
(c) identical arrangement of atoms and nearly same energies ☐
(d) the same number of paired and unpaired electrons ☐

ANSWERS : BRAIN STORMING PROBLEMS

1. (b)	**2.** (a)	**3.** (a)	**4.** (b)	**5.** (c)	**6.** (b)	**7.** (a)	**8.** (c)	**9.** (b)	**10.** (c)
11. (c)	**12.** (c)	**13.** (d)	**14.** (b)	**15.** (c)	**16.** (e)	**17.** (b)	**18.** (a)	**19.** (c,d)	**20.** (b)
21. (a)	**22.** (c)	**23.** (a, b)	**24.** (d)	**25.** (a)	**26.** (b)	**27.** (d)	**28.** (d)	**29.** (c)	**30.** (c)
31. (a)	**32.** (c)	**33.** (b)	**34.** (a)	**35.** (b, c, d)					

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

A polar covalent bond is formed between the two elements of different electronegativities. The polarity of a bond depends on the electronegativity difference, the bonding atoms and also on the shape of the molecule.

$$A - B$$

Let x_A and x_B are the electronegativities of bonding atoms A and B then, percentage ionic character of the bond can be calculated as,

$$\% \text{ ionic character} = 21|x_A \sim x_B| + 3.5|x_A - x_B|^2$$

Dipole moment of the bond (μ) depends on the bond length and the polarity of the bond.

$$\mu = q \times d$$

Here, q = charge of the dipoles

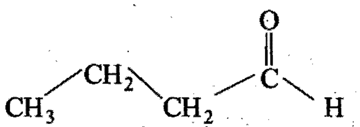
d = bond length

It is observed that the dipole moment increases with increase in the inductive effect.

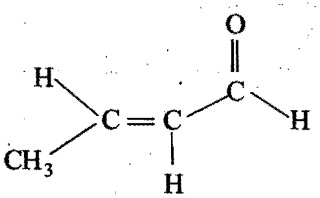
Answer the following questions as indicated :

Select code (a) if the statement is **true** and code (b) if the statement is **false.**

1. The dipole moment of $CH_3—X$ bond lies in the following sequence :
   $CH_3—I < CH_3—Br < CH_3—Cl$
   True (a) False (b)
2. Dipole moment of methanol is less than ethanol :
   True (a) False (b)
3. Dipole moment of C—Cl bond is greater than C—F bond :
   True (a) False (b)
4. Dipole moment of methyl alcohol (CH_3-O-H) is less than that of water :
   True (a) False (b)
5. Dipole moment of *trans*-2-butenal is greater than butanal :

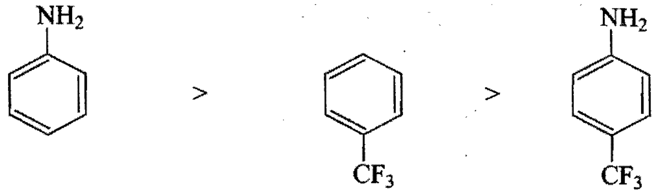


butanal



trans-2-butenal

   True (a) False (b)
6. Dipole moment of para-nitrophenol is greater than phenol :
   True (a) False (b)
7. Dipole moment of aniline, trifluoromethyl benzene and *p*-trifluoromethyl aniline lies in the following sequence :



True (a) False (b)

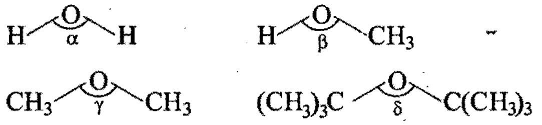
Passage 2

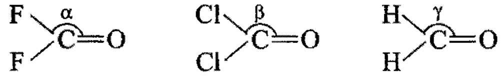
Geometry of organic compound is often described in terms of the valence shell electron pair repulsion theory. The VSEPR model rests on the premise that an electron pair, either bonded pair or an unshared pair, associated with a particular atom will be as far away from the atom's other electron pairs as possible.

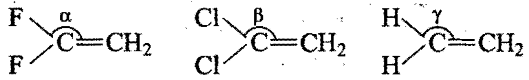
The tricoordinate carbon atoms of an alkene or carbonyl group also form bonds with angles near 120°. In these compounds, unsaturated double bonds have two electron pairs—those of the sigma and pi bonds. Repulsion by these two pairs are some what greater than those between single bonds, so that deviation from exact 120° trigonal geometry is observed.

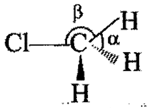
Another factor which has important influence on shapes is non bonded repulsion between the atoms within the molecule. Such repulsion is also referred to as **steric effects.**

Answer the following questions:

1. 

   Select the correct sequence of bond angles indicated in the above molecules.
   (a) $\alpha < \beta < \gamma < \delta$ (b) $\alpha = \beta = \gamma = \delta$
   (c) $\alpha > \beta > \gamma > \delta$ (d) $\alpha < \beta < \delta < \gamma$
2. 

   Select the correct sequence of indicated bond angles.
   (a) $\alpha < \beta < \gamma$ (b) $\alpha > \beta > \gamma$
   (c) $\alpha = \beta = \gamma$ (d) $\alpha < \beta > \gamma$
3. 

   Select the correct sequence of indicated bond angles.
   (a) $\alpha > \beta > \gamma$ (b) $\alpha = \beta = \gamma$
   (c) $\alpha < \beta < \gamma$ (d) $\alpha > \beta < \gamma$
4. 

   Which among the following is correct about the indicated bond angles?
   (a) $\alpha = \beta$ (b) $\alpha > \beta$
   (c) $\alpha < \beta$ (d) Can not be predicted

5. Which compound has bond angles nearest to 120°?
(a) $O{=}C{=}S$ (b) CHI_3
(c) $H_2C{=}O$ (d) $H-C{\equiv}C-H$
(e) CH_4

Passage 3

Double bond equivalents help in search for structure of a compound. It involves following steps:

- Calculate the expected number of hydrogen atoms in the saturated structure.
  - (a) For C_n there would be : $(2n+2)$ hydrogens if compound contains C, H, O only.
  - (b) For C_nN_m, there would be $(2n+2+m)$ hydrogens.
- Subtract the actual number of hydrogen and divide by 2. This gives the double bond equivalents.
- Ring is considered to possess single DBE.

Answer the following questions on DBE:

1. Double bond equivalent of compound $C_7H_{12}O$ is:
(a) 2 (b) 3
(c) 4 (d) 1

2. Double bond equivalent of benzene will be:
(a) 2 (b) 3
(c) 4 (d) 1

3. Which of the following is not correct?

	Compound	DBE
(a)	$C_7H_{10}O$	2
(b)	C_7H_8O	4
(c)	$C_7H_{17}N$	3
(d)	$C_7H_{13}NO$	2

4. Double bond equivalent of $C_7H_{16}O$ would be ...
(a) 0 (b) 1
(c) 2 (d) 3

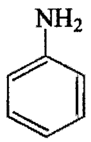
Passage 4

The hydrogen bond is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom like (F, O, N) of other molecule. Hydrogen bond is nearly an electrostatic attractive force and not a normal chemical bond. It is very weak (2 – 10 kcal/mol) as compared to a covalent bond (strength 50 – 100 kcal/mol).

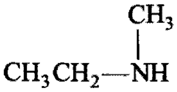
In intramolecular hydrogen bonding, the two or more than two molecules of the same or different substances are linked to form polymeric aggregate. Intermolecular hydrogen bonding increases the boiling point of the compound and also its solubility in water. Intramolecular hydrogen bonding occurs within two atoms of the same molecule. Intramolecular hydrogen bonding is also called chelation, since it involves ring formation. Intramolecular hydrogen bonding decreases the boiling point of the compound and also its solubility in water.

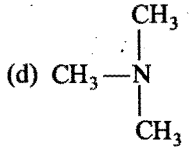
Answer the following questions:

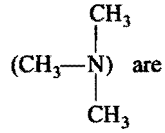
1. Which among the following has lowest boiling point?

(a) 

(b) $CH_3CH_2CH_2NH_2$

(c) 
$CH_3CH_2-\overset{CH_3}{\overset{|}{N}H}$

(d) 
$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{N}}}}$

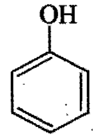
[**Hint :** Tertiary amines  $(CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{N}}}})$ are not involved in intermolecular hydrogen bonding, hence their boiling point is lowest as compared to corresponding primary and secondary amines.]

2. Which of the following molecules is dimerised when dissolved in nonpolar or organic solvent?

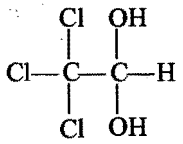
(a) $R-COOH$

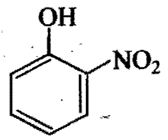
(b) 
$\underset{COOH}{\overset{COOH}{|}}$

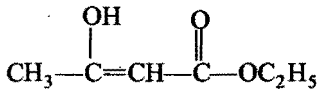
(c) $R-OH$

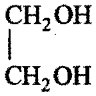
(d) 

3. Which of the following compounds is (are) stablised by intramolecular hydrogen bonding?

(a) 
$Cl-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H$

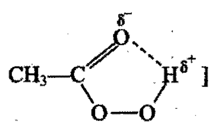
(b) 

(c) 
$CH_3-\overset{OH}{\overset{|}{C}}{=}CH-\overset{O}{\overset{\|}{C}}-OC_2H_5$

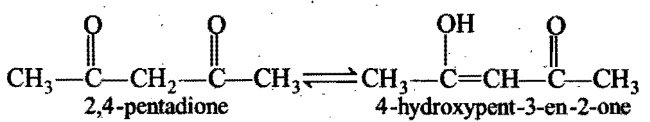
(d) 
$\underset{CH_2OH}{\overset{CH_2OH}{|}}$

4. Select the compound which involves intramolecular hydrogen bonding.
(a) $HCOOH$ (b) CH_3COOH
(c) C_6H_5COOH (d) CH_3COOOH

[**Hint :** Per acids form intramolecular hydrogen bond.



]

5. 
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}{=}CH-\overset{O}{\overset{\|}{C}}-CH_3$

2,4-pentadione (*A*) 4-hydroxypent-3-en-2-one (*B*)

Select the correct statement about above tautomers.
(a) Form (*A*) is more stable due to formation of intramolecular hydrogen bond
(b) Form (*B*) is more stable due to formation of intermolecular hydrogen bond

(c) Form (*B*) is more stable due to the formation of intramolecular hydrogen bond

(d) Form (*A*) is more stable due to the formation of intermolecular hydrogen bond

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	**1.** (a)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (a)	**6.** (a)	**7.** (b)
Passage 2	**1.** (a)	**2.** (b)	**3.** (a)	**4.** (b)	**5.** (c)		
Passage 3	**1.** (a)	**2.** (c)	**3.** (c)	**4.** (a)			
Passage 4	**1.** (d)	**2.** (a)	**3.** (a, b, c)	**4.** (d)	**5.** (c)		

2

MOLECULAR ANALYSIS OF ORGANIC COMPOUNDS

2.1 GENERAL

In order to establish the correct structure of an organic compound, it is necessary to know precisely its molecular formula. The following steps are involved in the determination of the molecular formula of a compound.

(i) Detection of elements (Qualitative analysis).
(ii) Estimation of elements (Quantitative analysis).
(iii) The determination of molecular mass.
(iv) Calculation of empirical and molecular formula.

2.2 DETECTION OF ELEMENTS (QUALITATIVE ANALYSIS)

Most of the organic compounds contain 2 to 5 different elements. The principal elements present are: carbon, hydrogen and oxygen. Less commonly present elements are: nitrogen, sulphur and halogens. In few organic compounds, phosphorus and metals may also be present. The order of abundance of these elements in organic compounds is given below:

Carbon —Always present
Hydrogen —Nearly always present
Oxygen —Generally present
Nitrogen, halogens, sulphur —Less commonly present
Phosphorus and metals —Rarely present

Detection of Carbon and Hydrogen

Carbon is always present in an organic compound and hydrogen, too, is rarely absent. However, the presence of these two elements is confirmed by the given common test.

A small amount of dry organic compound mixed with about eight times dry cupric oxide* is taken in a hard glass tube. The glass tube is clamped and fitted with a delivery tube carrying a bulb in the horizontal length. The end of the delivery tube is immersed in lime water. The bulb of the delivery tube contains anhydrous copper sulphate (colourless). The mixture is heated very strongly. Carbon and hydrogen present in the organic compound are oxidised by cupric oxide to carbon dioxide and water, respectively **(Copper Oxide Test).**

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$H_2 + CuO \xrightarrow{\Delta} Cu + H_2O$$

Carbon dioxide turns the lime water milky and water vapours turn anhydrous copper sulphate blue. Water vapours condense on the cooler part of the tube.

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{Milky}}{CaCO_3} + H_2O$$

$$\underset{\substack{\text{(Colourless)}\\\text{Anhydrous}}}{CuSO_4} + 5H_2O \longrightarrow \underset{\substack{\text{(Blue)}\\\text{Hydrated}}}{CuSO_4 \cdot 5H_2O}$$

If the substance under investigation is a volatile liquid or gas, the vapours are passed over heated copper oxide kept in combustion tube and the gaseous products are tested as above.

If the substance under examination contains sulphur also, the gases evolved are first passed through an acidified solution of potassium dichromate which absorbs all the sulphur dioxide and then through lime water which turns milky.

$$S + 2CuO \longrightarrow 2Cu + SO_2$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

[SO_2 like CO_2 turns lime water milky due to formation of $CaSO_3$.

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O]$$

---

*Cupric oxide, CuO, is hygroscopic. It is always ignited before use as to make it completely dry.

Organic compounds (suppose to contain phosphorus) are heated with oxidising agents (like sodium peroxide, Na_2O_2). The phosphorus present in the organic compound is oxidised to phosphate.

Detection of Nitrogen, Sulphur and Halogens

These elements are tested in an organic compound by **Lassaigne's test**. The organic compound (N, S or halogens) is fused with sodium metal as to convert these elements into ionisable inorganic substances, *i.e.*, nitrogen into sodium cyanide, sulphur into sodium sulphide and halogens into sodium halides.

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$2Na + X_2 \xrightarrow{\Delta} 2NaX \quad (X \text{ may be Cl, Br or I})$$

Note : Sodium metal should be in slight excess otherwise in compounds containing N and S together, sodium thiocyanate is formed. With excess of sodium, the thiocyanate formed decomposes into cyanide and sulphide.

$$Na + C + N + S \xrightarrow{\Delta} \underset{\text{Sodium thiocyanate}}{NaCNS}$$

$$NaCNS + 2Na \longrightarrow NaCN + Na_2S$$

The cyanide, sulphide or halide ions can be confirmed in the aqueous solution by usual tests. The aqueous solution is called **Lassaigne's filtrate.**

Instead of sodium metal, mixture of sodium carbonate and zinc can be used. It is called **Middleton's fusion method.**

Preparation of Lassaigne's filtrate : A small piece of sodium of pea size is freshly cut and dried between the folds of filter paper. It is taken in a fusion tube (ignition tube) and heated gently. When it melts to a shining globule, the tube is removed from the flame and a small amount of organic compound (0.05 g of solid or 3–4 drops of liquid) is added to the sodium. The tube is first gently heated till the reaction ceases and then strongly till it is red hot. It is now plunged directly into 10 to 15 mL of distilled water taken in a porcelain basin and crushed by the tip of the tongs. The contents are heated for five minutes and then filtered. The filtrate is known as **Lassaigne's filtrate** or **sodium extract.**

Organic compounds being covalents normally do not have ionisable groups, hence direct test is not possible.

Detection of Nitrogen

2 mL of Lassaigne's filtrate (sodium extract) is taken in a test tube and two or three drops of freshly prepared ferrous sulphate solution are added. As the solution is alkaline (excess of sodium reacts with water to form sodium hydroxide), a green precipitate of ferrous hydroxide appears. The mixture is boiled for two minutes, cooled and acidified with dilute sulphuric acid (H_2SO_4 dissolves ferrous hydroxide). Appearance of a green or prussian blue colour confirms the presence of nitrogen. Alternatively $FeCl_3$ and dilute HCl may be added.

Chemistry of the test : Lassaigne's filtrate consists of sodium cyanide and sodium hydroxide.

$$\underbrace{Na + C + N}_{\text{From organic compound}} \xrightarrow{\Delta} \underset{\text{Sodium cyanide}}{NaCN}$$

$$2Na + 2H_2O \longrightarrow \underset{\text{Sodium hydroxide}}{2NaOH} + H_2$$

When the filtrate is boiled with ferrous sulphate solution, the following reactions take place.

$$FeSO_4 + 2NaOH \longrightarrow \underset{\substack{\text{Ferrous hydroxide} \\ \text{(Green)}}}{Fe(OH)_2} + Na_2SO_4$$

$$Fe(OH)_2 + 6NaCN \longrightarrow \underset{\substack{\text{Sodium ferrocyanide} \\ \text{[Sodium} \\ \text{hexacyanoferrate (II)]}}}{Na_4[Fe(CN)_6]} + 2NaOH$$

At the same time some ferrous sulphate is converted to ferric sulphate. This reacts with sodium ferrocyanide to form ferric ferrocyanide or iron (III) hexacyanoferrate (II) which gives prussian blue colour or precipitate.

$$3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \rightarrow \underset{\substack{\text{Ferric ferrocyanide} \\ \text{(Prussian blue)}}}{Fe_4[Fe(CN)_6]_3} + 6Na_2SO_4$$

In case ferric chloride ($FeCl_3$) is added, the following reaction occurs.

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$$

Note : (i) Sometimes when the amount of nitrogen present is small, the prussian blue is present in colloidal form and the solution looks green.

(ii) When the alkaline solution is acidified with HCl, the yellow colour of ferric chloride produced by the acid with ferric ions makes the blue colour to appear as green.

(iii) When the organic substance contains both N and S, sodium thiocyanate is formed which gives a blood red colouration of ferric sulphocyanide (or ferric thiocyanate) with ferric ions.

$$3NaCNS + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric sulphocyanide} \\ \text{(Blood red in colour)}}}{Fe(CNS)_3} + 3NaCl$$

(iv) This test fails in case of diazo compounds.

Detection of Sulphur

1. Lassaigne's test : Sulphur is present in the sodium extract in the form of sodium sulphide.

$$S + 2Na \xrightarrow{\Delta} Na_2S$$

(When sulphur and nitrogen both are present, sodium thiocyanate is formed. Both are tested simultaneously with ferric chloride solution, when a blood red colouration appears).

Sulphur is tested in the sodium extract in the following manner:

(i) To a little of sodium extract, freshly prepared solution of sodium nitroprusside is added; a deep violet colour indicates the presence of sulphur.

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(NO)(CN)_5]} \longrightarrow \underset{\substack{\text{(Violet coloured complex)}\\ \text{Sodium thionitroprusside}}}{Na_3[Fe(ONSNa)(CN)_5]}$$

$$\text{or} \quad \underset{\text{(Purple colour complex)}}{Na_4[Fe(CN)_5NOS]}$$

(ii) To another test portion of sodium extract, a few drops of acetic acid and lead acetate are added. A black precipitate of lead sulphide is formed.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{(Black ppt.)}}{PbS} + 2CH_3COONa$$

(iii) To a small portion of sodium extract, a few drops of acetic acid and cadmium acetate are added. Yellow precipitate of cadmium sulphide is formed.

$$Na_2S + (CH_3COO)_2Cd \longrightarrow \underset{\text{(Yellow ppt.)}}{CdS} + 2CH_3COONa$$

2. Oxidation test : Sulphur can also be tested by oxidation test. The organic compound is fused with fusion mixture (a mixture of sodium carbonate and potassium nitrate). The sulphur, if present in the organic compound, is oxidised to sodium sulphate.

$$Na_2CO_3 + S + 3O \longrightarrow Na_2SO_4 + CO_2$$

The fused mass is dissolved in water and the solution is acidified with hydrochloric acid. Barium chloride solution is then added. The formation of a white precipitate indicates the presence of sulphur.

$$Na_2SO_4 + BaCl_2 \longrightarrow \underset{\text{(White ppt.)}}{BaSO_4} + 2NaCl$$

Detection of Halogens

1. Lassaigne's test : Chlorine, bromine and iodine are present in the sodium extract in the form of sodium chloride, sodium bromide and sodium iodide, respectively. For the test of halogens, it is necessary to remove sodium cyanide and sodium sulphide from the sodium extract if nitrogen and sulphur are present. This is done by boiling the sodium extract with concentrated nitric acid.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$

$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S\uparrow$$

[If NaCN and Na_2S are not decomposed, white or black precipitate of AgCN and Ag_2S respectively are formed with silver nitrate solution.]

To the sodium extract (free from NaCN and Na_2S), silver nitrate solution is added after acidifying it with dilute nitric acid. Appearance of white precipitate (AgCl) or pale yellow precipitate (AgBr) or yellow precipitate (AgI) indicates the presence of chlorine, bromine or iodine in the organic compound, respectively.

$$NaCl + AgNO_3 \longrightarrow \underset{\text{(White ppt.)}}{AgCl} + NaNO_3$$

The precipitate of AgCl dissolves in ammonium hydroxide.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{(Pale yellow ppt.)}}{AgBr} + NaNO_3$$

The precipitate of AgBr is sparingly soluble in ammonium hydroxide.

$$NaI + AgNO_3 \longrightarrow \underset{\text{(Yellow ppt.)}}{AgI} + NaNO_3$$

AgI is insoluble in ammonium hydroxide.

2. Chlorine water test for bromine and iodine : From the colour of AgBr and AgI, it is difficult to judge whether the organic compound contains bromine or iodine. To confirm the presence of bromine or iodine, the above test is supplemented by the chlorine water test **(layer test).**

A small portion of sodium extract is acidified with dilute HNO_3 or H_2SO_4 and then 1 mL of chloroform or carbon tetrachloride is added. Now shake it vigorously with excess of chlorine water. If chloroform layer becomes yellow or brown, bromine is present and if violet, iodine is present.

$$2NaBr + Cl_2 \longrightarrow \underset{\text{(Turns } CS_2 \text{ layer orange)}}{2NaCl} + Br_2$$

Br_2 dissolves in $CHCl_3$ or CCl_4 giving yellow or brown colour (layer).

$$2NaI + Cl_2 \longrightarrow \underset{\text{(Turns } CS_2 \text{ layer violet)}}{2NaCl} + I_2$$

I_2 dissolves in $CHCl_3$ or CCl_4 giving violet colour (layer).

Note : The presence of NaCN or Na_2S in sodium extract does not interfere in this test.

3. Beilstein test or copper wire test : The copper wire is flattened at one end. The flattened end is heated in an oxidising flame of the burner till it ceases to impart any green or blue colour to the flame. A small quantity of organic substance is taken on the flattened end of the wire and introduced in the flame. A green or blue colour of the flame indicates the presence of halogen(s). The green or blue colour is produced due to the interaction of halogen with copper to form volatile copper halides.

Note : This test, though very sensitive, is not always reliable. Substances which do not contain halogens such as urea, thiourea, pyridine, quinoline and purines, etc., also impart colour to the flame.

Detection of Phosphorus

The organic compound is fused with the fusion mixture (sodium carbonate and potassium nitrate) or sodium peroxide. The phosphorus present in the organic compound is converted into sodium phosphate. The fused product is extracted with water and the aqueous solution obtained is boiled with concentrated nitric acid and ammonium molybdate. A yellow precipitate or colouration indicates the presence of phosphorus. The yellow precipitate is due to the formation of ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$.

$$[P + Na_2O_2 \xrightarrow{\text{Boil}} Na_3PO_4]$$

$$3Na_2CO_3 + 2P + 5O \longrightarrow 2Na_3PO_4 + 3CO_2$$

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\substack{\text{Ammonium phosphomolybdate}\\ \text{(Yellow ppt.)}}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Detection of Oxygen

There is no satisfactory qualitative method for the detection of oxygen. However, its presence can be inferred indirectly.

(i) If the organic compound is heated alone in a dry test tube in presence of nitrogen, the formation of water drops on cooler parts of the tube may indicate the presence of oxygen.

(ii) The presence of oxygen can be inferred by testing the presence of functional groups known to contain oxygen, *e.g.*, hydroxyl (—OH), aldehydic (—CHO), carboxyl (—COOH), and nitro (—NO_2), etc.

2.3 ESTIMATION OF ELEMENTS (QUANTITATIVE ANALYSIS)

After qualitative analysis of elements, the next step in the determination of molecular formula of an organic compound is the estimation of various elements by mass, *i.e.*, finding the percentage composition of the substance by mass. The various methods commonly employed for the estimation of principal elements are discussed below:

Estimation of Carbon and Hydrogen

Carbon and hydrogen are estimated simultaneously by **Liebig's combustion method.**

Principle : When a known mass of an organic compound is strongly heated with dry cupric oxide, carbon and hydrogen present are quantitatively oxidised to carbon dioxide and water, respectively. The masses of carbon dioxide and water thus formed are determined and the amounts of carbon and hydrogen in the original compound are calculated.

$$C_xH_y + (x + y/4)O_2 \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O$$

Observations :

(i) Let the **mass of the organic compound be W g.**

(ii) Increase in the mass of U-tube = y g

So, Mass of water formed = y g

Increase in the mass of potash bulbs (or saphnolite tube) = x g

So, **Mass of carbon dioxide formed** = x g

Calculations :

(a) $$\underset{2\,g}{H_2} + \frac{1}{2}O_2 \longrightarrow \underset{18\,g}{H_2O}$$

18 g of water contain 2 g of hydrogen

y g of water will contain $= \frac{2}{18} \times y$ g of hydrogen

$$\textbf{Percentage of hydrogen} = \frac{2}{18} \times \frac{y}{W} \times 100$$

(b) $$\underset{12\,g}{C} + O_2 \longrightarrow \underset{44\,g}{CO_2}$$

44 g of CO_2 contain 12 g of carbon

x g of CO_2 will contain $= \frac{12}{44} \times x$ g of carbon

$$\textbf{Percentage of carbon} = \frac{12}{44} \times \frac{x}{W} \times 100$$

Liebig's method is most suitable in case of organic compounds containing C, H and oxygen only. If, however, the organic compound contains nitrogen, halogens and sulphur also, some modifications are made.

1. Substances containing nitrogen : The oxidation of nitrogen present in the organic compound occurs and oxides of nitrogen (N_2O, NO and NO_2) are formed. These oxides are also absorbed by caustic potash solution along with CO_2. The oxides of nitrogen are decomposed again into nitrogen by placing a bright copper gauze roll near the exit end. Nitrogen so produced is not absorbed by KOH solution.

$$4Cu + 2NO_2 \longrightarrow 4CuO + N_2$$

$$Cu + N_2O \longrightarrow CuO + N_2$$

2. Substances containing halogens : Halogens present in organic compounds form copper halides during combustion. Copper halides are volatile and partly decompose at high temperature forming free halogens. These halogens and copper halides are absorbed in the absorption apparatus. This can be prevented by placing a bright silver gauze roll near the exit end. Non-volatile silver halides are formed.

$$2Ag + X_2 \longrightarrow 2AgX$$

$$2Ag + CuX_2 \longrightarrow 2AgX + Cu$$

3. Substances containing sulphur alone or sulphur and halogen : The sulphur present in the organic compound is oxidised to sulphur dioxide which is absorbed in potash bulbs. A layer of fused lead chromate is placed near the exit end. SO_2 reacts to produce nonvolatile lead sulphate.

$$2PbCrO_4 \longrightarrow 2PbO + Cr_2O_3 + 3O$$

$$PbO + SO_2 + O \longrightarrow PbSO_4$$

It also reacts with copper halides and free halogens to form lead halides which are retained in the combustion tube.

SOME SOLVED PROBLEMS

Problem 1. 0.92 *g of an organic compound containing carbon, hydrogen and oxygen was analysed by combustion method. The increase in mass of the U-tube and the potash bulbs at the end of the operation was found to be* 1.08 *g and* 1.76 *g, respectively. Determine the percentage composition of the compound.*

Solution : Increase in mass of U-tube = 1.08 g

Mass of water formed = 1.08 g

Since, 18 g of water contain hydrogen = 2 g

$$1.08 \text{ g of water contain hydrogen} = \frac{2}{18} \times 1.08 \text{ g}$$

Mass of compound taken for analysis = 0.92 g

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{1.08}{0.92} \times 100 = 13.04$$

Increase in mass of potash bulbs = 1.76 g

Mass of carbon dioxide formed = 1.76 g

Since, 44 g of carbon dioxide contain carbon = 12 g

$$1.76 \text{ g of carbon dioxide contain carbon} = \frac{12}{44} \times 1.76 \text{ g}$$

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{1.76}{0.92} \times 100 = 52.17$$

Percentage of oxygen = 100 – (per cent of C + per cent of H)

$$= 100 - (52.17 + 13.04)$$
$$= 100 - 65.21 = 34.79$$

Composition of the compound : C = 52.17%; H = 13.04%; O = 34.79%

Estimation of Nitrogen

The following two methods are used for the estimation of nitrogen in an organic substance:

(i) Duma's method

(ii) Kjeldahl's method

1. Duma's method : This method can be applied in case of all nitrogenous compounds.

The elemental nitrogen is converted into molecular nitrogen and its volume is changed to STP data.

$$\underset{28\text{g}}{2\text{N}} \longrightarrow \underset{22.4\text{L at STP}}{\text{N}_2(g)}$$

Principle : A nitrogenous compound of formula $C_xH_yN_z$ when strongly heated with cupric oxide, in the atmosphere of CO_2, nitrogen is set free along with the formation of carbon dioxide and water. Part of nitrogen may be oxidised into oxides of nitrogen. When the gaseous mixture is passed over a roll of heated bright copper gauze, the oxides of nitrogen are reduced again into nitrogen.

$$C_xH_yN_z + \underset{\text{(Excess)}}{(2x + y/2)\text{CuO}} \longrightarrow x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O} + \frac{z}{2}\text{N}_2 + (2x + y/2)\text{Cu}$$

$$\text{Oxide of nitrogen} + \text{Cu} \xrightarrow{\text{Heat}} \text{N}_2 + \text{CuO}$$

The resultant mixture is collected over concentrated KOH solution in a nitrometer. All the gases (CO_2, SO_2, H_2O) except nitrogen are absorbed. The volume of nitrogen collected over KOH solution is measured.

Observations :

(i) Mass of the organic substance taken = ***W* g**

(ii) Volume of moist nitrogen in nitrometer = v mL

(iii) Room temperature = t°C = $(t + 273)$ K

(iv) Atmospheric pressure = p mm

(v) Aqueous tension at room temperature = p_1 mm

∴ Pressure of dry N_2 gas formed = $(p - p_1)$ mm

Alternately, volume of the vapours is changed to STP values.

Calculation:

Experimental values at STP

$P_1 = (p - p_1)$ mm $\qquad P_2 = 760$ mm

$V_1 = V$ mL $\qquad V_2 = ?$

$T_1 = (273 + t°\text{C})$ $\qquad T_2 = 273$

$$\text{Thus,} \quad \frac{760 \times V_2}{273} = \frac{(p - p_1) \times V}{(273 + t)}$$

(1 mol of every gaseous substance has volume 22.4 L at STP)

So, volume of N_2 (by gas equation)

$$V_2 = \frac{(p - p_1) \times V}{(t + 273)} \times \frac{273}{760} = \mathbf{V\ mL}$$

Percentage of Nitrogen :

22400 mL of N_2 weigh at STP = 28 g

$$\text{Therefore,} \quad V \text{ mL of N}_2 \text{ weigh at STP} = \frac{28}{22400} \times V \text{ g}$$

∴ **Percentage of nitrogen in the given compound**

$$= \frac{\mathbf{28}}{\mathbf{22400}} \times \frac{V}{W} \times \mathbf{100}$$

2. Kjeldahl's method : This is a very convenient method but its use is restricted. This method is suitable for estimating nitrogen in those organic compounds in which nitrogen is linked to carbon and hydrogen. The method is not used in the case of nitro, azo and azoxy compounds and to the compounds containing nitrogen in the ring (*e.g.*, pyridine quinoline, isoquinoline, etc.). The method is extensively used for estimating nitrogen in food, fertilizers and agricultural products.

Principle : The method is based on the fact that when the nitrogenous compound is heated with concentrated sulphuric acid in presence of copper sulphate (as catalyst) and potassium sulphate solid, the nitrogen present in the compound is quantitatively converted to ammonium sulphate.

$$\text{Organic compound} + \text{Conc. H}_2\text{SO}, \xrightarrow[\Delta]{\text{CuSO}_4 + \text{K}_2\text{SO}_4} (\text{NH}_4)_2\text{SO}_4$$

The ammonium sulphate so formed is decomposed by heating with excess of alkali and the ammonia evolved is absorbed in known excess volume of a standard acid (H_2SO_4). The excess acid left after neutralisation with ammonia is estimated by back titration with standard alkali. The percentage of nitrogen is then calculated from the amount of ammonia.

Observations :

(i) Mass of the organic compound taken $= \mathbf{W}$ **g**

(ii) Normality of the standard acid $= \mathbf{N_1}$

(iii) Volume of the acid taken $= V_1$ mL

(iv) Volume of the acid left after NH_3 absorption $= V_2$ mL (Determined by titrating with standard alkali solution)

(v) Volume of N_1 acid used, *i.e.*, neutralised by ammonia $= (V_1 - V_2)$ mL $= \mathbf{V}$ **mL**

Calculations : Since, V mL N_1 acid $= V$ mL N_1 NH_3

and $\quad$ 1000 mL N NH_3 = 17 g NH_3 ≡ 14 g nitrogen

So $\quad$ $V \text{ mL } N_1 \text{ NH}_3 = \frac{17}{1000} \times N_1 \times V \text{ g NH}_3$

$$= \frac{14}{1000} \times N_1 \times V \text{ g nitrogen}$$

$$\text{Percentage of nitrogen} = \frac{14}{1000} \times N_1 \times V \times \frac{100}{W}$$

$$= \frac{\mathbf{1.4 \times N_1 \times V}}{\mathbf{W}}$$

Problem 2. *An organic compound was analysed by Duma's method. 0.45 g of the compound on combustion gave 48.6 mL nitrogen at 27°C and 756 mm pressure. Calculate the percentage of nitrogen.*

Solution: $V_1 = 48.6$ mL $\quad V_2 = ?$

$P_1 = 756$ mm $\quad P_2 = 760$ mm

$T_1 = 27 + 273 = 300$ K $\quad T_2 = 273$ K

$$\text{Applying general gas equation, } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\text{Volume of nitrogen at STP, } V_2 = \frac{P_1V_1}{T_1} \cdot \frac{T_2}{P_2}$$

$$= \frac{756 \times 48.6}{300} \times \frac{273}{760}$$

$$= 43.99 \text{ mL}$$

Mass of organic compound = 0.45 g

$$\text{Percentage of nitrogen in the compound} = \frac{28}{22400} \times \frac{V_2}{W} \times 100$$

$$= \frac{28}{22400} \times \frac{43.99}{0.45} \times 100$$

$$= \mathbf{12.22\%}$$

Problem 3. *0.2 g of an organic compound was analysed by Kjeldahl's method. Ammonia evolved was absorbed in 60 mL $N/5$ H_2SO_4. Unused acid required 40 mL of $N/10$ NaOH for complete neutralisation. Find the percentage of nitrogen in the compound.*

Solution : Mass of organic compound = 0.2 g

$$\text{Unused acid required} = 40 \text{ mL } \frac{N}{10} \text{ NaOH}$$

$$40 \text{ mL } \frac{N}{10} \text{ NaOH} \equiv 40 \text{ mL } \frac{N}{10} \text{ H}_2\text{SO}_4$$

$$\equiv 20 \text{ mL } \frac{N}{5} \text{ H}_2\text{SO}_4$$

Acid used for absorption of ammonia

$$= (60 - 20) \text{ mL } \frac{N}{5} \text{ H}_2\text{SO}_4$$

$$= 40 \text{ mL } \frac{N}{5} \text{ H}_2\text{SO}_4$$

$$\text{Percentage of nitrogen} = \frac{1.4 \times N_1 \times V}{W} = \frac{1.4 \times \frac{1}{5} \times 40}{0.2}$$

$$= \frac{1.4 \times 40}{0.2 \times 5} = \mathbf{56\%}$$

Problem 4. *1.216 g of an organic compound was reacted under Kjeldahl's method and the ammonia evolved was absorbed in 100 mL N H_2SO_4. The remaining acid solution was made up to 500 mL by addition of water. 20 mL of this dilute solution required 32 mL of N/10 caustic soda solution for complete neutralisation. Calculate the percentage of nitrogen in the compound.*

Solution : 20 mL dilute unreacted acid soln. required

$$= 32 \text{ mL } \frac{N}{10} \text{ NaOH soln.}$$

500 mL dilute unreacted acid soln. required

$$= \frac{32}{20} \times 500 \text{ mL } \frac{N}{10} \text{ NaOH soln.}$$

$$= \frac{32}{20} \times \frac{500}{10} \text{ mL } N \text{ NaOH}$$

$$= 80 \text{ mL } N \text{ NaOH}$$

80 mL N NaOH ≡ 80 mL N H_2SO_4

Acid used for the neutralisation of NH_3

$$= (100 - 80) \text{ mL } N \text{ H}_2\text{SO}_4$$

$$= 20 \text{ mL } N \text{ H}_2\text{SO}_4$$

$$\text{Percentage of nitrogen} = 1.4 \times N_1 \times \frac{V}{W}$$

$N_1 = 1$, $V = 20$ mL and $W = 1.216$ g

So, $\quad$ $\text{percentage of nitrogen} = \frac{1.4 \times 1 \times 20}{1.216} = \mathbf{23.03\%}$

Estimation of Halogens

The estimation of halogens (Cl, Br or I) in organic compounds is usually done by **Carius method**.

Principle : The method is based on the fact that when an organic compound containing halogen (Cl, Br or I) is heated in a sealed tube (Carius tube) with fuming nitric acid in presence of excess of silver nitrate, silver halide is formed.

From the mass of silver halide formed, the percentage of the halogen can be calculated.

Calculations : Mass of the organic substance = W g

Mass of the silver halide = W_1 g

(a) Chlorine : $\underset{143.5\text{ g}}{AgCl} \equiv \underset{35.5\text{ g}}{Cl}$

143.5 g of AgCl contains chlorine = 35.5 g

W_1 g AgCl contains chlorine $= \frac{35.5}{143.5} \times W_1$ g

Percentage of chlorine $= \frac{35.5}{143.5} \times \frac{W_1}{W} \times 100$

(b) Bromine : $\underset{188\text{ g}}{AgBr} \equiv \underset{80\text{ g}}{Br}$

188 g of AgBr contains bromine = 80 g

W_1 g of AgBr contains bromine $= \frac{80}{188} \times W_1$ g

Percentage of bromine $= \frac{80}{188} \times \frac{W_1}{W} \times 100$

(c) Iodine : $\underset{235\text{ g}}{AgI} \equiv \underset{127\text{ g}}{I}$

235 g of AgI contains iodine = 127 g

W_1 g AgI contains iodine $= \frac{127}{235} \times W_1$ g

Percentage of iodine $= \frac{127}{235} \times \frac{W_1}{W} \times 100$

Problem 5. 0.5264 *g silver bromide is obtained from* 0.5124 *g of an organic compound. Calculate the percentage of bromine in the compound.*

Solution : Mass of organic compound, $W = 0.5124$ g

Mass of silver bromide, $W_1 = 0.5264$ g

$\underset{188\text{ g}}{AgBr} \equiv \underset{80\text{ g}}{Br}$

$$\text{Percentage of bromine} = \frac{80}{188} \times \frac{W_1}{W} \times 100$$

$$= \frac{80}{188} \times \frac{0.5264}{0.5124} \times 100 = \mathbf{43.71\%}$$

Problem 6. 0.156 *g of an organic compound on heating with fuming* HNO_3 *and* $AgNO_3$ *gives* 0.235 *g of* AgI. *Calculate the percentage of iodine in the compound.*

Solution : Mass of organic compound, $W = 0.156$ g

Mass of AgI, $W_1 = 0.235$ g

$\underset{235\text{ g}}{AgI} \equiv \underset{127\text{ g}}{I}$

$$\text{Percentage of iodine} = \frac{127}{235} \times \frac{W_1}{W} \times 100$$

$$= \frac{127}{235} \times \frac{0.235}{0.156} \times 100 = \mathbf{81.41\%}$$

Problem 7. 0.1170 *g of an organic compound on heating with conc.* HNO_3 *and silver nitrate in Carius furnace gave* 0.42 *g of* AgCl. *Find the percentage of chlorine in the compound.*

Solution : Mass of organic compound, $W = 0.1170$ g

Mass of AgCl, $W_1 = 0.42$ g

$\underset{143.5\text{ g}}{AgCl} \equiv \underset{35.5\text{ g}}{Cl}$

$$\text{Percentage of chlorine} = \frac{35.5}{143.5} \times \frac{W_1}{W} \times 100$$

$$= \frac{35.5}{143.5} \times \frac{0.42}{0.1170} \times 100 = \mathbf{88.80\%}$$

Halogens can also be estimated by **Schiff's** and **Piria method.**

In this method the accurately weighed organic compound is taken in a small platinum crucible with a mixture of lime and sodium carbonate, ($CaO + Na_2CO_3$). It is now heated strongly and then cooled and dissolved in dilute nitric acid in a beaker. The solution is then filtered and the halide is precipitated with silver nitrate solution. Halogen is now calculated as in Carius method.

Estimation of Sulphur

Sulphur in organic compounds may be estimated by any one of the following method:

(a) Carius method
(b) Messengers method
(c) Fusion method

The most common method for the estimation of sulphur is **Carius method.**

Principle : When an organic compound containing sulphur is heated with fuming nitric acid, sulphur is quantitatively oxidised to sulphuric acid. This is precipitated as barium sulphate by adding barium chloride solution. From the amount of barium sulphate, percentage of sulphur can be calculated.

$$S + HNO_3\text{ (fuming)} \xrightarrow{\text{Heat}} H_2SO_4$$

$$H_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2HCl$$

Calculations : Mass of organic compound = W g

Mass of barium sulphate = W_1 g

$\underset{233\text{ g}}{BaSO_4} \equiv \underset{32\text{ g}}{S}$

233 g of barium sulphate contains sulphur = 32 g

W_1 g of barium sulphate contains sulphur $= \frac{32}{233} \times W_1$ g

Percentage of sulphur $= \frac{32}{233} \times \frac{W_1}{W} \times 100$

Problem 8. *On heating* 0.32 *g of an organic compound with concentrated nitric acid and barium chloride,* 0.932 *g barium sulphate was obtained. Calculate the percentage of sulphur in the given compound.*

Solution : Mass of organic compound, $W = 0.32\,\text{g}$

Mass of barium sulphate, $W_1 = 0.932\,\text{g}$

$$\underset{233\text{ g}}{\text{BaSO}_4} \equiv \underset{32\text{ g}}{\text{S}}$$

$$\text{Percentage of sulphur} = \frac{32}{233} \times \frac{W_1}{W} \times 100$$

$$= \frac{32}{233} \times \frac{0.932}{0.32} \times 100 = 40\%$$

Estimation of Phosphorus

It is also estimated by Carius method. The organic compound containing phosphorus is heated with fuming nitric acid. Phosphorus is oxidised to phosphoric acid. It is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$ by heating it with conc. HNO_3 and then adding ammonium molybdate. The yellow precipitate is filtered, washed, dried and weighed.

Alternatively phosphoric acid is precipitated as magnesium ammonium phosphate, $MgNH_4PO_4$, by the addition of magnesia mixture $(MgSO_4 + NH_4OH + NH_4Cl)$. The magnesium ammonium phosphate is washed, dried and ignited when it is converted to magnesium pyrophosphate $(Mg_2P_2O_7)$.

$$P \xrightarrow[\Delta]{HNO_3} H_3PO_4$$

$$\underset{\text{Phosphoric acid}}{H_3PO_4} \xrightarrow[(Mg^{2+} + NH_4OH)]{\text{Magnesia mixture}} \underset{\text{Magnesium ammonium phosphate}}{MgNH_4PO_4}$$

$$2MgNH_4PO_4 \xrightarrow{\text{Heat}} Mg_2P_2O_7 + 2NH_3 + H_2O$$

From the mass of magnesium pyrophosphate, the percentage of phosphorus in the compound can be calculated.

Calculations : Mass of organic compound $= W$ g

Mass of magnesium pyrophosphate $= W_1$ g

$$\underset{222\text{ g}}{Mg_2P_2O_7} \equiv \underset{62\text{ g}}{2P}$$

$$\textbf{Percentage of phosphorus} = \frac{62}{222} \times \frac{W_1}{W} \times 100$$

Estimation of Oxygen

The usual method of determining the percentage of oxygen in an organic compound is by the method of difference. All the elements except oxygen present in the organic compound are estimated and the total of their percentages is subtracted from 100 to get the percentage of oxygen.

Percentage of oxygen = 100 − (Sum of the percentages of all other elements)

However, a direct method for the estimation of oxygen was discovered in 1947. This is known as Aluise's method. A known amount of organic compound is subjected to pyrolysis (decomposition by heat) in a stream of nitrogen. The oxygen and other gaseous products formed during pyrolysis are passed over heated carbon at 1100°C. The oxygen combines with carbon forming carbon monoxide.

$$\text{Compound} \xrightarrow{\text{Pyrolysis}} \text{Oxygen} + \text{Gaseous products}$$

$$O_2 + 2C(\text{graphite}) \xrightarrow{1100^\circ C} 2CO$$

The gas is then passed through a tube containing iodine pentoxide at 175°C to liberate iodine.

$$5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$$

By determining the amount of CO_2 or I_2 produced, the percentage of oxygen in the organic compound can be calculated.

The resulting gaseous mixture $(CO_2 \text{ and } I_2)$ is passed through potassium iodide which absorbs iodine and the CO_2 left is then absorbed in KOH. Knowing the increase of weight of KOH, *i.e.*, the weight of CO_2, the percentage of oxygen can be calculated.

$$\underset{16\text{ g}}{O} \equiv CO \equiv \underset{44\text{ g}}{CO_2}$$

$$\textbf{Percentage of oxygen} = \frac{16}{44} \times \frac{\textbf{mass of CO}_2}{\textbf{mass of org. compd.}} \times 100$$

Now a days, the estimation of elements (C, H and N) in an organic compound is done by taking only very small (micro) quantities (about 1–3 mg) of the substance with the help of instrumental automatic experiment techniques **(CHN elemental analyzer)** and the results are obtained on a screen (LED) within a short time.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Lassaigne's test for the detection of nitrogen will fail in the case of :

(a) NH_2CONH_2 (b) $NH_2CONHNH_2 \cdot HCl$

(c) $NH_2NH_2 \cdot HCl$ (d) $C_6H_5NHNH_2 \cdot 2HCl$

[**Ans.** (c)]

[**Hint :** For Lassaigne's test of nitrogen, compound must contain N in addition to carbon to form NaCN in sodium extract.]

2. The function of boiling the sodium extract with conc. HNO_3 before testing for halogen is:

(a) to make the solution acidic

(b) to make the solution clear

(c) to convert Fe^{2+} to Fe^{3+}

(d) to destroy CN^- and S^{2-} ions

[**Ans.** (d)]

[**Hint :** If N and S are already present, they will hinder in test of halogens as NaCN and Na_2S will give white or black precipitate with $AgNO_3$. Boiling conc. HNO_3 is thus used to remove CN^- and S^{2-} ions in the form of volatile HCN and H_2S.]

3. Sodium nitroprusside when added to an alkaline solution of sulphide ions produces a colouration : **[AFMC 2005]**

(a) red (b) blue

(c) brown (d) purple

[Ans. (d)]
[Hint : Purple (deep violet) colour is due to the formation of sodium thionitroprusside, $Na_4[Fe(CN)_5NOS]$.]

4. In Kjeldahl's method, nitrogen present is estimated as:
(a) N_2 (b) NH_3
(c) NO_2 (d) none of these
[Ans. (b)]
[Hint : In this method the nitrogen present is quantitatively converted into $(NH_4)_2SO_4$ on heating with conc. H_2SO_4. The $(NH_4)_2SO_4$ is then treated with standard alkali solution to liberate NH_3, which is absorbed in H_2SO_4 to obtain percentage of nitrogen.]

5. In Kjeldahl's method, nitrogen present is quantitatively converted to :
(a) N_2 (b) $(NH_4)_2SO_4$
(c) NO_2 (d) none of these
[Ans. (b)]

6. In Kjeldahl's method of estimation of nitrogen, K_2SO_4 acts as:
(a) an oxidising agent (b) catalytic agent
(c) hydrolysing agent (d) boiling point elevator
[Ans. (d)]
[Hint: Addition of K_2SO_4 increases the boiling point of H_2SO_4.]

7. Positive Beilstein test shows that:
(a) halogens are surely present
(b) halogens are absent
(c) halogens may be present
(d) none of the above
[Ans. (c)]
[Hint : Beilstein test is also given by some other compounds such as urea, pyridine thiourea and organic acids, etc., which imparts colour to the flame.]

8. In an organic compound, the phosphorus is estimated as: **[AFMC 2010]**
(a) $Mg_2P_2O_7$ (b) $Mg_3(PO_4)_2$
(c) H_3PO_4 (d) P_2O_5
[Ans. (a)]

2.4 DETERMINATION OF MOLECULAR MASS

The molecular mass of the organic compounds can be determined by various methods. The methods may be divided into two groups:

1. **Physical methods :** These are of two types:
   - **(i) For volatile compounds**
     - (a) Victor Meyer's method
     - (b) Duma's method
     - (c) Hofmann's method
   - **(ii) For non-volatile compounds**
     - (a) Ebullioscopic method or elevation in boiling point method
     - (b) Cryoscopic method or depression in freezing point method
2. **Chemical methods**:
   - (i) Silver salt method for acids
   - (ii) Platinichloride method for bases
   - (iii) Volumetric method for both acids and bases

1. (i) Physical Methods for Volatile Compounds

(a) Victor Meyer's method : Molecular mass of volatile liquids and solids can be easily determined from the application of **Avogadro hypothesis** according to which the mass of 22.4 litres or 22400 mL of the vapour of any volatile substance at NTP is equal to the molecular mass of the substance.

In Victor Meyer's method, a known mass of the volatile substance is vaporised in a Victor Meyer's tube, The vapours formed displace an equal volume of air into a graduated tube. The volume of air collected in graduated tube is measured under experimental conditions. This volume is converted to NTP conditions.

Calculations : Mass of the organic substance $= W$ g

Let the volume of the air displaced be $= V_1$ mL

Temperature $= T_1$ K

Pressure (after deducting aqueous tension) $= p_1$ mm

Let the volume at NTP be $= V_2$ mL

Applying gas equation,

$$V_2 = \frac{p_1 \times V_1}{T_1} \times \frac{273}{760}$$

22400 mL of vapours weigh at NTP $= M$ (mol. mass)

V_2 mL of vapours weigh at NTP $= W$ g

22400 mL of vapours weigh at NTP $= \frac{W}{V_2} \times 22400 = M$

or Vapour density of substance

$$= \frac{\text{Mass of 1 mL of vapours at NTP}}{\text{Mass of 1 mL of hydrogen at NTP}}$$

or

$$\text{V.D.} = \frac{W/V_2}{0.00009}$$

or

$$\text{V.D.} = \frac{W}{V_2 \times 0.00009}$$

$$\text{Mol. mass, } M = 2 \times \text{V.D.} = \frac{2W}{V_2 \times 0.00009}$$

Note: Alternately volume of the vapours is changed to STP values. (1 mol of every gaseous substance has volume 22.4 L at STP)

Problem 9. *In a Victor Meyer's determination, the following observations have been made :*

Mass of compound $= 0.17$ *g*

Volume of air collected $= 34.2$ *mL*

Temperature $= 15°C$

Atmospheric pressure $= 750$ *mm*

Vapour pressure of water at $15°C = 13$ *mm.*

Calculate the vapour density and molecular mass of the compound.

Solution : Given

$$\left.\begin{array}{ll} V_1 = 34.2 \text{ mL} & V_2 = ? \\ P_1 = (750 - 13) = 737 \text{ mm} & P_2 = 760 \text{ mm} \\ T_1 = (15 + 273) = 288 \text{ K} & T_2 = 237 \text{ K} \end{array}\right\} \text{NTP conditions}$$

By gas equation,

$$V_2 = \frac{737 \times 34.2}{288} \times \frac{273}{760} = 31.4376 \text{ mL}$$

$$\text{Vapour density} = \frac{W}{V_2 \times 0.00009} = \frac{0.17}{31.4376 \times 0.00009} = \mathbf{60.08}$$

$$\text{Mol. mass} = 2 \times \text{Vapour density} = 2 \times 60.08 = \mathbf{120.16}$$

(b) Duma's method : The apparatus consists of a glass bulb of about 250 mL capacity with a narrow outlet tube. It is cleaned, dried and weighed at the room temperature. A few mL of the organic substance (liquid) is placed in the bulb. The bulb is now placed in a bath and clamped. The bath consists of a liquid having 30–40° C higher boiling point than that of the substance whose molecular mass is to be determined. The bath is now heated to about 20°C higher than the boiling point of the substance kept inside the bulb. When whole of the substance inside the bulb has vaporised and no more vapours come out, the mouth of the bulb is sealed with a blow pipe flame. The bulb is now taken out of the bath, cleaned and dried from outside. It is now weighed. The volume of the bulb is determined by breaking the end of the sealed mouth under water and weighing the bulb full of water along with broken pieces of glass.

Calculations :

(i) Mass of bulb + air = W_1 g

(ii) Mass of bulb + vapours = W_2 g

(iii) Mass of bulb + water = W_3 g

Mass of water in bulb = $(W_3 - W_1)$ g

So Volume of bulb = $(W_3 - W_1)$ mL

(iv) Room temperature = T_1 K and pressure after deducting vapour pressure of water = p_1 mm

Volume of the air in the bulb at NTP

$$= \frac{(W_3 - W_1) \times p_1}{T_1} \times \frac{273}{760} = V_1 \text{ mL}$$

So Mass of air = $V_1 \times 0.00129$

(density of air at NTP = 0.00129 g / mL)

(v) Temperature of the bath = T_2 K

Hence, Mass of empty bulb = $(W_1 - V_1 \times 0.00129)$ g

So Mass of vapour = $[W_2 - (W_1 - V_1 \times 0.00129)]$ g

Mol. mass of the substance

$$= \frac{[W_2 - (W_1 - V_1 \times 0.00129)]}{V_2} \times 22400$$

$$\left[V_2 = \text{volume of vapours at NTP} = \frac{(W_3 - W_1) \times p_1}{T_2} \times \frac{273}{760}\right]$$

Problem 10. *A Duma's bulb full of air weighs* 22.567 *g at* 20°C *and* 755 *mm pressure. Full of vapours of a substance at* 120°C *and the same pressure, it weighs* 22.8617 *g. The capacity of the bulb is* 200 *mL. Find out the molecular mass of the substance.* [*Density of air* = 0.00129 *g/mL*]

Solution : Given

$$\left.\begin{array}{ll} V_1 = \text{volume of bulb} = 200 \text{ mL} & V_2 = ? \\ T_1 = (20 + 273) = 293 \text{ K} & T_2 = 273 \text{ K} \\ P_1 = 755 \text{ mm} & P_2 = 760 \text{ mm} \end{array}\right\} \text{NTP conditions}$$

So V_2 = Volume of bulb at NTP

$$= \frac{200 \times 755}{293} \times \frac{273}{760} = 185.122 \text{ mL}$$

$$\text{Mass of air} = V_2 \times 0.00129 = 185.122 \times 0.00129 = 0.2388 \text{ g}$$

$$\text{Mass of empty bulb} = (22.567 - 0.2388) = 22.3282 \text{ g}$$

$$\text{Mass of vapours} = (22.8617 - 22.3282) = 0.5335 \text{ g}$$

Let the volume of vapours at NTP be V.

$$V = \frac{200 \times 755}{393} \times \frac{273}{760} = 138 \text{ mL}$$

$$\text{Mol. mass of the substance} = \frac{\text{mass of vapours}}{\text{vol. of vapours at NTP}} \times 22400$$

$$= \frac{0.5335}{138} \times 22400 = \mathbf{86.59}$$

(c) Hofmann's method : The method is applied to those substances which are not stable at their boiling points, but which may be volatilised without decomposition under reduced pressure. A known mass of the substance is vaporised above a mercury column in a barometric tube and the volume of the vapour formed is recorded. It is then reduced to NTP conditions. The molecular mass of the organic substance can be calculated by the application of following relationship:

$$\text{Mol. mass} = \frac{\text{mass of the substance}}{\text{volume of the vapours at NTP}} \times 22400$$

(ii) Physical Methods for Non-volatile Substances

The molecular mass of a non-volatile organic compound can be determined by noting either the elevation in boiling point of the solvent **(Ebullioscopic method)** or the depression in freezing point of the solvent **(Cryoscopic method)** produced by dissolving a definite mass of the substance in a known mass of the solvent. The molecular mass of the compound can be calculated from the following mathematical relationships:

Vapour pressure of water at $15°C = 13$ *mm.*

Calculate the vapour density and molecular mass of the compound.

Solution : Given

$$\left.\begin{array}{ll} V_1 = 34.2\text{ mL} & V_2 = ? \\ P_1 = (750-13) = 737\text{ mm} & P_2 = 760\text{ mm} \\ T_1 = (15+273) = 288\text{ K} & T_2 = 237\text{ K} \end{array}\right\}\text{NTP conditions}$$

By gas equation,

$$V_2 = \frac{737 \times 34.2}{288} \times \frac{273}{760} = 31.4376\text{ mL}$$

$$\text{Vapour density} = \frac{W}{V_2 \times 0.00009} = \frac{0.17}{31.4376 \times 0.00009} = \mathbf{60.08}$$

$$\text{Mol. mass} = 2 \times \text{Vapour density} = 2 \times 60.08 = \mathbf{120.16}$$

(b) Duma's method : The apparatus consists of a glass bulb of about 250 mL capacity with a narrow outlet tube. It is cleaned, dried and weighed at the room temperature. A few mL of the organic substance (liquid) is placed in the bulb. The bulb is now placed in a bath and clamped. The bath consists of a liquid having 30–40° C higher boiling point than that of the substance whose molecular mass is to be determined. The bath is now heated to about 20°C higher than the boiling point of the substance kept inside the bulb. When whole of the substance inside the bulb has vaporised and no more vapours come out, the mouth of the bulb is sealed with a blow pipe flame. The bulb is now taken out of the bath, cleaned and dried from outside. It is now weighed. The volume of the bulb is determined by breaking the end of the sealed mouth under water and weighing the bulb full of water along with broken pieces of glass.

Calculations :

(i) Mass of bulb + air $= W_1$ g

(ii) Mass of bulb + vapours $= W_2$ g

(iii) Mass of bulb + water $= W_3$ g

Mass of water in bulb $= (W_3 - W_1)$ g

So Volume of bulb $= (W_3 - W_1)$ mL

(iv) Room temperature $= T_1$ K and pressure after deducting vapour pressure of water $= p_1$ mm

Volume of the air in the bulb at NTP

$$= \frac{(W_3 - W_1) \times p_1}{T_1} \times \frac{273}{760} = V_1\text{ mL}$$

So Mass of air $= V_1 \times 0.00129$

(density of air at NTP $= 0.00129$ g / mL)

(v) Temperature of the bath $= T_2$ K

Hence, Mass of empty bulb $= (W_1 - V_1 \times 0.00129)$ g

So Mass of vapour $= [W_2 - (W_1 - V_1 \times 0.00129)]$ g

Mol. mass of the substance

$$= \frac{[W_2 - (W_1 - V_1 \times 0.00129)]}{V_2} \times 22400$$

$$\left[V_2 = \text{volume of vapours at NTP} = \frac{(W_3 - W_1) \times p_1}{T_2} \times \frac{273}{760}\right]$$

Problem 10. *A Duma's bulb full of air weighs 22.567 g at 20°C and 755 mm pressure. Full of vapours of a substance at 120°C and the same pressure, it weighs 22.8617 g. The capacity of the bulb is 200 mL. Find out the molecular mass of the substance. [Density of air = 0.00129 g/mL]*

Solution : Given

$$\left.\begin{array}{ll} V_1 = \text{volume of bulb} = 200\text{ mL} & V_2 = ? \\ T_1 = (20+273) = 293\text{ K} & T_2 = 273\text{ K} \\ P_1 = 755\text{ mm} & P_2 = 760\text{ mm} \end{array}\right\}\text{NTP conditions}$$

So V_2 = Volume of bulb at NTP

$$= \frac{200 \times 755}{293} \times \frac{273}{760} = 185.122\text{ mL}$$

$$\text{Mass of air} = V_2 \times 0.00129 = 185.122 \times 0.00129 = 0.2388\text{ g}$$

$$\text{Mass of empty bulb} = (22.567 - 0.2388) = 22.3282\text{ g}$$

$$\text{Mass of vapours} = (22.8617 - 22.3282) = 0.5335\text{ g}$$

Let the volume of vapours at NTP be V.

$$V = \frac{200 \times 755}{393} \times \frac{273}{760} = 138\text{ mL}$$

$$\text{Mol. mass of the substance} = \frac{\text{mass of vapours}}{\text{vol. of vapours at NTP}} \times 22400$$

$$= \frac{0.5335}{138} \times 22400 = \mathbf{86.59}$$

(c) Hofmann's method : The method is applied to those substances which are not stable at their boiling points, but which may be volatilised without decomposition under reduced pressure. A known mass of the substance is vaporised above a mercury column in a barometric tube and the volume of the vapour formed is recorded. It is then reduced to NTP conditions. The molecular mass of the organic substance can be calculated by the application of following relationship:

$$\text{Mol. mass} = \frac{\text{mass of the substance}}{\text{volume of the vapours at NTP}} \times 22400$$

(ii) Physical Methods for Non-volatile Substances

The molecular mass of a non-volatile organic compound can be determined by noting either the elevation in boiling point of the solvent **(Ebullioscopic method)** or the depression in freezing point of the solvent **(Cryoscopic method)** produced by dissolving a definite mass of the substance in a known mass of the solvent. The molecular mass of the compound can be calculated from the following mathematical relationships:

(a) Elevation in boiling point :

$$\text{Mol. mass} = \frac{1000K_b \times w}{W \times \Delta T}$$

where

K_b = Molal elevation constant of the solvent

w = Mass of the compound

W = Mass of the solvent

ΔT = Elevation in boiling point of the solvent (determined experimentally).

(b) Depression in freezing point :

$$\text{Mol. mass} = \frac{1000K_f \times w}{W \times \Delta T}$$

where

K_f = Molal depression constant of the solvent

w = Mass of the compound

W = Mass of the solvent

ΔT = Depression in freezing point of the solvent (determined experimentally)

2. Chemical Methods

(i) Silver salt method for acids : It is based on the fact that silver salt of an organic acid on heating gives residue of metallic silver.

$$\underset{\text{Silver salt}}{RCOOAg} \xrightarrow{\text{Heat}} \underset{\substack{\text{Silver}\\ \text{(residue)}}}{Ag}$$

From the mass of silver salt taken and the mass of the silver residue obtained, the equivalent mass of the silver salt can be calculated.

$$\frac{\text{Equivalent mass of silver salt}}{\text{Equivalent mass of silver}} = \frac{\text{Mass of silver salt}}{\text{Mass of silver}}$$

Knowing the equivalent mass of silver salt, the equivalent mass of the acid can be obtained. The molecular mass of an acid can be determined with the help of the following relationship:

Mol. mass of the acid = Equivalent mass of the acid × basicity

Procedure : The organic acid is treated with excess of NH_4OH. The ammonium salt is formed which remains in dissolved form.

$$RCOOH + NH_4OH \longrightarrow RCOONH_4 + H_2O$$

The unreacted ammonia is boiled off. The neutral solution is then treated with silver nitrate solution. The precipitated silver salt is filtered, washed and dried.

$$RCOONH_4 + AgNO_3 \longrightarrow RCOOAg + NH_4NO_3$$

A known mass of silver salt (about 0.2 g) is heated in a platinum crucible when metallic silver is obtained as residue. It is weighed.

Calculations :

(i) Mass of silver salt taken = w g

(ii) Mass of metallic silver = x g

$$\frac{\text{Eq. mass of silver salt}}{\text{Eq. mass of silver}} = \frac{w}{x}$$

or $$\text{Eq. mass of silver salt} = \frac{w}{x} \times 108$$

Let the equivalent mass of the acid be E. In the preparation of silver salt, a hydrogen atom of the carboxylic group is replaced by a silver atom.

Thus, Equivalent mass of silver salt $= E - 1 + 108$
$= E + 107$

Thus, $$E + 107 = \frac{w}{x} \times 108$$

or $$E = \left[\frac{w}{x} \times 108 - 107\right]$$

If n be the basicity of the acid, then

$$\textbf{Mol. mass of the acid} = \left[\frac{w}{x} \times 108 - 107\right] \times n$$

Problem 11. 0.38 *g of a silver salt of a dibasic acid on ignition gave* 0.27 *g of silver. Calculate the molecular mass of the acid.*

Solution : Mass of silver salt = 0.38 g

Mass of silver = 0.27 g

$$\frac{\text{Eq. mass of silver salt}}{\text{Eq. mass of silver}} = \frac{\text{Mass of silver salt}}{\text{Mass of silver}}$$

$$\text{Eq. mass of silver salt} = \frac{0.38}{0.27} \times 108$$

or $$E + 107 = \frac{0.38}{0.27} \times 108 \qquad (E = \text{Eq. mass of acid})$$

or $$E = \left[\frac{0.38}{0.27} \times 108 - 107\right] = 45$$

Mol. mass of the acid = Eq. mass × basicity $= 45 \times 2 = 90$

(ii) Platinichloride method for bases : Organic bases combine with chloroplatinic acid, H_2PtCl_6, to form insoluble platinichlorides, which, on ignition, leave a residue of metallic platinum. Knowing the mass of platinum salt and the mass of metallic platinum, the molecular mass of the platinum salt can be determined. Let B represents one molecule of the base. If the base is mono-acidic, the formula of the double salt will be $B_2H_2PtCl_6$.

$$2B \xrightarrow{HCl} 2B \cdot HCl \xrightarrow{PtCl_4} B_2H_2PtCl_6$$

$$\underset{\substack{\text{Double salt}\\ (2B + 410)}}{B_2H_2PtCl_6} \xrightarrow{\text{Heat}} \underset{\substack{\text{Platinum (residue)}\\ (195)}}{Pt}$$

$$\frac{\text{Molecular mass of the salt}}{\text{Atomic mass of platinum}} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

Let E be the equivalent mass of the base.

$$\text{Molecular mass of the salt} = 2E + 2 + 195 + 213$$
$$= 2E + 410$$

So, $$\frac{2E+410}{195} = \frac{w}{x} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

$$2E = \left[\frac{w}{x} \times 195 - 410\right]$$

$$E = \frac{1}{2}\left[\frac{w}{x} \times 195 - 410\right]$$

$$\text{Mol. mass of the base} = \text{Eq. mass} \times \text{acidity of the base}$$
$$= E \times n$$

where n is the acidity of the base.

Problem 12. 0.49 *g of the chloroplatinate of a diacid base gave on ignition* 0.195 *g of platinum. Calculate the molecular mass of the base.*

Solution :

$$\frac{\text{Mol. mass of chloroplatinate}}{\text{At. mass of platinum}} = \frac{\text{Mass of chloroplatinate taken}}{\text{Mass of platinum left}}$$
$$= \frac{0.49}{0.195}$$

Let B be the equivalent mass of the base.

$$\frac{2B+410}{195} = \frac{0.49}{0.195}$$

or $$2B = \left[\frac{0.49}{0.195} \times 195 - 410\right] = 80$$

or $$B = 40$$

Mol. mass of the base = Eq. mass × acidity $= 40 \times 2 = \mathbf{80}$

(iii) Volumetric method for acids and bases : The molecular mass of an acid can be determined by dissolving a known mass of the acid in water and titrating the solution against a standard solution of an alkali using phenolphthalein as indicator. Knowing the volume of alkali solution used, the mass of the acid, which will require 1000 mL of a normal alkali solution for complete neutralisation can be calculated. This mass of the acid will be its equivalent mass.

$$\underbrace{\text{1000 mL 1 } N \text{ alkali solution}}_{\text{One gram equivalent of alkali}} \equiv \text{One gram equivalent of the acid}$$

Calculations : Suppose w g of the organic acid requires V mL N_1 alkali solution for complete neutralisation.

$$V \text{ mL } N_1 \text{ alkali solution} \equiv w \text{ g acid}$$

$$\text{So, 1000 mL } N_1 \text{ alkali solution} \equiv \frac{w}{V \times N_1} \times 1000 \text{ g acid}$$
$$\equiv \text{one gram equivalent acid}$$

$$\text{Equivalent mass of the acid} \equiv \frac{w}{V \times N_1} \times 1000$$

Thus, Molecular mass of the acid = Eq. mass × basicity

In the case of organic bases, the known mass of the base is titrated against a standard solution of an acid. Knowing the volume of the acid solution used, the mass of the organic base which will require 1000 mL of a normal acid solution for complete neutralisation can be calculated. This mass will be the equivalent mass of the base.

$$\underbrace{\text{1000 mL } N \text{ acid solution}}_{\text{One gram equivalent of the acid}} \equiv \text{One gram equivalent of the base}$$

$$\text{Molecular mass of the base} = \text{Eq. mass} \times \text{acidity}$$

Problem 13. 1.575 *g of an organic acid was dissolved in* 250 *mL of water.* 20 *mL of this solution required* 16 *mL of N/8 alkali solution for complete neutralisation. If the basicity of the acid is two, find its molecular mass.*

Solution :

$$16 \text{ mL } N/8 \text{ alkali solution} \equiv 20 \text{ mL of acid solution}$$
$$2 \text{ mL } 1\ N \text{ alkali solution} \equiv 20 \text{ mL of acid solution}$$
$$\frac{2 \times 250}{20} \text{ mL } 1\ N \text{ alkali solution} \equiv 250 \text{ mL of acid solution}$$
$$25 \text{ mL } 1\ N \text{ alkali solution} \equiv 1.575 \text{ g acid}$$
$$1000 \text{ mL } 1\ N \text{ alkali solution} \equiv \frac{1.575}{25} \times 1000 \text{ g acid}$$
$$\text{Eq. mass of the acid} = 63 \text{ g acid}$$
$$\text{Mol. mass of the acid} = 63 \times 2 = 126$$

Problem 14. 2.65 *g of a diacidic base was dissolved in* 500 *mL of water.* 20 *mL of this solution required* 12 *mL of* $\frac{N}{6}$ HCl *solution. Calculate the equivalent mass and molecular mass of the base.*

Solution :

$$12 \text{ mL } \frac{N}{6} \text{ HCl solution} \equiv 20 \text{ mL of base solution}$$

or $$2 \text{ mL } 1\ N \text{ HCl solution} \equiv 20 \text{ mL of base solution}$$

or $$\frac{2}{20} \times 500 \text{ mL } 1\ N \text{ HCl solution} \equiv 500 \text{ mL of base solution}$$

or $$50 \text{ mL } 1\ N \text{ HCl solution} \equiv 2.65 \text{ g of base}$$

$$1000 \text{ mL } 1\ N \text{ HCl solution} \equiv \frac{2.65}{50} \times 1000 = 53 \text{ g base}$$

$$\text{Eq. mass of the base} = 53$$

Mol. mass of the base = Eq. mass × acidity $= 53 \times 2 = \mathbf{106}$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

9. Molecular mass of a volatile organic solid can be determined by:

(a) silver chloride method (b) platinichloride method
(c) Victor Meyer's method (d) Kjeldahl's method
[**Ans.** (c)]

10. Molecular mass of a non-volatile organic solid can be determined by:

(a) Victor Meyer's method
(b) elevation in boiling point
(c) silver salt method
(d) depression in freezing point
[**Ans.** (b) and (d)]

11. Equivalent mass of an organic acid can be determined by:
    - (a) silver salt method
    - (b) cryoscopic method
    - (c) ebullioscopic method
    - (d) platinichloride method

    [**Ans.** (a)]

12. Equivalent mass of an organic base can be determined by:
    - (a) silver salt method
    - (b) depression in freezing point
    - (c) elevation in boiling point
    - (d) platinichloride method

    [**Ans.** (d)]

2.5 EMPIRICAL FORMULA AND MOLECULAR FORMULA

The empirical formula of a compound is the simplest formula which expresses the simple whole number ratio of the atoms of constituent elements present in the molecule. For example, CH_2O is the empirical formula of acetic acid. It expresses that the simplest whole number ratio between carbon, hydrogen and oxygen atoms present in one molecule of acetic acid is 1 : 2 : 1. The empirical formula does not tell us the exact number of various atoms of different elements present in one molecule of the substance. However, the exact number of atoms of different elements present in one molecule is always a simple multiple of ratio of atoms in the empirical formula. **The formula which gives the actual number of atoms of various elements present in the molecule of the substance is termed the molecular formula.**

Thus, Molecular formula = $n \times$ [Empirical formula]

where n is a whole number.

$$\text{Molecular formula of acetic acid} = 2 \times \text{Empirical formula}$$
$$= 2 \times CH_2O$$
$$= C_2H_4O_2 (CH_3COOH)$$

The value of 'n' can be obtained by dividing the molecular mass by empirical formula mass.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

For example,

Molecular mass of acetic acid = 60

and Empirical formula mass (CH_2O) = $(12 + 2 + 16) = 30$

$$n = \frac{60}{30} = 2$$

The percentage composition of the compound can be calculated from its empirical formula. For example :

Empirical formula of acetic acid = CH_2O

$$\text{Empirical formula mass} = (12 + 2 + 16) = 30$$

$$\text{Percentage of C} = \frac{12}{30} \times 100 = 40.00$$

$$\text{Percentage of H} = \frac{2}{30} \times 100 = 6.66$$

$$\text{Percentage of O} = \frac{16}{30} \times 100 = 53.34$$

Thus, the simplest formula of a substance capable of expressing its percentage composition can be called its empirical formula.

Calculation of empirical formula : Empirical formula is calculated from the percentage composition. The steps involved in the calculation are as follows:

Step 1 : The percentage of each element is divided by its atomic mass. This gives the relative number of different atoms present in the molecule.

Step 2 : The relative numbers of different atoms obtained in Step 1 are divided by the lowest one amongst them as to get simple ratio of atoms present in the molecule.

Step 3 : The values obtained in Step 2 may or may not be whole numbers. In case one or more values are fractional, these are multiplied by a suitable integer to get simplest ratio in whole numbers. Minor fractions are neglected.

Step 4 : The symbols of each element present are written side by side in a line with the number of atoms as determined in Step 2 or Step 3 as subscripts to the lower corner of each. This gives the empirical or simplest formula.

Knowing the empirical formula, the molecular formula can be ascertained if the molecular mass of the substance is known. It may be the same as the empirical formula of the substance or an exact multiple of it.

Molecular formula = $n \times$ (Empirical formula)

The value of 'n' can be determined if molecular mass of the substance is known.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

An alternative method of molecular formula determination.

In this method, molecular formula can be determined without determining empirical formula. It is very simple method and comparatively less time taking.

Following relation is used to calculate number of moles of an element in the compound :

Number of moles of element

$$= \frac{\%\text{ of element}}{100} \times \frac{\text{Molecular mass}}{\text{Atomic mass of element}}$$

Problem 15. *An organic compound contains* 40% C, 6.66% H *and rest oxygen. Its vapour density is* 30. *Calculate its empirical and molecular formulas.*

Solution : Calculation of empirical formula :

Element	**Percentage**	**At. mass**	**Relative number of atoms**	**Simplest ratio**
Carbon	40.0	12	$\frac{40}{12} = 3.33$	$\frac{3.33}{3.33} = 1$
Hydrogen	6.66	1	$\frac{6.66}{1} = 6.66$	$\frac{6.66}{3.33} = 2$
Oxygen	53.34 (by difference)	16	$\frac{53.34}{16} = 3.33$	$\frac{3.33}{3.33} = 1$

$$\text{Empirical formula} = CH_2O$$

$$\text{Empirical formula mass} = (12+2+16) = 30$$

$$\text{Mol. mass} = 2 \times \text{V.D.} = 2 \times 30 = 60$$

$$n = \frac{\text{Mol. mass}}{\text{Emp. mass}} = \frac{60}{30} = 2$$

$$\text{Molecular formula} = 2 \times (\text{Empirical formula}) = 2 \times (CH_2O) = C_2H_4O_2$$

Alternatively

Number of moles of carbon

$$= \frac{\%\text{ of carbon}}{100} \times \frac{\text{Molecular mass}}{\text{Atomic mass of element}}$$

$$= \frac{40}{100} \times \frac{60}{12} = 2$$

Number of moles of hydrogen

$$= \frac{\%\text{ of hydrogen}}{100} \times \frac{\text{Molecular mass}}{\text{Atomic mass of hydrogen}}$$

$$= \frac{6.66}{100} \times \frac{60}{1} = 4$$

Number of moles of oxygen

$$= \frac{\%\text{ of oxygen}}{100} \times \frac{\text{Molecular mass}}{\text{Atomic mass of oxygen}}$$

$$= \frac{53.34}{100} \times \frac{60}{16} = 2$$

$$\text{Molecular formula} = C_2H_4O_2$$

Problem 16. *A dibasic organic acid gave the following results :* $C = 34.62\%$, $H = 3.84\%$. $0.1075\, g$ *of this acid consumes* $20\, mL$ *of* $0.1\, N$ NaOH *for complete neutralisation. Find out the molecular formula of the acid.*

Solution : Calculation of empirical formula :

Element	Percentage	At. mass	Relative number of atoms	Simplest ratio of atoms
Carbon	34.62	12	$\frac{34.62}{12} = 2.88$	$\frac{2.88}{2.88} = 1 \times 3 = 3$
Hydrogen	3.84	1	$\frac{3.84}{1} = 3.84$	$\frac{3.84}{2.88} = 1.33 \times 3 = 4$
Oxygen	61.54 (by difference)	16	$\frac{61.54}{16} = 3.84$	$\frac{3.84}{2.88} = 1.33 \times 3 = 4$

$$\text{Empirical formula of the acid} = C_3H_4O_4$$

$$\text{Empirical formula mass} = (3 \times 12) + (4 \times 1) + (4 \times 16) = 104$$

Calculation of molecular mass :

$$20\text{ mL } 0.1\, N \text{ NaOH} \equiv 0.1075\text{ g acid}$$

$$20 \times 0.1\text{ mL } 1\, N \text{ NaOH} \equiv 0.1075\text{ g acid}$$

So, $$1000\text{ mL } 1\, N \text{ NaOH} \equiv \frac{0.1075}{20 \times 0.1} \times 1000\text{ g acid}$$

$$\equiv 53.75\text{ g acid}$$

$$\text{Eq. mass of the acid} = 53.75$$

$$\text{Mol. mass of the acid} = \text{Eq. mass} \times \text{basicity} = 53.75 \times 2 = 107.50$$

$$n = \frac{\text{Mol. mass}}{\text{Emp. mass}} = \frac{107.50}{104.0} \approx 1$$

$$\text{Molecular formula} = C_3H_4O_4$$

Problem 17. *An organic compound contains* $C = 48\%$, $H = 8\%$. $0.48\, g$ *of the compound was Kjeldahlised and the liberated ammonia required* $19.2\, mL$ $N/2\, H_2SO_4$. *Find the empirical formula of the compound.*

Solution : Percentage of nitrogen $= \frac{1.4 \times N_1 \times V_1}{W}$

$$W = \text{Mass of organic compound} = 0.48\text{ g}$$

$$N_1 = \frac{1}{2} = 0.5, \quad V_1 = 19.2\text{ mL}$$

$$\text{Percentage of } N = \frac{1.4 \times 0.5 \times 19.2}{0.48} = 28$$

$$\text{Percentage of oxygen} = 100 - (48 + 8 + 28) = 16$$

Calculation of empirical formula:

Element	Percentage	At. mass	Relative number of atoms	Simplest ratio of atoms
Carbon	48.0	12	$\frac{48}{12} = 4$	$\frac{4}{1} = 4$
Hydrogen	8.0	1	$\frac{8}{1} = 8$	$\frac{8}{1} = 8$
Nitrogen	28.0	14	$\frac{28}{14} = 2$	$\frac{2}{1} = 2$
Oxygen	16.0	16	$\frac{16}{16} = 1$	$\frac{1}{1} = 1$

$$\text{Empirical formula} = C_4H_8N_2O$$

Problem 18. *Haemoglobin is a chromoprotein having four atoms of* Fe *in each molecule. Analysis showed* 0.35% Fe. *What is the molecular weight of haemoglobin?*

Solution: Atomic mass of iron = 56 amu

Mass of iron in a molecule of haemoglobin

$$= 56 \times 4 = 224\text{ amu}$$

$\because$ 0.35 amu of Fe is present in 100 amu of haemoglobin.

$\therefore$ 224 amu of Fe will be present in $\frac{100}{0.35} \times 224$ amu of haemoglobin, *i.e.*, 64000 amu

Thus, molecular mass of haemoglobin = **64000 amu**

2.6 MOLECULAR FORMULA OF GASEOUS HYDROCARBONS

The molecular formula of gaseous hydrocarbons can be determined even without knowing their percentage composition. A known volume of hydrocarbon is taken in **eudiometer tube** and exploded with an excess of known volume of oxygen. The carbon and hydrogen of the hydrocarbon are oxidised to carbon dioxide and water respectively according to the following general reaction :

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

After explosion, the tube is allowed to cool to room temperature. The volume of the gaseous mixture is recorded.

The volume corresponds to unreacted oxygen and carbon dioxide. The volume of carbon dioxide is determined by the decrease in volume of the gaseous mixture when caustic potash solution is introduced into the eudiometer tube. The caustic potash solution absorbs whole of carbon dioxide. The gas left behind is the unreacted oxygen. Volume of oxygen used is then calculated by subtracting the volume of unreacted oxygen from the total volume of the oxygen taken initially.

The molecular formula of the hydrocarbon can be evaluated by knowing (i) the volume of gaseous hydrocarbon taken, (ii) the volume of oxygen used, and (iii) the volume of carbon dioxide produced.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

13. An organic compound has C and H percentage in the ratio 6 : 1 and C and O percentage in the ratio 3 : 4. The compound is:

(a) HCHO (b) CH_3OH

(c) CH_3CH_2OH (d) $(COOH)_2$

[**Ans.** (a)]

[**Hint :** % ratio of C : H is 6 : 1 and % ratio of C : O is 3 : 4. So, % ratio of C : H : O is 6 : 1 : 8.

Therefore, % of C comes to be 3.33, % of H is 6.66 and % of O is 3.33. Simplest ratio of C : H : O is 1 : 2 : 1, *i.e.*, CH_2O.]

14. A hydrocarbon (X) was found to have a molecular weight of 80–85. A 10.02 mg sample took up 8.40 mL of H_2 gas measured at 0°C and 760 mm pressure. Ozonolysis of (X) yields only HCHO and OHC—CHO. What was hydrocarbon?

(a) C_6H_8 (b) C_6H_{10}

(c) C_6H_{12} (d) C_6H_{14}

[**Ans.** (a)] *i.e.*, Hexa-1,3,5-triene ($H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$)

[**Hint :** Moles of H_2 taken up

$$= \frac{8.40\times10^{-3}}{22.4} = 3.75\times10^{-4}$$

$$\text{Moles of compound} = \frac{10.02\times10^{-3}}{22.4} = 1.253\times10^{-4}$$

Thus, moles of H_2 taken up by 1 mole of compound

$$= \frac{3.75\times10^{-4}}{1.253\times10^{-4}} = 3$$

Therefore, molecules has three double bonds and it may be hexa-1,3,5-triene.]

Problem 19. *5 mL of a gas containing only carbon and hydrogen were mixed with an excess of oxygen (30 mL) and the mixture exploded by means of an electric spark. After the explosion, the volume of the mixed gases remaining was 25 mL. On adding a concentrated solution of potassium hydroxide, the volume further diminished to 15 mL, the residual gas being pure oxygen. All volumes have been reduced to NTP. Calculate the molecular formula of the hydrocarbon gas.*

Solution : Let the formula of the hydrocarbon be C_xH_y. Its combustion can be shown by the following equation:

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

$$\begin{array}{lll} 1 \text{ vol.} & \left(x+\frac{y}{4}\right)\text{mL} & x \text{ vol.} \\ 5 \text{ mL} & 5\left(x+\frac{y}{4}\right)\text{mL} & 5x \text{ vol.} \end{array}$$

Volume of carbon dioxide produced = (25 − 15) = 10 mL

$$5x = 10$$

or $$x = 2$$

Volume of oxygen used = (30 − 15) = 15 mL

$$5\left[x+\frac{y}{4}\right] = 15 \quad \text{or} \quad x+\frac{y}{4} = \frac{15}{5} = 3$$

or $$2+\frac{y}{4} = 3$$

or $$\frac{y}{4} = 3-2 = 1$$

or $$y = 4$$

Thus, the molecular formula of the hydrocarbon = C_2H_4

Problem 20. *10 mL of a gaseous hydrocarbon was exploded with oxygen. After explosion, there was a contraction of 20 mL in volume. On shaking the residual gaseous mixture with* KOH, *there was a further concentration of 20 mL in volume. Calculate the molecular formula. All the volumes were recorded at same temperature and pressure.*

Solution : Let the formula of the hydrocarbon be C_xH_y. The combustion of the hydrocarbon can be shown as :

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

$$\begin{array}{lll} 10 \text{ mL} & 10\left(x+\frac{y}{4}\right)\text{mL} & 10x \text{ mL} \end{array}$$

The first reduction in volume after explosion

$$= 10+10\left(x+\frac{y}{4}\right)-10x = 20$$

$$= 10+\frac{10y}{4} = 20$$

Thus, $$y = \frac{10\times4}{10} = 4$$

Volume of carbon dioxide produced = 20 mL

Thus, $$10x = 20$$

$$x = \frac{20}{10} = 2$$

Hence, the molecular formula of the hydrocarbon = C_2H_4

2.7 MODERN METHODS OF STRUCTURE ELUCIDATION

Several new techniques have been designed during the last three or four decades which help in complete elucidation of the structure of an organic compound. These techniques not only help in determination of the molecular mass and various functional groups present in the molecule but also help to determine the complete three-dimensional structure of the molecule including bond length and bond angle, etc. These methods are broadly divided into two groups:

roscopic methods : These methods are based either on the absorption or radiation or the emission of radiation. The molecular mass is easily determined by the use of **Mass spectrometry. The infrared (IR), ultraviolet (UV),** and **nuclear magnetic resonance (NMR)** techniques are used these days to detect the presence of functional groups in the molecule.

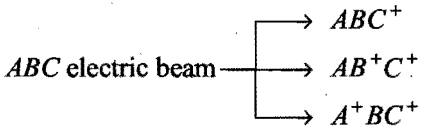
(2) Diffraction methods : X-ray diffraction, neutron diffraction and **electron diffraction techniques** are commonly used to determine the three-dimensional structure. These methods also help in the measurement of bond lengths and bond angles.

Mass Spectrometry

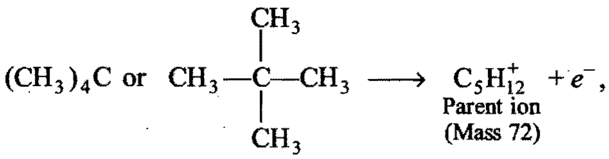
Mass spectrometry is the most accurate method for determining the molecular mass of a compound and its elemental composition like molecular formula and molecular structure of an unknown compound. When the vapour of a compound in high vacuum is bombarded with a moving beam of high energy electrons ($\approx 70\,\text{eV}$), ionisation of some molecule occurs with the formation of a radical cation.

$$\underset{\text{(M)}}{\text{Molecule}} + e^- \longrightarrow \underset{\text{Radical cation (or M}^+\text{)}}{(\text{Molecule})^+ + 2e^-}$$

Most of these ions carry a unit positive charge. The parent molecular ion possess so much excess energy that they often break up to give new smaller positive ions called **fragment ions** through various bond cleavages.

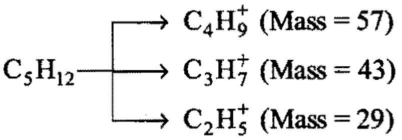


For example, a molecule of 2,2-dimethyl propane (neo-pentane) may break up as:



$$(CH_3)_4C \text{ or } CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3 \longrightarrow \underset{\substack{\text{Parent ion}\\ \text{(Mass 72)}}}{C_5H_{12}^+} + e^-,$$

2,2-Dimethyl propane (C_5H_{12})



Energy required to knock ion from an electron (ionisation potential) is only about 10–15 eV. Since, energy of the electron in practice is approximately 50–75 eV, the molecular ion is formed with an excess energy which is large enough to further break it down into a mixture of neutral and positively charged fragments.

Each kind of ion has a particular mass-to-charge ratio or m/Z value. For most of the ions, the charge (Z) is (+1), so that m/Z usually represents the mass of the ion. All positive ions are accelerated in an electric field and then passed through a magnetic field when these get separated. Ions having the same mass to charge ratio are, thus collected into beams.

Gases, liquids or solids may be used in the determination of mass spectra.

IMPORTANT POINTS TO REMEMBER (SUMMARY)

Qualitative analysis of a pure organic compound is carried out for **detection of elements** present in it.

Nitrogen, sulphur, halogens and phosphorus are detected by **Lassaigne's test.** Carbon and hydrogen are estimated by determining the amounts of carbon dioxide and water produced **(Liebig's method).** Nitrogen is estimated by **Duma's** or **Kjeldahl's method** and halogens by **Carius method.** Sulphur and phosphorus are estimated by oxidising them to sulphuric and phosphoric acids respectively **(Carius method).**

Relations for the estimation of elements in organic compounds:

Percentage of carbon (Liebig's method)

$$=\frac{12}{44}\times\frac{\text{Mass of CO}_2\text{ formed}}{\text{Mass of the compound}}\times 100$$

Percentage of hydrogen (Liebig's method)

$$=\frac{2}{18}\times\frac{\text{Mass of H}_2\text{O formed}}{\text{Mass of the compound}}\times 100$$

Percentage of nitrogen (Duma's method)

$$=\frac{28}{22{,}400}\times\frac{\text{Volume of N}_2\text{ at NTP}}{\text{Mass of the compound}}\times 100$$

Percentage of nitrogen (Kjeldahl's method)

$$=\frac{1.4\times\text{Normality of acid used}\times\text{Volume of acid used}}{\text{Mass of the compound}}$$

Percentage of halogens (X) (Carius method)

$$=\frac{\text{Atomic mass of }X}{(108+\text{Atomic mass of }X)}\times\frac{\text{Mass of Ag}X\text{ formed}}{\text{Mass of the compound}}\times 100$$

[For Cl ($X = 35.5$), Br ($X = 80$), I ($X = 127$)]

Percentage of sulphur (Carius method)

$$=\frac{32}{233}\times\frac{\text{Mass of BaSO}_4\text{ formed}}{\text{Mass of the compound}}\times 100$$

Percentage of phosphorus (Carius method)

$$=\frac{62}{222}\times\frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7\text{ formed}}{\text{Mass of the compound}}\times 100$$

The **percentage of oxygen** is usually determined by difference between the total percentage (100) and the sum of percentages of all other elements present.

Molecular mass determination can be done by the following methods:

(a) For volatile compounds	(i) Victor Meyer's method (ii) Duma's method (iii) Hofmann's method
(b) For non-volatile compounds	(i) Elevation in boiling point method (ii) Depression in freezing point method
(c) Chemical methods	(i) Silver salt method for acids (ii) Platinichloride method for bases (iii) Volumetric methods for both acids and bases

QUESTIONS

➢ VERY SHORT ANSWER TYPE

1. Fill in the blanks:
   (a) Lassaigne's test can be applied for the detection of ......, sulphur and ...... in organic compounds.
   (b) In the Lassaigne's test, the sulphur present in the organic compound is converted into ......
   (c) In the Lassaigne's test, the nitrogen present in the organic compound is converted into ......
   (d) The formation of violet colour by the addition of sodium nitroprusside to the Lassaigne's solution is the indication of...... element in the organic compound.
   (e) In the Kjeldahl's process, the nitrogen present in the organic compound is changed into ...... by heating the compound with concentrated H_2SO_4.
   (f) In Lassaigne's test for halogens, concentrated HNO_3 is used to destroy ...... and ......
   (g) In Carius method, sulphur is oxidised to ...... with fuming nitric acid.
   (h) In Duma's method, the nitrogen present in an organic compound is released as ...... gas.
   (i) To determine the amount of halogen in an organic compound, the compound is heated with fuming HNO_3 in presence of ......
   (j) In the Lassaigne's solution with nitrogen present in the organic compound, ferrous sulphate solution is added and then boiled. It is neutralised with dilute H_2SO_4. A bright ...... solution is formed.
   (k) Molecular mass of the base = Equivalent mass × ......
   (l) Equivalent mass of the acid

$$=\left(\frac{\text{Mass of ......}}{\text{Mass of silver}}\times 108-107\right)$$

   (m) 1000 mL 1 N alkali solution = ... of the acid.
   (n) Molecular mass of a gaseous hydrocarbon can be determined even without knowing its percentage composition by ......
   (o) Empirical formula indicates ...... present in one molecule of a compound.
   (p) Molecular formula indicates ...... of each of the constituent elements present in one molecule.
   (q) Molecular formula = n × empirical formula

   where $n=\frac{......}{......}$

   (r) Empirical formula of C_6H_6 is ......
   (s) Empirical formula of $C_6H_{12}O_6$ is ......
   (t) The vapour density of NH_2CONH_2 is ......
   (u) The sodium extract of an organic compound on boiling with HNO_3 and treatment with ammonium molybdate solution gives a yellow precipitate. It indicates the presence of ...... in the compound.
   (v) When an organic compound is heated with dry cupric oxide and the gases evolved are passed through lime water which turns milky, the gas may be ...... or ......
   (w) If nitrogen and sulphur both are present in an organic compound and it is fused with sodium. The sodium compound formed is ......
   (x) The percentage of carbon in CH_4 is ......
   (y) Equivalent mass of a base

$$=\frac{1}{2}\left[\frac{..............}{\text{Mass of platinum}}\times 195-410\right]$$

   (z) The basicity of the acid is ...... if its molecular mass is 104 and equivalent mass is 52.

2. State whether the following statements are **True** or **False**:
   (a) All organic compounds contain carbon and hydrogen both.
   (b) Carbon and hydrogen are detected simultaneously in an organic compound by Liebig method.
   (c) Beilstein test is reliable test for halogens in organic compounds.
   (d) Sulphur is estimated by Carius method as barium sulphate.
   (e) Mol. mass of an acid = Equivalent mass × acidity.
   (f) Victor Meyer's method is used for the determination of molecular mass of a non-volatile compound.
   (g) Duma's method can be applied for estimation of nitrogen in all nitrogenous organic compounds.
   (h) A red solution is obtained when ferric chloride solution is added to sodium extract. It indicates both nitrogen and sulphur are present in the organic compound.
   (i) In Lassaigne's test of nitrogen, the final product formed is sodium ferrocyanide.
   (j) Kjeldahl's method is applicable to all nitrogenous organic compounds.
   (k) Phosphorus is estimated by Carius method as magnesium pyrophosphate.
   (l) Ordinary CuO is used in Liebig's combustion method for estimation of carbon and hydrogen in organic compounds.
   (m) An organic base, B, whose acidity is one when combines with H_2PtCl_6 forms insoluble compound of formula $B_2H_2PtCl_6$.
   (n) $\frac{\text{Molecular mass}}{\text{Empirical formula mass}}=n$, where n is always a whole number.
   (o) Silver salt method is a chemical method for the determination of equivalent mass of organic bases.
   (p) Estimation of oxygen in an organic compound can be made by Aluise method.
   (q) In the Carius method, the sealed Carius tube containing organic compound, fuming nitric acid and

silver nitrate is heated at 300°C for six hours in the estimation of halogens.

(r) In Kjeldahl's method, during digestion of the organic compound with conc. H_2SO_4, potassium sulphate and sodium sulphate are also added.

(s) An organic compound containing nitrogen, on heating strongly with H_2SO_4 gives ammonium sulphate which on treatment with excess of NaOH liberates ammonia.

(t) The simplest formula that shows the ratio of the atoms of the various elements present in the molecule is called the molecular formula.

(u) The molecular mass of a non-volatile organic compound is determined either by the Victor Meyer's method or Duma's method.

(v) The gas displaced in Victor Meyer's method is air.

(w) The gas estimated in Duma's method is nitrogen.

(x) A Lassaigne's solution is boiled with dilute HNO_3, cooled and $AgNO_3$ added. It gives a yellow precipitate, sparingly soluble in ammonia. This indicates the presence of iodine in the organic compound.

(y) A black precipitate is formed when lead acetate solution is added to acidified sodium extract of an organic compound containing sulphur.

(z) Copper wire is used in Beilstein test.

3. Give reasons:

(i) During the test for nitrogen in Lassaigne's filtrate, sometimes red colouration is obtained when ferric chloride is added.

(ii) Why is sodium extract made acidic with acetic acid before the addition of lead acetate in the test of sulphur?

(iii) In the test of nitrogen, freshly prepared solution of ferrous sulphate is always used.

(iv) During the test for halogens, why is sodium extract first boiled with a few drops of conc. HNO_3?

(v) Why the organic compound is fused with sodium metal during detection of nitrogen, sulphur, halogens, etc.?

(vi) What is the role of copper sulphate and potassium sulphate in Kjeldahl's process for the estimation of nitrogen in an organic compound?

(vii) Is Beilstein test a satisfactory test for detection of halogens?

4. Match the following:

Property to be determined	**Method used for determination**
(a) Molecular mass of a volatile organic solid	1. Silver salt method
(b) Molecular mass of a non-volatile organic solid	2. Liebig method
(c) Estimation of chlorine in carbon tetrachloride	3. Platinichloride method
(d) Estimation of nitrogen in aniline	4. Victor Meyer's method
(e) Equivalent mass of an organic acid	5. Depression in freezing point
(f) Equivalent mass of an organic base	6. Carius method
(g) Estimation of carbon and hydrogen in an organic compound	7. Kjeldahl's method

5. Complete the following:

(i) $(CH_3COO)_2Pb + Na_2S \xrightarrow{H^+} \ldots\ldots + \ldots\ldots$

(ii) $Fe^{3+} + 3NaCNS \longrightarrow \ldots\ldots + \ldots\ldots$

(iii) $NaI + AgNO_3 \longrightarrow \ldots\ldots + \ldots\ldots$

(iv) $4FeCl_3 + 3Na_4Fe(CN)_6 \longrightarrow \ldots\ldots + \ldots\ldots$

(v) $FeSO_4 + 6NaCN \longrightarrow \ldots\ldots + \ldots\ldots$

(vi) $Na_2S + Na_2Fe(CN)_5NO \longrightarrow \ldots\ldots$

(vii) $(NH_4)_2SO_4 + 2NaOH \longrightarrow \ldots\ldots + \ldots\ldots + \ldots\ldots$

(viii) $5CO + I_2O_5 \longrightarrow \ldots\ldots + \ldots\ldots$

(ix) $RCOONH_4 + AgNO_3 \longrightarrow \ldots\ldots + \ldots\ldots$

(x) $C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow \ldots\ldots + \ldots\ldots$

➤ SHORT ANSWER TYPE

6. Describe the following:

(i) Chemistry of Lassaigne's test for the detection of nitrogen in an organic compound.

(ii) Chemistry of Lassaigne's test for the detection of sulphur in an organic compound.

(iii) Chemistry of Lassaigne's test for the detection of halogens in an organic compound.

(iv) Chemistry of Kjeldahl's method for the estimation of nitrogen in an organic compound.

(v) Platinichloride method of determination of molecular mass of an organic base.

(vi) Silver salt method of determination of molecular mass of an organic acid.

(vii) Principle of Duma's method for the estimation of nitrogen in an organic compound.

(viii) Liebig method for the estimation of carbon and hydrogen in an organic compound.

(ix) Carius method for the estimation of sulphur in an organic compound.

(x) Carius method for the estimation of halogens in an organic compound.

(xi) How is molecular formula of a hydrocarbon derived by eudiometry?

(xii) The difference between empirical and molecular formula and the relationship between them.

(xiii) Layer test for bromine and iodine in an organic compound.

(xiv) Aluise's method for the estimation of oxygen in an organic compound.

(xv) Beilstein test or copper wire test.

ANSWERS

1. (a) nitrogen, halogens; (b) sodium sulphide; (c) sodium cyanide; (d) sulphur; (e) ammonium sulphate; (f) HCN and H_2S; (g) H_2SO_4; (h) nitrogen; (i) $AgNO_3$; (j) blue coloured; (k) acidity; (l) silver salt; (m) equivalent mass; (n) eudiometry; (o) simplest ratio of atoms of constituent elements; (p) actual number of atoms;

(q) $\dfrac{\text{Molecular mass}}{\text{Empirical formula mass}}$; (r) CH; (s) CH_2O; (t) 30; (u) phosphorus; (v) CO_2, SO_2; (w) NaCNS; (x) 75; (y) mass of platinum salt; (z) two.

2. (a) False—hydrogen is not always present; (b) True; (c) False—sometimes the test fails; (d) True; (e) False—molecular mass of an acid = equivalent mass × basicity; (f) False—used for a volatile compound; (g) True; (h) True; (i) False—the final product formed is ferri-ferro cyanide; (j) False—not applicable to pyridine, compounds containing N—N, N—O, etc. bonds; (k) True; (l) False—dry CuO is used; (m) True; (n) True; (o) False—for the determination of equivalent mass of organic acids; (p) True; (q) True; (r) False—potassium sulphate and copper sulphate are added; (s) True; (t) False—is called empirical formula; (u) False—determined by either elevation in boiling point method or depression in freezing point method; (v) True; (w) True; (x) False—indicates the presence of bromine; (y) True; (z) True.

3. (i) When nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed which gives red colouration with $FeCl_3$.
   (ii) Lead acetate is hydrolysed by NaOH present in sodium extract. It is neutralised first with acetic acid before the addition of lead acetate.
   (iii) Ferrous sulphate gets hydrolysed if its solution is stored.
   (iv) As to decompose NaCN or Na_2S if present in the sodium extract.
   (v) As to convert nitrogen, sulphur or halogens present in an organic compound into ionisable substances.
   (vi) Copper sulphate acts as a catalyst while potassium sulphate raises the boiling point of H_2SO_4.
   (vii) It is not always reliable. Substances such as urea, thiourea, pyridine, organic acids, etc., also impart colour to flame.

4. (a—4); (b—5); (c—6); (d—7); (e—1); (f—3); (g—2).

5. (i) $2CH_3COONa + PbS$ (ii) $Fe(CNS)_3 + 3Na^+$
(iii) $AgI + NaNO_3$ (iv) $Fe_4[Fe(CN)_6]_3 + 12NaCl$
(v) $Na_4[Fe(CN)_6] + Na_2SO_4$ (vi) $Na_4[Fe(CN)_5NOS]$
(vii) $2NH_3 + Na_2SO_4 + 2H_2O$ (viii) $I_2 + 5CO_2$
(ix) $RCOOAg + NH_4NO_3$ (x) $xCO_2 + \frac{y}{2}H_2O$

NUMERICAL PROBLEMS FOR PRACTICE

1. 0.45 g of an organic compound gave on combustion 0.792 g of CO_2 and 0.324 g of water. 0.24 g of the same substance was Kjeldahlised and the ammonia formed was absorbed in 50 mL of 0.25 N H_2SO_4. The excess of acid required 77.0 mL of 0.1 N NaOH for complete neutralisation. Calculate the empirical formula of the compound.
[Ans. $C_4H_8N_2O$]

2. A compound contains 40% C, 6.66% H and 53.33% O. An examination reveals that 9.0 g of the compound dissolved in 500 g of water raises the boiling point of water by 0.051°C. What is the molecular formula of the compound? [$K_f = 0.51\,\text{K mol}^{-1}\,\text{kg}$]
[Ans. $C_6H_{12}O_6$]

3. Tyrosine is one of the amino acids present in protein. Its content in the protein is 0.22% and its molecular weight is 181 g mol^{-1}. What is the lowest molecular weight of the protein?
[Ans. 82272]

4. A molecule was known by its mode of synthesis to contain 10 atoms of carbon per molecule, along with unknown number of chlorine, hydrogen and oxygen. Analysis indicates that it contains 60.5% carbon, 5.55% hydrogen, 16.1% oxygen and 17.9% chlorine. Derive molecular formula.
[Ans. $C_{10}H_{11}O_2Cl$]

5. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10 litre (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula (ii) molar mass of the gas (iii) molecular formula.
[Ans. (i) CH_2 (ii) 26 (iii) C_2H_2]

6. 0.33 mole cholesterol gives 9 mole CO_2 on combustion. It was observed that cholesterol contains 83.85% C; 12% H and 4.15% O. Find its molecular formula and molecular mass.
[Ans. $C_{27}H_{46}O$; 386]

7. An automobile antifreeze consists of 38.7% carbon; 9.7% hydrogen and remaining oxygen by weight. When 0.93 g of it are vaporised at 200°C and 1 atm pressure, 582 mL of vapour are formed. Find molecular formula of antifreeze.
[Ans. $C_2H_6O_2$]

8. The compound $[Pd(C_xH_yN_z)](ClO_4)_2$ contains 30.15% carbon and 5.06% hydrogen. The compound $[Pd(C_xH_yN_z)](SCN)_2$ contains 40.46% carbon and 5.94% hydrogen. Calculate x, y, z.
[Ans. $x = 14$, $y = 28$, $z = 4$]

9. Methyl orange, an acid base indicator, is the sodium salt of an acid that contains C, H, N, S and oxygen. Quantitative analysis gave C = 51.4%, H = 4.3%, N = 12.8%, S = 9.8% and Na = 7.0%. What is the empirical formula of methyl orange?
[Ans. $C_{14}H_{14}N_3SO_3Na$]

10. The sulphur content of cystine is 26.7%. Given that cystine contains two sulphur atoms, what is the molecular weight of cystine?
[Ans. 239.7 g]
[Hint: Atomic mass of sulphur is 32, hence for two sulphur atoms, the molecular formula will have 64 g sulphur.
Thus, if 26.7 g sulphur, then molecular weight = 100 g.
and if 64 g sulphur is present, molecular weight
$$= \frac{100 \times 64}{26.7} = 239.7 \text{ g mol}^{-1}]$$

OBJECTIVE QUESTIONS

SET I : This set contains the questions with single correct answer.

1. Carbon and hydrogen are estimated in organic compounds by:
(a) Kjeldahl's method ☐ (b) Duma's method ☐
(c) Liebig's method ☐ (d) Carius method ☐

2. Lassaigne's test is used for the detection of:
(a) carbon only ☐
(b) hydrogen only ☐
(c) oxygen only ☐
(d) nitrogen, sulphur and halogens ☐

3. In Lassaigne's test, the organic compound is fused with sodium metal as to:
(a) hydrolyse the compound ☐
(b) form a sodium derivative ☐
(c) convert nitrogen, sulphur or halogens if present into soluble ionic sodium compound ☐
(d) burn the compound ☐

4. Nitrogen containing organic compound when fused with sodium metal forms: **[CET (Karnataka) 2006]**
(a) $NaNO_2$ ☐ (b) NaCN ☐
(c) $NaNH_2$ ☐ (d) NaNC ☐

5. The sodium extract of an organic compound on treatment with $FeSO_4$ solution, $FeCl_3$ and HCl gives a red solution. The organic compound contains:
(a) both nitrogen and sulphur ☐
(b) nitrogen only ☐
(c) sulphur only ☐
(d) halogen ☐

6. The prussian blue colour obtained during the test of nitrogen by Lassaigne's test is due to the formation of: **[AIEEE 2004; AFMC 2010]**
(a) $Fe_4[Fe(CN)_6]_3$ ☐ (b) $Na_3[Fe(CN)_6]$ ☐
(c) $Fe(CN)_3$ ☐ (d) $Na_4[Fe(CN)_5NOS]$ ☐

7. Which of the following sodium compound/compounds are formed when an organic compound containing both nitrogen and sulphur is fused with sodium?
(a) Cyanide and sulphide ☐ (b) Thiocyanate ☐
(c) Sulphite and cyanide ☐ (d) Nitrate and sulphide ☐

8. When N and S both are present in an organic compound, the sodium extract with $FeCl_3$ gives:
(a) green colour ☐ (b) blue colour ☐
(c) yellow colour ☐ (d) red colour ☐

9. The sodium extract of an organic compound on acidification with acetic acid and addition of lead acetate solution gives a black precipitate. The organic compound contains:
(a) nitrogen ☐ (b) halogen ☐
(c) sulphur ☐ (d) phosphorus ☐

10. The sodium extract of an organic compound on boiling with HNO_3 and addition of ammonium molybdate solution gives a yellow precipitate. The compound contains:
(a) nitrogen ☐ (b) phosphorus ☐
(c) sulphur ☐ (d) chlorine ☐

11. Which of the following compounds gives blood red colouration when its Lassaigne's extract is treated with alkali and ferric chloride? **[DPMT 2009]**
(a) Thiourea ☐ (b) Benzamide ☐
(c) Phenyl hydrazine ☐ (d) Diphenyl sulphide ☐

12. Copper wire test of halogens is known as:
(a) Liebig's test ☐ (b) Lassaigne's test ☐
(c) Fusion test ☐ (d) Beilstein's test ☐

13. Duma's method involves the determination of nitrogen content in the organic compound in the form of : **[BHU 2005]**
(a) NH_3 ☐ (b) N_2 ☐
(c) NaCN ☐ (d) $(NH_4)_2SO_4$ ☐

14. In Lassaigne's solution, pink/violet colouration is produced when sodium nitroprusside solution is added. It indicates the presence of:
(a) sulphur ☐ (b) nitrogen ☐
(c) chlorine ☐ (d) none of these ☐

15. An organic compound on heating with CuO produces CO_2 but no water. It may be:
(a) CH_4 ☐ (b) C_2H_5I ☐
(c) $CHCl_3$ ☐ (d) CCl_4 ☐

16. In an organic compound, Kjeldahl's method is used for the estimation of:
(a) halogens ☐ (b) sulphur ☐
(c) nitrogen ☐ (d) oxygen ☐

17. In Lassaigne's test for the detection of halogens, the sodium fusion extract is first boiled with concentrated nitric acid. This is : **[PET (Kerala) 2010]**
(a) to remove silver halides ☐
(b) to decompose Na_2S and NaCN, if present ☐
(c) to dissolve Ag_2S ☐
(d) to dissolve AgCN, if formed ☐
(e) because Ag_2S and AgCN are insoluble in nitric acid ☐

18. In Kjeldahl's method of estimation of nitrogen, copper sulphate acts as: **[UPSEE 2008]**
(a) an oxidising agent ☐ (b) a reducing agent ☐
(c) a catalytic agent ☐ (d) a hydrolysing agent ☐

19. In the Duma's method for the estimation of nitrogen in an organic compound, nitrogen is determined in the form of:
(a) gaseous nitrogen ☐ (b) gaseous ammonia ☐
(c) ammonium sulphate ☐ (d) sodium cyanide ☐

20. An organic compound which produces a bluish green coloured flame on heating in presence of copper is : **[CET (Karnataka) 2006]**

(a) benzaldehyde ☐ (b) benzoic acid ☐
(c) aniline ☐ (d) chlorobenzene ☐

21. In organic compounds, halogens are estimated by:
(a) Carius method ☐ (b) Liebig's method ☐
(c) Kjeldahl's method ☐ (d) Duma's method ☐

22. In the estimation of sulphur in an organic compound, fuming nitric acid is used to convert sulphur into:
(a) SO_2 ☐ (b) H_2S ☐
(c) H_2SO_3 ☐ (d) H_2SO_4 ☐

23. Schiff's and Piria method is used for the estimation of:
(a) nitrogen ☐ (b) sulphur ☐
(c) halogens ☐ (d) oxygen ☐

24. Prussian blue colour is obtained by mixing together aqueous solution of Fe^{3+} salt with : **[CET (J&K) 2007]**
(a) ferricyanide ☐ (b) ferrocyanide ☐
(c) hydrogen cyanide ☐ (d) sodium cyanide ☐

25. The blood red colour in the combination test of nitrogen and sulphur in organic compound is due to the formation of:
(a) ferric sulpho cyanide ☐
(b) ferric acetate ☐
(c) ferrous sulpho cyanide ☐
(d) ferric cyanide ☐

26. The violet colour obtained during the test of sulphur by Lassaigne's test is due to the formation of: **[PMT (Kerala) 2006; CMC (Vellore) 2008]**
(a) $Na_2[Fe(CN)_5S]$ ☐ (b) $Na_2[Fe(CN)_5NO]$ ☐
(c) $Na_2[Fe(CN)_6]$ ☐ (d) $Na_4[Fe(CN)_5NOS]$ ☐

27. Chloro acetic acid is heated with fuming nitric acid in presence of $AgNO_3$ in Carius tube. After filtration and washing, a white precipitate is obtained. This precipitate is:
(a) $AgNO_3$ ☐ (b) Ag_2O ☐
(c) AgCl ☐ (d) $ClCH_2COOAg$ ☐

28. Mark the incorrect statement in nitrogen Kjeldahl's method of estimation:
(a) nitrogen gas is collected over caustic potash solution ☐
(b) potassium sulphate is used as boiling point elevator of H_2SO_4 ☐
(c) copper sulphate or mercury acts as a catalyst ☐
(d) nitrogen is quantitatively decomposed to give ammonium sulphate ☐

29. In the estimation of carbon and hydrogen, if the substance also contains nitrogen, then near the exit, it is placed:
(a) a roll of silver ☐
(b) a bright copper gauge spiral ☐
(c) ammonium sulphate ☐
(d) a layer of lead chromate ☐

30. In the estimation of carbon and hydrogen, if the substance also contains halogens, then near the exit, it is placed:
(a) a roll of silver ☐
(b) a layer of lead chromate ☐
(c) both, a roll of silver and a layer of lead chromate ☐
(d) a bright copper gauge spiral ☐

31. In the estimation of carbon and hydrogen, if the substance also contains both halogen and sulphur, then near the exit, it is placed:
(a) a roll of silver ☐
(b) a layer of lead chromate ☐
(c) a bright copper gauge spiral ☐
(d) none of the above ☐

32. In carbon and hydrogen estimation, the saphnolite (a resin) absorbs:
(a) N_2 ☐ (b) water vapours ☐
(c) both CO_2 and H_2O ☐ (d) only CO_2 ☐

33. Catalyst used in Kjeldahl's method for the estimation of nitrogen is:
(a) sodium ☐ (b) magnesium ☐
(c) mercury ☐ (d) copper ☐

34. Formula which represents a simple ratio of atoms of different elements present in a molecule of the substance is called:
(a) molecular formula ☐ (b) empirical formula ☐
(c) structural formula ☐ (d) none of these ☐

35. An organic compound contains carbon, hydrogen and oxygen. Its elemental analysis gave C, 38.71% and H, 9.67%. The empirical formula of the compound would be: **[CBSE (Med.) 2008]**
(a) CH_2O ☐ (b) CH_4O ☐
(c) CH_3O ☐ (d) CHO ☐

36. An alkaloid contains 17.28% of nitrogen and its molecular mass is 162. The number of nitrogen atoms present in one molecule of alkaloid is: **[Punjab CET (Engg.) 2008]**
(a) 3 ☐ (b) 2 ☐
(c) 5 ☐ (d) 4 ☐

37. A hydrocarbon contains 10.5 g carbon and 1 g hydrogen. Its 0.36 g has 1 litre volume at 1 atm and 127° C, the hydrocarbon is: **[UPSEAT 2003]**
(a) C_6H_7 ☐ (b) C_7H_8 ☐
(c) C_5H_6 ☐ (d) None of these ☐

38. Which of the following reagents is used for the separation of acetaldehyde from acetophenone? **[AIIMS 2004]**
(a) NH_2OH ☐ (b) $NaOHI_2$ ☐
(c) $NaHSO_3$ ☐ (d) $C_6H_5NHNH_2$ ☐

39. The formula of gas is $[CO]_x$. If its vapour density is 70, the value of x will be: **[DCE 2004]**
(a) 2.5 ☐ (b) 3.0 ☐
(c) 5.0 ☐ (d) 6.0 ☐

40. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium hydroxide solution for complete neutralization. The organic compound is: **[AIEEE 2004]**
(a) urea ☐ (b) thiourea ☐
(c) acetamide ☐ (d) benzamide ☐

41. How will you separate a solution (miscible) of benzene + $CHCl_3$? **[AFMC 2005]**

(a) Sublimation ☐ (b) Filtration ☐
(c) Distillation ☐ (d) Crystallisation ☐

42. An organic compound having molecular mass 60 is found to contain $C = 20\%$, $H = 6.67\%$ and $N = 46.67\%$ while rest is oxygen. On heating it gives NH_3 along with a solid residue. The solid residue gives violet colour with alkaline copper sulphate solution. The compound is: **[AIEEE 2005; PMT (Kerala) 2008]**

(a) CH_3NCO ☐ (b) CH_3CONH_2 ☐
(c) $(NH_4)_2CO$ ☐ (d) $CH_3CH_2CONH_2$ ☐

43. A compound containing only carbon, hydrogen and oxygen, has a molecular weight of 44. On complete oxidation it is converted into a compound of molecular weight 60. The original compound is: **(KCET 2005)**

(a) an aldehyde ☐ (b) an acid ☐
(c) an alcohol ☐ (d) an ether ☐

44. 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 ml of 0.1 *M* HCl solution. The excess of acid required 15 ml of 0.1 *M* NaOH solution for complete neutralisation. The percentage of nitrogen in the compound is: **[AIEEE 2010]**

(a) 29.5 ☐ (b) 59.0 ☐
(c) 23.7 ☐ (d) 47.4 ☐

45. An aromatic hydrocarbon with empirical formula C_5H_4 on treatment with concentrated H_2SO_4 gave a monosulphonic acid. 0.104 g of the acid required 10 ml of *N*/20 NaOH for complete neutralisation. The molecular formula of hydrocarbon is: **[PET (Kerala) 2007]**

(a) C_5H_4 ☐ (b) $C_{10}H_8$ ☐
(c) $C_{15}H_{12}$ ☐ (d) $C_{20}H_{16}$ ☐
(e) $C_{15}H_{20}$ ☐

46. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene ($K_f = 1.72$ K kg mol^{-1}), a freezing point depression of 2K is observed. The van't Hoff factor (*i*) is: **[IIT 2007]**

(a) 0.5 ☐ (b) 1 ☐
(c) 2 ☐ (d) 3 ☐

47. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in presence of air gives a prussian blue precipitate. The blue colour is due to the formation of: **[IIT 2007]**

(a) $Fe_4[Fe(CN)_6]_3$ ☐ (b) $Fe_3[Fe(CN)_6]_2$ ☐
(c) $Fe_4[Fe(CN)_6]_2$ ☐ (d) $Fe_3[Fe(CN)_6]_3$ ☐

48. Camphor is often used in molecular mass determination because: **[UGET (Med.) 2007]**

(a) it is readily available ☐
(b) it has a very high cryoscopic constant ☐
(c) it is volatile ☐
(d) it is solvent for organic substances ☐

49. Match the following:

Property to be determined	**Method used for determination**
(A) Estimation of carbon and hydrogen in an organic compound	(i) Lassaigne's test
(B) Estimation of nitrogen in aniline	(ii) Carius method
(C) Estimation of chlorine in carbon tetrachloride	(iii) Liebig's method
(D) Detection of nitrogen, sulphur and halogens	(iv) Kjeldahl's method

	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iv)	(iii)	(i)	(ii)
(c)	(ii)	(i)	(iv)	(iii)
(d)	(iii)	(iv)	(ii)	(i)

50. Match the following:

(A) Equivalent mass of an organic acid	(i) Depression in freezing point
(B) Equivalent mass of an organic base	(ii) Victor Meyer's method
(C) Molecular mass of a volatile organic solid	(iii) Platinichloride method
(D) Molecular mass of a non-volatile organic solid	(iv) Silver salt method

	A	B	C	D
(a)	(iv)	(iii)	(ii)	(i)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(iii)	(i)	(iv)	(ii)
(d)	(ii)	(iv)	(i)	(iii)

SET II : This set contains the questions with one or more correct answers.

51. Which of the following compounds may give blood red colouration while performing Lassaigne's test for nitrogen?

(a) $(NH_2)_2CO$ ☐ (b) $(NH_2)_2C{=}S$ ☐
(c) $p\text{-}NH_2C_6H_4SO_3H$ ☐ (d) $C_6H_5SO_3H$ ☐

52. The desiccants used for absorbing water during Liebig's method for estimation of carbon and hydrogen are:

(a) Anhydrous $CaCl_2$ ☐ (b) Anhydrous Na_2SO_4 ☐
(c) $MgSO_4 \cdot 7H_2O$ ☐ (d) $Mg(ClO_4)_2$ ☐

53. The empirical formula of a compound is CH_2. To which of the hydrocarbon series does it belong?

(a) Alkanes ☐ (b) Alkenes ☐
(c) Alkynes ☐ (d) Cycloalkanes ☐

54. An organic compound contains about 52% carbon. It could be:

(a) ethanol ☐ (b) dimethyl ether ☐
(c) acetic acid ☐ (d) phenol ☐

55. Presence of halogen in a compound is tested by:

(a) Iodoform test ☐ (b) Millon's test ☐
(c) Silver nitrate test ☐ (d) Beilstein test ☐

56. The weights of carbon, hydrogen and oxygen in an organic compound are in the ratio 6 : 1 : 8 respectively. The molecular formula of the compound may be:
(a) CH_2O ☐ (b) $C_2H_4O_2$ ☐
(c) CH_2O_2 ☐ (d) $C_3H_6O_3$ ☐

57. Which of the organic compounds will give white precipitate with $AgNO_3$?
(a) $C_6H_5NH_3^+Cl^-$ ☐
(b) NaCl ☐
(c) C_6H_5Cl ☐
(d) 2,6,6-Trinitrochlorobenzene ☐

58. Violet coloured complex obtained in the detection of sulphur is : **[AFMC 2010]**
(a) $Na_2[Fe(NO)(CN)_5]$ ☐
(b) $Na_3[Fe(ONSNa)(CN)_5]$ ☐
(c) $Na_4[Fe(CN)_5NOS]$ ☐
(d) both (b) and (c) ☐

ASSERTION-REASON TYPE QUESTIONS

Section A : IIT Type Questions

These questions consist of an **Assertion (A)** and the **Reason (R).** Use the following keys to choose the appropriate answer:

(a) If both **assertion** and **reason** are correct and **reason** is the correct explanation of the **assertion.**
(b) If both **assertion** and **reason** are correct but **reason** is not the correct explanation of the **assertion.**
(c) If **assertion** is correct but **reason** is incorrect.
(d) If **assertion** is incorrect but **reason** is correct.

1. (A) Lassaigne's test can be used to detect nitrogen in hydrazine.
(R) During fusion with sodium metal, nitrogen and carbon of the organic compound combine to form sodium cyanide.

2. (A) If sulphur and nitrogen are also present in organic compound along with halogen then $AgNO_3$ solution is added in acidified sodium fusion extract.
(R) On acidification, NaCN and Na_2S decompose.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$
$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S\uparrow$$

3. (A) Litmus is not used in Lassaigne's test.
(R) It generally forms covalent compounds.

4. (A) In Victor Meyer's method, vapour density is considered to be one-half of molecular weight.
(R) Vapour density is other name of density.

5. (A) Nitrogen cannot be estimated in nitrobenzene by Kjeldahl's method.
(R) Nitrobenzene evolves ammonia gas on acid treatment.

6. (A) All compounds containing an odd number of nitrogen atoms have odd masses and those which contain even number of nitrogen atoms have even masses.
(R) Nitrogen rule can be applied to both aliphatic and aromatic compounds.

Section B : AIIMS Type Questions

Choose the correct answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If both (A) and (R) are incorrect.

7. (A) p-$NH_2C_6H_5SO_3H$ gives blood red colouration while performing Lassaigne's test for nitrogen.
(R) Sodium fusion extract containing NaCNS gives blood red colour on treatment with $FeCl_3$.

8. (A) Lassaigne's test is not shown by diazonium compounds.
(R) Diazonium compounds lose N_2 on heating before they combine with fused sodium.

9. (A) If two compounds have the same empirical formula but different molecular formula, they have same vapour density.
(R) g/mL is the unit of vapour density.

10. (A) Duma's method is more applicable to nitrogen containing organic compounds than Kjeldahl's method.
(R) Kjeldahl's method does not give satisfactory results for compounds in which nitrogen is linked to oxygen.

11. (A) Hydrazine contains nitrogen but does not give Lassaigne's test for nitrogen.
(R) Hydrazine reacts with fused sodium to give H_2 gas.

12. (A) Sodium fusion extract of a compound gives black precipitate with lead acetate.
(R) Sulphur containing compounds form Na_2S in sodium fusion extract.

ANSWERS

OBJECTIVE QUESTIONS

1. (c) **2.** (d) **3.** (c) **4.** (b) **5.** (a) **6.** (a) **7.** (b) **8.** (d) **9.** (c) **10.** (b)
11. (a) **12.** (d) **13.** (b) **14.** (a) **15.** (d) **16.** (c) **17.** (b) **18.** (c) **19.** (a) **20.** (d)
21. (a) **22.** (d) **23.** (c) **24.** (b) **25.** (a) **26.** (d) **27.** (c) **28.** (a) **29.** (b) **30.** (c)
31. (b) **32.** (d) **33.** (c) **34.** (b) **35.** (c) **36.** (b) **37.** (b) **38.** (c) **39.** (c) **40.** (a)
41. (c) **42.** (c) **43.** (a) **44.** (c) **45.** (c) **46.** (a) **47.** (a) **48.** (c) **49.** (d) **50.** (a)
51. (b,c) **52.** (a,d) **53.** (b,d) **54.** (a,b) **55.** (c,d) **56.** (a,b,d) **57.** (a,d) **58.** (d)

ASSERTION-REASON TYPE QUESTIONS

1. (d) **2.** (a) **3.** (a) **4.** (c) **5.** (c) **6.** (b) **7.** (a) **8.** (a) **9.** (d) **10.** (b)
11. (a) **12.** (b)

BRAIN STORMING PROBLEMS

1. Which among the following is not correctly matched with their colour?

Compound	**Colour**	
(a) $Na_4[Fe(CN)_5NOS]$	purple	☐
(b) $Fe_4[Fe(CN)_6]_3$	blue	☐
(c) $Fe(CNS)_3$	blood red	☐
(d) AgCl	light yellow	☐

2. In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. If sodium fusion is carried out with excess of sodium, sodium thiocyanate decomposes. Which of the following compounds is/are present in the extract after decomposition?

(a) NaCN ☐ (b) Na_2S ☐
(c) Both ☐ (d) None of these ☐

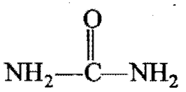
3. 0.0833 mole of a carbohydrate of empirical formula CH_2O contains 1.00 g of hydrogen. The molecular formula of the carbohydrate is:

(a) $C_5H_{10}O_5$ ☐ (b) $C_3H_4O_3$ ☐
(c) $C_{12}H_{22}O_{11}$ ☐ (d) $C_6H_{12}O_6$ ☐

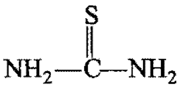
[**Hint :** 1 mole of carbohydrate will contain $\frac{1}{0.0833}$ g of hydrogen, *i.e.,* 12 g hydrogen.
∴ The molecular formula of the compound will be $C_6H_{12}O_6$]

4. Select the organic compounds, which will give red colour in Lassaigne's test?

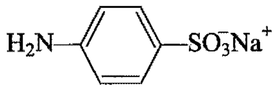
(a) NaCNS ☐

(b)  ☐

$NH_2—\overset{\overset{O}{\|}}{C}—NH_2$

(c)  ☐

$NH_2—\overset{\overset{S}{\|}}{C}—NH_2$

(d)  ☐

5. The desiccants used for absorbing water during Liebig's method for estimation of carbon and hydrogen are:

(a) $CaCl_2$ ☐ (b) Na_2SO_4 ☐
(c) $MgSO_4 \cdot 7H_2O$ ☐ (d) $Mg(ClO_4)_2$ ☐

[**Hint :** Anhydrous $CaCl_2$ and $Mg(ClO_4)_2$ are used as desiccants because they are efficient absorbent of water.]

6. Kjeldahl's method can not be used for estimation of nitrogen in:

(a) pyridine ☐ (b) azobenzene ☐
(c) nitrobenzene ☐ (d) all of these ☐

7. 9.9 g amide with molecular formula $C_4H_5N_xO_y$ on heating with alkali liberated 1.7 g of ammonia. If the percentage of oxygen is 33.33% then the ratio of 'N' and 'O' atoms in the compound is:

(a) 1 : 1 ☐ (b) 1 : 2 ☐
(c) 2 : 3 ☐ (d) 3 : 2 ☐

[**Hint :** Amide $C_4H_5N_xO_y$ will give x mol NH_3.

∴ Molecular mass of amide $= \frac{9.9}{1.7} \times 17x = 99x$

% Nitrogen in the amide $= \frac{14x}{99x} \times 100 = 14.14$

% Oxygen in the amide = 33.33

Ratio of number of atoms of 'N' and 'O'

$$= \frac{14.14}{14} : \frac{33.33}{16} = 1 : 2]$$

8. Lassaigne's test is not shown by diazonium salts because they:

(a) form NH_3 gas on heating much before the reaction with sodium ☐
(b) form N_2 gas on heating much before the reaction with sodium ☐
(c) are highly volatile and evaporate before the reaction with sodium ☐
(d) all of the above ☐

9. 0.28 g of a nitrogenous compound was Kjeldahlised to produce 0.17 g of NH_3. The percentage of nitrogen in the organic compound is:

(a) 5 ☐ (b) 30 ☐
(c) 50 ☐ (d) 80 ☐

[**Hint :** 0.17 g NH_3 will contain $\left(\frac{14}{17} \times 0.17\right)$ g of nitrogen, *i.e.,* 0.14 g of nitrogen

$$\% \text{ Nitrogen} = \frac{\text{Mass of nitrogen}}{\text{Mass of compound}} \times 100$$

$$= \frac{0.14}{0.28} \times 100 = 50\%]$$

10. Kjeldahl's method cannot be used for estimation of nitrogen in:

(I) $C_6H_5CONH_2$
(II) Pyridine
(III) $C_6H_5—N{=}N—C_6H_5$ (IV) $C_6H_5NHCOCH_3$

(a) I, III ☐ (b) II, III ☐
(c) III, IV ☐ (d) I, II ☐

ANSWERS : BRAIN STORMING PROBLEMS

1. (d) **2.** (c) **3.** (d) **4.** (c,d) **5.** (a,d) **6.** (d) **7.** (b) **8.** (b) **9.** (c) **10.** (b)

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Empirical formula of a substance gives the simplest whole number ratio between the atoms of the various elements present in one molecule of the substance. Molecular formula on the other hand gives the actual number of atoms present in one molecule of the substance.

Molecular formula = $n \times$ Empirical formula

where n is a simple integer 1, 2, 3, ..., etc., given by the equation;

$$n = \frac{\text{Molecular mass of the compound}}{\text{Empirical formula mass of the compound}}$$

Answer the following questions :

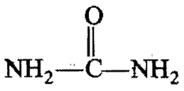
Select (a) if True and (b) if False.

1. Empirical and molecular formula of a compound may be same.
   True (a) False (b)
2. Empirical formula of two different compounds cannot be same.
   True (a) False (b)
3. If two compounds have the same empirical formula but different molecular formula, they have same vapour density.
   True (a) False (b)
4. The two compounds having same empirical formula have same percentage composition.
   True (a) False (b)
5. Empirical formula of benzene is C_2H_2.
   True (a) False (b)
6. The compounds having same empirical formula must have same properties.
   True (a) False (b)
7. Cyclo alkanes and alkenes have same empirical formula.
   True (a) False (b)

Passage 2

Combustion of 0.42 g of a compound gave 0.924 g CO_2 and 0.243 g H_2O. Due to distillation of 0.208 g of compound with NaOH, ammonia evolved required 30 mL of $\frac{N}{20}$ H_2SO_4 for complete neutralization. Vapour density of the compound is 69.5.

Answer the following questions :

1. The compound has empirical formula:
   (a) $C_7H_9O_2N$ (b) $C_6H_5NO_2$
   (c) C_3H_7—$CONH_2$ (d)
   
   $NH_2-\overset{\overset{\large O}{\|}}{C}-NH_2$
2. Percentage composition of carbon in the compound is .... .
   (a) 6.43 (b) 23.48
   (c) 60 (d) 10.09
3. What is the percentage composition of nitrogen in the compound?
   (a) 23.48 (b) 10.09
   (c) 6.43 (d) 60
4. What is the percentage composition of hydrogen in the compound?
   (a) 6.43 (b) 10.09
   (c) 60 (d) 23.48
5. What is the value of 'n' for the given compound?
   where $n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$
   (a) 2 (b) 3
   (c) 1 (d) 4

Passage 3

0.9 g of an organic compound gave on combustion :
(i) 1.584 g CO_2 (ii) 0.648 g H_2O

When 0.24 g of the substance was Kjeldahlised and the ammonia formed was absorbed in 50 cm^3 of $\frac{N}{4}$ H_2SO_4. The excess acid required 77 cm^3 of $N/10$ NaOH for complete neutralization. Molecular mass of the compound is estimated to be 100.

Answer the following questions:

1. The compound has maximum percentage composition of which of the following elements?
   (a) C (b) H
   (c) N (d) O
2. What is the percentage composition of carbon in the compound?
   (a) 16% (b) 8%
   (c) 28% (d) 48%
3. Percentage composition of nitrogen in the compound will be :
   (a) 16 (b) 61
   (c) 6 (d) 28
4. Which among the following is the empirical formula of the compound?
   (a) $C_8H_4NO_2$ (b) $C_4H_8N_2O$
   (c) C_4H_8NO (d) C_8H_4NO
5. Molecular formula of the compound will be:
   (a) $C_8H_4NO_2$ (b) $C_4H_8N_2O$
   (c) C_4H_8NO (d) C_8H_4NO

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	1. (a)	2. (b)	3. (b)	4. (a)	5. (b)	6. (b)	7. (a)
Passage 2	1. (a)	2. (c)	3. (b)	4. (a)	5. (c)		
Passage 3	1. (a)	2. (d)	3. (d)	4. (b)	5. (b)		

3

CLASSIFICATION AND NOMENCLATURE OF ORGANIC COMPOUNDS

3.1 CLASSIFICATION OF ORGANIC COMPOUNDS

Organic compounds have been classified on the basis of carbon skeleton (structure) or functional groups or the concept of homology.

(A) Classification Based on Structure

All the known organic compounds have been divided into two main types:

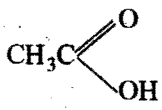
1. **Acyclic or Open-chain compounds :** These are the compounds in which the carbon atoms are linked to each other in such a manner that the molecule is having an open-chain structure. The chain of the carbon atoms may be **straight** or **branched**. These compounds are also called as **aliphatic compounds**. The term aliphatic has been derived from the Greek word *aleiphatos* meaning fats, since the earliest compounds to be studied were fatty acids or compounds found in fats. Some of the examples are:

$CH_3CH_2CH_3$
Propane

$CH_3-\overset{\overset{\large CH_3}{|}}{CH}-CH_3$

Isobutane

$H_2C=CH_2$
Ethylene



Acetic acid

$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3$

Acetone

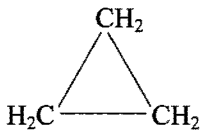
CH_3CH_2OH
Ethyl alcohol

2. **Cyclic or Closed-chain compounds :** These are the compounds in which carbon atoms are linked to each other or to the atoms of other elements in such a manner that the molecule has a closed-chain or cyclic or ring structure. One or more closed-chains or rings may be present in the molecule. The compounds with only one ring of atoms in the molecule are known as **monocyclic** but those with more than one ring of atoms are termed as **polycyclic**. These are further divided into two subgroups:

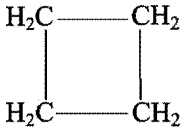
(a) Homocyclic or Carbocyclic, (b) Heterocyclic.

(a) Homocyclic or Carbocyclic : These are the compounds having a ring or rings of carbon atoms only in the molecule. The carbocyclic or homocyclic compounds may again be divided into two types: (i) Alicyclic compounds and (ii) Aromatic compounds.

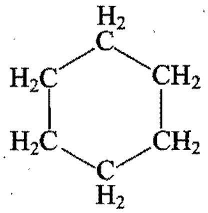
(i) Alicyclic compounds : These are the compounds which contain rings of three or more carbon atoms. These resemble with aliphatic compounds than aromatic compounds in many respects. That is why these are named alicyclic, *i.e.*, aliphatic cyclic. These are also termed as polymethylenes. Some of the examples are:



Cyclopropane



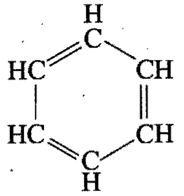
Cyclobutane



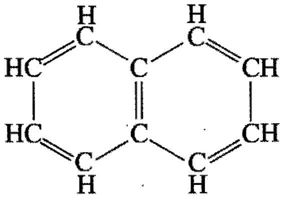
Cyclohexane

(ii) Aromatic compounds : These compounds consist of at least one benzene ring, *i.e.*, a six-membered carbocyclic ring having alternate single and double bonds. Generally, these compounds have some fragrant odour and hence, named as aromatic (Greek word *aroma* meaning sweet smell).

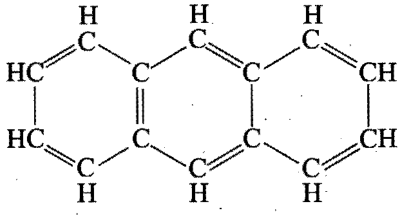
Examples are:



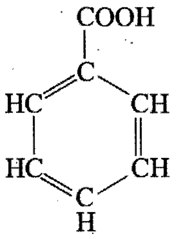
Benzene
(Monocyclic)



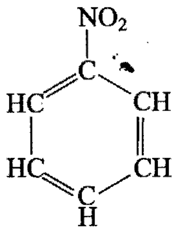
Naphthalene
(Bicyclic)



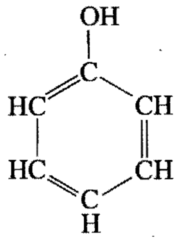
Anthracene
(Tricyclic)



Benzoic acid

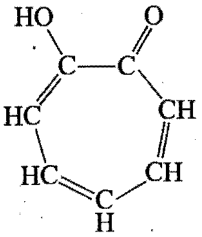


Nitrobenzene

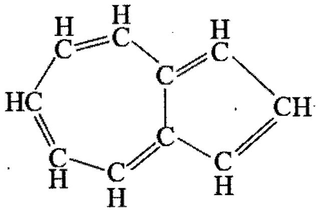


Phenol

The above compounds are also known as **benzenoid aromatics** as their molecules consist of benzene ring or rings. However, there are aromatic compounds, which have structural units different from benzenoid type, and are known as **non-benzenoid aromatics**. Tropolone and azulene are the examples of non-benzenoid aromatics.

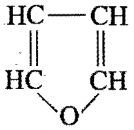


Tropolone

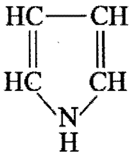


Azulene

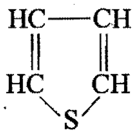
(b) Heterocyclic compounds : These are cyclic compounds having ring or rings built up of more than one kind of atoms. The most common other atoms (hetero-atoms) besides carbon are O, N and S. A few examples of this class are:



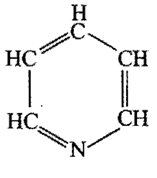
Furan



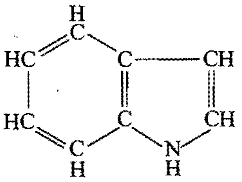
Pyrrole



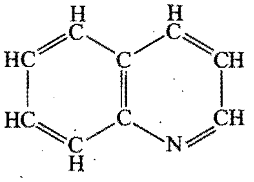
Thiophene



Pyridine

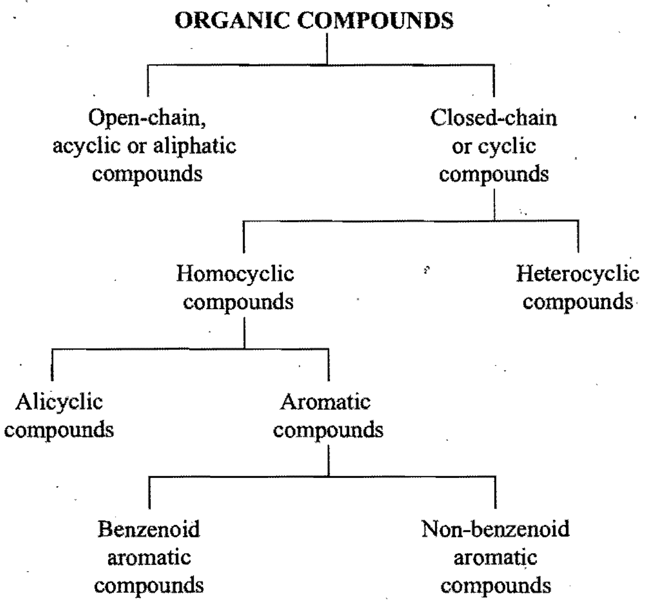


Indole



Quinoline

The classification may be summarised as follows:



(B) Classification Based on Functional Groups

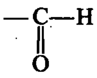
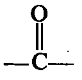
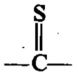
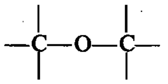
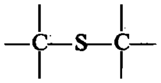
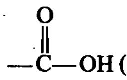
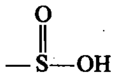
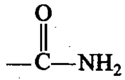
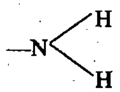
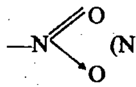
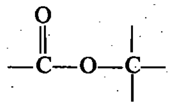
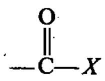
The compounds of only carbon and hydrogen are called hydrocarbons. Hydrocarbons are considered as the parents of all the organic compounds. All other compounds are obtained from hydrocarbons by the replacement of one or more hydrogen atoms with other atoms or groups.

$$\underset{\text{Hydrocarbon}}{R\text{—H}} \xrightarrow[+X]{-\text{H}} \underset{\text{Derivative of hydrocarbon}}{R\text{—}X}$$

Thus, most of the organic compounds consist of two parts, each of which is called a group or radical. Both of these groups are responsible for the properties of the compound. The group R represents the carbon-hydrogen framework which mainly affects the physical properties while group X is known as **functional group** which is responsible for the chemical properties of the compound.

A functional group is an atom or group of atoms present in a molecule that gives the molecule its characteristic chemical properties. Double and triple bonds are also considered as functional groups. Functional group is actually the action group or the site of chemical reactivity in a compound. Compounds having same functional group show similar characteristic chemical properties.

Functional groups, thus, serve to classify organic compounds into classes/families. All compounds with the same functional group belong to the same class. Various classes of compounds having some of the common functional groups are listed in the table on next page.

Class	Functional group
Olefins/Alkenes	$>C{=}C<$
Acetylenes/Alkynes	$—C{\equiv}C—$
Halides	—F, —Cl, —Br, —I (Halo)
Alcohols	—OH (Hydroxy)
Thiols	—SH
Aldehydes	 $-\underset{\underset{O}{\Vert}}{C}-H$ (Aldehydic)
Ketones	 $-\overset{\overset{O}{\Vert}}{C}-$ (Ketonic)
Thioketones	 $-\overset{\overset{S}{\Vert}}{C}-$
Ethers	 $-\overset{\vert}{\underset{\vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$ (Alkoxy)
Thioethers	 $-\overset{\vert}{\underset{\vert}{C}}-S-\overset{\vert}{\underset{\vert}{C}}-$
Carboxylic acid	 $-\overset{\overset{O}{\Vert}}{C}-OH$ (Carboxyl)
Sulphinic acid	 $-\overset{\overset{O}{\Vert}}{S}-OH$
Amides	 $-\overset{\overset{O}{\Vert}}{C}-NH_2$ (Amide)
Amines	 $-N\begin{matrix}H\\H\end{matrix}$ (Amino)
Cyanides/Nitriles	$—C{\equiv}N$ (Cyano)
Nitro compounds	 $-N\begin{matrix}O\\O\end{matrix}$ (Nitro)
Esters	 $-\overset{\overset{O}{\Vert}}{C}-O-\overset{\vert}{\underset{\vert}{C}}-$ (Ester)
Acid halides	 $-\overset{\overset{O}{\Vert}}{C}-X$ (Acylhalide)

Certain compounds contain more than one functional groups. Such compounds are called **polyfunctional compounds**. The properties of each **functional group may be modified by the presence of the others.**

Homologous series : Organic compounds belonging to a main class can be divided into different families, known as homologous series, on the basis of similarity in structure and chemical properties. All compounds having same carbon framework (skeleton) and same functional group in their molecules possess similar properties. Such compounds when arranged in order of their molecular masses constitute a series called **homologous series** and the individual members are called **homologues**. The property by virtue of which a number of organic compounds form a homologous series is termed 'homology'.

A homologous series can be defined as a group of compounds in which the various members have similar structural features and similar chemical properties and the successive members differ in their molecular formula by CH_2.

The general characteristics of a homologous series are:

(i) All compounds in the series are composed of same elements and contain the same functional group.

(ii) All compounds in the series can be represented by one general formula, *e.g.*, the homologous series of monohydric alcohols can be represented by the general formula* $C_nH_{2n+1}OH$. The formula of various homologues can be written by giving the values 1, 2, 3, . . . to *n*.

n	$C_nH_{2n+1}OH$	
1	CH_3OH	
2	C_2H_5OH	CH_2
3	C_3H_7OH	CH_2
4	C_4H_9OH	CH_2

The molecular formula of each member differs from the members above and below it by one CH_2 group.

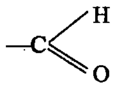
(iii) The molecular mass of every two adjacent members differs by 14 ($CH_2 = 12 + 2 \times 1 = 14$).

(iv) All compounds in the series have similar chemical properties because of the presence of same functional group.

(v) The members of the series show a gradual gradation in their physical properties like solubility, density, melting and boiling points. The physical properties generally increase as the molecular mass increases.

(vi) The homologues can be prepared by almost similar methods. These are known as general methods of preparation.

There are a number of homologous series in organic compounds. Some important series of aliphatic compounds are listed below:

Homologous series	General formula	Functional group
1. Alkanes	C_nH_{2n+2}	—
2. Alkenes	C_nH_{2n}	$>C{=}C<$
3. Alkynes	C_nH_{2n-2}	$—C{\equiv}C—$
4. Monohydric alcohols	$C_nH_{2n+1}OH$	—OH
5. Aldehydes	$C_nH_{2n}O$	 $-C\begin{matrix}H\\O\end{matrix}$

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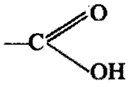
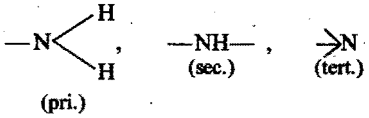
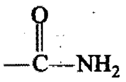
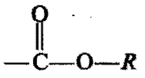
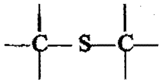
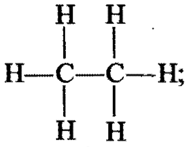
*C_nH_{2n+1} = CH_3, C_2H_5, etc., alkyl groups (*R*).

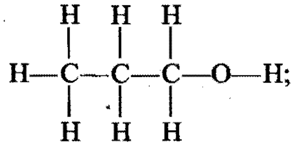
Contd.

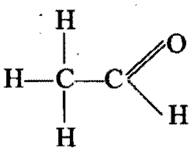
	Homologous series	General formula	Functional group
6.	Ketones	$C_nH_{2n}O$	$>C=O$
7.	Monocarboxylic acids	$C_nH_{2n}O_2$	
8.	Ethers	$C_nH_{2n+2}O$	 or $—O—R$
9.	Amines (pri., sec., tert.)	$C_nH_{2n+1}NH_2$ ($C_nH_{2n+3}N$)	
10.	Amides	$C_nH_{2n+1}CONH_2$	
11.	Esters	$C_nH_{2n}O_2$	
12.	Nitriles	$C_nH_{2n+1}CN$	$—C\equiv N$
13.	Thiols	$C_nH_{2n+1}SH$	$—SH$
14.	Thioethers	$C_nH_{2n+2}S$	

3.2 SATURATED AND UNSATURATED COMPOUNDS

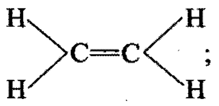
If, in an organic compound containing two or more carbon atoms, there are only single bonds between carbon atoms, then the compound is said to be **saturated**, *e.g.*, ethane, *n*-propyl alcohol, acetaldehyde, etc.


Ethane

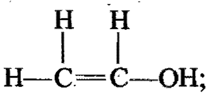

n-propyl alcohol

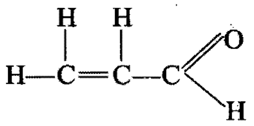

Acetaldehyde

On the other hand, if the compound contains at least one pair of adjacent carbon atoms linked by a multiple bond, then that compound is said to be **unsaturated,** *e.g.*, ethylene, acetylene, vinyl alcohol, acraldehyde, etc.


Ethylene

$H—C\equiv C—H$;
Acetylene


Vinyl alcohol


Acraldehyde

Note : The double bond between carbon and oxygen atoms is not a sign of unsaturation as in acetaldehyde or acetone.

3.3 NOMENCLATURE OF ORGANIC COMPOUNDS

Nomenclature means the assignment of names to organic compounds. The naming of organic compounds is an important aspect in the study of organic chemistry as their number is very large and variety of molecular structures exist in their molecules. The field has become more complex on account of the phenomenon of isomerism. There are two main systems of nomenclature of organic compounds :

I. Trivial system, II. IUPAC system.

I. Trivial System

This is the oldest system of naming organic compounds. Whenever a new compound was discovered, it was given an individual name. Such a name was assigned at the whim of the discoverer and had no system. These trivial names are called **common names** and generally based on the source, from which they were obtained. Quite frequently, the names chosen had Latin or Greek roots. The following examples justify the above statement:

(a) Acetic acid derives its name from vinegar of which it is the chief constituent (Latin : *acetum* = vinegar).

(b) Formic acid was named as it was obtained from red ants. The Greek word for the red ants is *formicus*.

(c) The names oxalic acid (*oxalus*), malic acid (*pyrus malus*), citric acid (*citrus*) have been derived from botanical sources given in parentheses.

(d) Urea and uric acid have derived their names from urine in which both are present.

(e) The liquid obtained by the destructive distillation of wood was named as wood spirit. Later on, it was named methyl alcohol (Greek : *methu* = spirit; *hule* = wood).

(f) Names like glucose (sweet), pentane (five), hexane (six), etc., were derived from Greek words describing their properties or structures.

(g) Methane was named as **marsh gas** because it was produced in marshes. It was also named as fire damp as it formed explosive mixture with air.

The IUPAC names have become very popular these days but certain common or trivial names are so familiar that their use could not be completely discarded. A few of these common names have become a part of the IUPAC system while some others continue to be used along with the corresponding IUPAC names. These common names may include simple compounds such as acetone, acetic acid, glycol, glycerol, benzene, toluene, phenol, etc; or complex compounds such as penicillin, streptomycin, quinine, morphine, vitamin-A, etc. **A student must be familiar with both common and IUPAC names of organic compounds** as both the names are generally used in the standard text books on organic chemistry. A brief description of important members of various families with their **common names** has been made here.

(1) Saturated hydrocarbons : Hydrocarbons are compounds that contain only carbon and hydrogen. The saturated hydrocarbons contain only single bonds between carbon atoms. These are also called paraffins (Latin : *parum* = small, and *affinis* = affinity) as these are chemically less reactive and represented by the general formula C_nH_{2n+2}. The first four members are known as methane, ethane, propane and butane. The names of the higher members have Greek prefixes indicating the number of carbon atoms in the molecule.

Name	Molecular formula
Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}
Heptane	C_7H_{16}
Octane	C_8H_{18}
Nonane	C_9H_{20}
Decane	$C_{10}H_{22}$

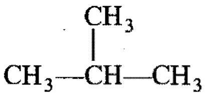
Chain isomerism (see chapter 4) starts from butane. All isomeric paraffins have same parent name. The names of various isomers are distinguished by prefixes.

(a) Prefix *n*- is used for those paraffins in which all the carbon atoms are in one continuous chain. The prefix *n*-stands for normal or straight chain.

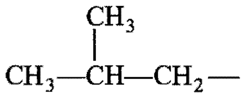
$CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2CH_3$,
n-Butane *n*-Pentane

$CH_3CH_2CH_2CH_2CH_2CH_3$
n-Hexane

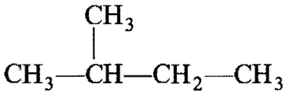
(b) Prefix iso- is used for those paraffins in which methyl group is attached to the second last carbon atom of the continuous chain.


$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3$

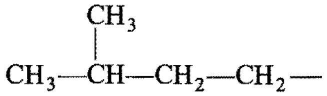
Isobutane
(continuous chain)


$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-$

Isobutyl

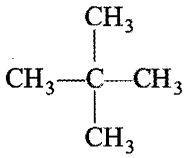

$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_3$

Isopentane
(continuous chain)

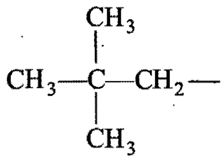

$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-$

Isopentyl

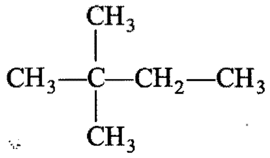
(c) Prefix neo- is used for those paraffins in which two methyl groups are attached to the second last carbon atom of the continuous chain.


$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

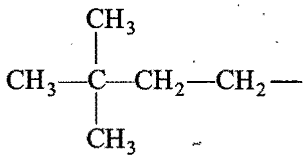
Neopentane
(continuous chain)


$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-$

Neopentyl


$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$

Neohexane
(continuous chain)


$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-$

Neohexyl

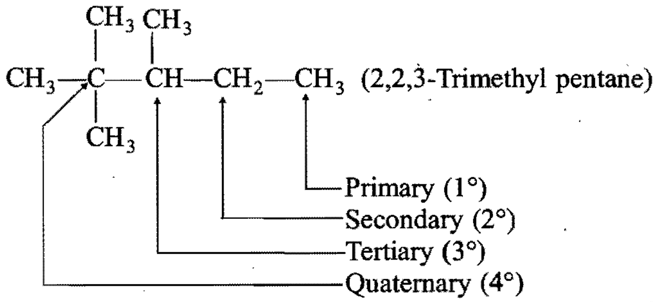
There are four types of carbons in the carbon chain.

(i) Primary carbon : A carbon atom attached to one (or no) other carbon atom is termed primary carbon or 1° carbon atom.

(ii) Secondary carbon : A carbon atom attached to two other carbon atoms is termed secondary carbon or 2° carbon atom.

(iii) Tertiary carbon : A carbon atom attached to three other carbon atoms is termed tertiary carbon or 3° carbon atom.

(iv) Quaternary carbon : A carbon atom attached to four other carbon atoms is termed quaternary carbon or 4° carbon atom.



[The hydrogen atoms attached to primary, secondary and tertiary carbon atoms are correspondingly termed as primary, secondary and tertiary hydrogen atoms respectively.]

Normal hydrocarbons contain either only primary or both primary and secondary carbon atoms. No branching is present.

Iso-hydrocarbons contain a tertiary carbon atom, *i.e.*, $(CH_3)_2CH$—.

Neo-hydrocarbons contain a quaternary carbon atom, *i.e.*, $(CH_3)_3C$—.

The isomers of butanes (2) and pentanes (3) can be named by using prefixes (*n*-, iso-, neo-) but it will be difficult to name properly all the hexanes (5), heptanes (9) and decanes (75) by this method.

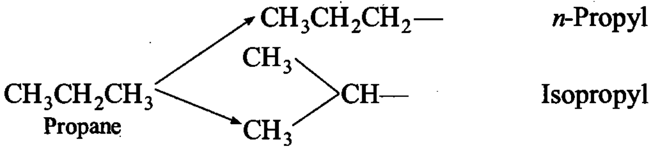
Alkyl groups : These are univalent groups or radicals obtained by the removal of one hydrogen atom from a molecule of a paraffin. The symbol '*R*' is often used to represent an alkyl group.

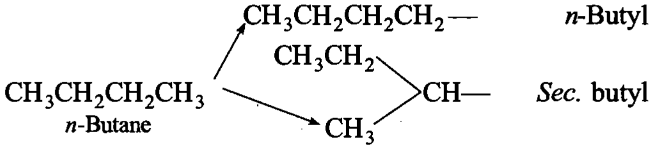
$$\text{(Alkane)}\ \underset{(R\text{—H})}{C_nH_{2n+2}} \xrightarrow{-\text{H}} \underset{(R\text{—})}{C_nH_{2n+1}}\ \text{(Alkyl group)}$$

Alkyl groups are named by dropping -ane from the name of corresponding paraffin and adding the ending -yl.

Parent saturated hydrocarbon	Name of the alkyl group	Structure
Methane	Methyl	CH_3—
Ethane	Ethyl	CH_3—CH_2—
Propane	*n*-Propyl	CH_3—CH_2—CH_2—
Butane	*n*-Butyl	CH_3—CH_2—CH_2—CH_2—

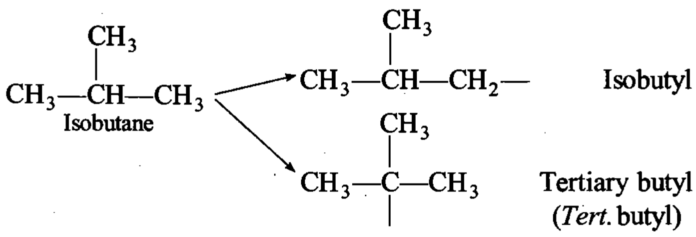
Alkyl groups derived from saturated hydrocarbons having three or more carbon atoms exist in isomeric forms.





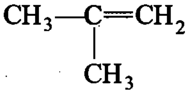
or

$$(CH_3\text{—}\underset{|}{C}H\text{—}CH_2CH_3)$$



Beyond butyl, the number of isomeric groups derived from each paraffin becomes so great that it is impracticable to designate them all by various prefixes.

(2) Olefins : These are unsaturated hydrocarbons containing two hydrogen atoms less than the corresponding paraffin, *i.e.*, there is one double bond between two carbon atoms in their molecules. They have the general formula C_nH_{2n}. The first member of the series is C_2H_4. These unsaturated hydrocarbons are named olefins (Latin: *oleum* = oil; *fiant* = making). The names are derived by substituting the suffix -ane of the corresponding paraffin by -ylene.

$H_2C{=}CH_2$	Ethylene
CH_3—$CH{=}CH_2$	Propylene
CH_3—CH_2—$CH{=}CH_2$	Butylene
 $CH_3\text{—}\underset{\underset{CH_3}{|}}{C}{=}CH_2$	Isobutylene

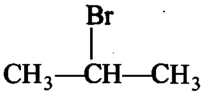
$\text{Alkene} \xrightarrow[(-e+\text{yl})]{-\text{H}} \text{Alkenyl}$	Alkenyl
$\underset{\text{Ethene}}{H_2C{=}CH_2} \xrightarrow{-\text{H}} H_2C{=}CH\text{—}$	Ethenyl (Vinyl)
$H_2C{=}CH\text{—}CH_3 \xrightarrow{-\text{H}} H_2C{=}CH\text{—}CH_2\text{—}$	2-Propenyl (Allyl)
$H_3C\text{—}CH{=}CH_2 \xrightarrow{-\text{H}} H_3C\text{—}CH{=}CH\text{—}$	1-Propenyl

(3) Acetylenes : These are unsaturated hydrocarbons containing four hydrogen atoms less than corresponding paraffin. There is one triple bond between two carbon atoms. These have general formula C_nH_{2n-2}. The first member of the series is C_2H_2. The various homologues are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl groups.

$HC{\equiv}CH$	Acetylene
CH_3—$C{\equiv}CH$	Methyl acetylene (Allylene)
CH_3—$C{\equiv}C$—CH_3	Dimethyl acetylene (Crotonylene)

$\text{Alkyne} \xrightarrow[(-e+\text{yl})]{-\text{H}} \text{Alkynyl}$	
$HC{\equiv}CH \xrightarrow{-\text{H}} HC{\equiv}C\text{—}$	Ethynyl
$H_3C\text{—}C{\equiv}CH \xrightarrow{-\text{H}} H_3C\text{—}C{\equiv}C\text{—}$	1-Propynyl
$HC{\equiv}C\text{—}CH_3 \xrightarrow{-\text{H}} HC{\equiv}C\text{—}CH_2\text{—}$	2-Propynyl (Propargyl)

(4) Alkyl halides : These are monohalogen derivatives of paraffins and are obtained by the replacement of one hydrogen atom by halogen atom *X* (*X* = F, Cl, Br or I). These have the general formula $C_nH_{2n+1}X$. Common names are obtained by naming the alkyl groups and adding the name of the halide as separate word. The position of the halogen atom is indicated by primary, secondary or tertiary prefix.

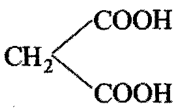
CH_3Br ; CH_3CH_2Cl ;  $CH_3\text{—}\overset{\overset{Br}{|}}{C}H\text{—}CH_3$

Methyl bromide ; Ethyl chloride ; Isopropyl bromide

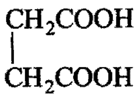
Dicarboxylic acids : These compounds contain two carboxylic groups attached to same or different carbon atoms. The names of the individual acids are generally derived from some source of the acid.

$\underset{COOH}{\overset{COOH}{|}}$;

Oxalic acid

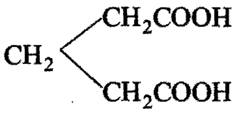


Malonic acid



$\underset{CH_2COOH}{\overset{CH_2COOH}{|}}$;

Succinic acid



Glutaric acid

(10) Acid derivatives : These are the compounds which are obtained by the replacement of hydroxyl part of the carboxyl group with other groups.

(i) Acid chlorides : OH part of the $—\overset{\overset{O}{\|}}{C}—OH$ group is replaced by Cl atom. These are named by removing the ending -ic acid of the carboxylic acid and adding -yl chloride.

CH_3COCl	Acetyl chloride
C_2H_5COCl	Propionyl chloride
$CH_3CH_2CH_2COCl$	*n*-Butyryl chloride

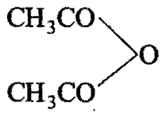
(ii) Amides : OH part of the $—\overset{\overset{O}{\|}}{C}—OH$ group is replaced by NH_2. These are named by replacing -ic acid of the carboxylic acid by -amide.

$HCONH_2$	Formamide
CH_3CONH_2	Acetamide
$CH_3CONHCH_3$	*N*-Methyl acetamide
$CH_3CON(CH_3)_2$	*N,N*-Dimethyl acetamide
$HCON(CH_3)_2$	*N,N*-Dimethyl formamide (DMF)
$CH_2{=}CHCONH_2$	Acrylamide

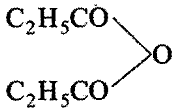
(iii) Esters : OH part of the $—\overset{\overset{O}{\|}}{C}—OH$ group is replaced by O*R*. They are named as alkyl salts of the parent acid by replacing -ic acid of the carboxylic acid by -ate.

$HCOOCH_3$	Methyl formate
$CH_3COOC_2H_5$	Ethyl acetate
$C_2H_5COOCH_3$	Methyl propionate
$C_3H_7COOC_2H_5$	Ethyl butyrate

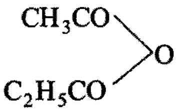
(iv) Acid anhydrides : OH part of $—\overset{\overset{O}{\|}}{C}—OH$ group is replaced by OCO*R*. They are named by changing the suffix acid to anhydride.



Acetic anhydride



Propionic anhydride



Acetic propionic anhydride

(11) Amines : They are the derivatives of ammonia and are obtained by the replacement of hydrogen atoms of ammonia by alkyl groups. They are called primary, secondary and tertiary amines depending on the number of hydrogen atoms of ammonia replaced. The common names are obtained by adding the names of alkyl groups to the suffix amine.

CH_3NH_2 ; $CH_3—NH—CH_3$;

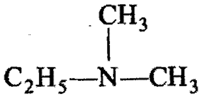
Methyl amine (1°) Dimethyl amine (2°)

$CH_3—\overset{\overset{CH_3}{|}}{N}—CH_3$

Trimethyl amine (3°)

$C_2H_5NH_2$; $CH_3NHC_2H_5$;

Ethyl amine (1°) Ethyl methyl amine (2°)



$C_2H_5—\overset{\overset{CH_3}{|}}{N}—CH_3$

Ethyl dimethyl amine (3°)

$CH_3CH_2CH_2NH_2$; $C_2H_5NH—CH(CH_3)_2$

n-Propyl amine (1°) Ethyl isopropyl amine (2°)

$(C_2H_5)_2N—CH_3$

Diethyl methyl amine (3°)

(12) Cyanides : These compounds contain —CN group attached to an alkyl group and are named as alkyl cyanide or carbonitrile (Replacing -ic acid of their carboxylic acid by -Onitrile).

CH_3CN ; C_2H_5CN

Methyl cyanide (Acetonitrile) Ethyl cyanide (Propiononitrile)

$CH_3CH_2CH_2CN$; $(CH_3)_2CHCN$

n-Propyl cyanide (Butyro nitrile) Isopropyl cyanide (Isobutyro nitrile)

$H_2C{=}CHCN$

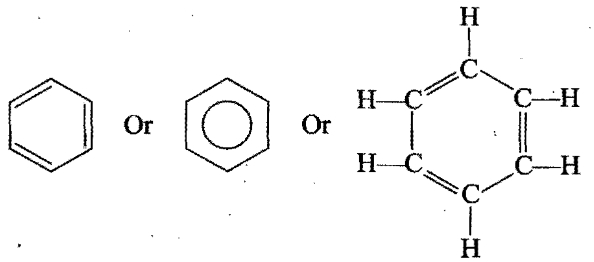
Vinyl cyanide (Acrylo nitrile)

(13) Isocyanides : These compounds contain —NC group attached to an alkyl group and named as alkyl isocyanide or alkane isonitrile. They are also called alkyl carbylamine.

CH_3NC ; C_2H_5NC

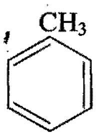
Methyl isocyanide (Methyl carbylamine or Methane isonitrile) Ethyl isocyanide (Ethyl carbylamine or Ethane isonitrile)

(14) Common names of aromatic compounds : The simplest aromatic compound is the hydrocarbon, C_6H_6. It is called benzene and represented as:

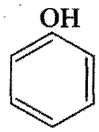


For naming aromatic compounds, no special rules are required, but they are named as substituted benzene.

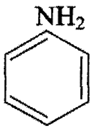
The monosubstituted derivatives of benzene are those in which a hydrogen of the ring is replaced by another substituent. These are named by prefixing the name of the substituent to the word benzene. Some derivatives have special names.



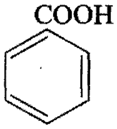
Toluene (Methylbenzene)



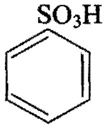
Phenol



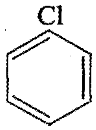
Aniline



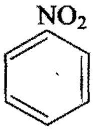
Benzoic acid



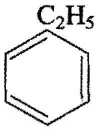
Benzene sulphonic acid



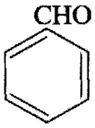
Chlorobenzene



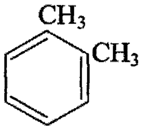
Nitrobenzene



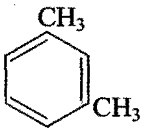
Ethylbenzene



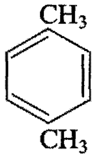
Benzaldehyde



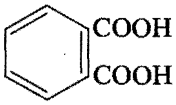
o-Xylene



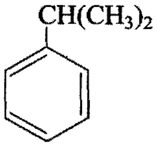
m-Xylene



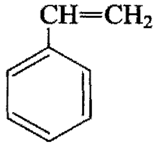
p-Xylene



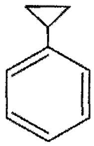
Phthalic acid



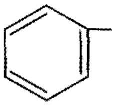
Cumene (Isopropyl benzene)

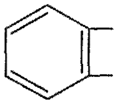


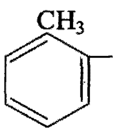
Styrene (Vinyl benzene)


Cyclopropyl benzene

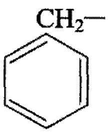
The following names are given to certain aromatic hydrocarbon residues formed by the loss of one or more hydrogen atoms from the parent hydrocarbon.


C_6H_5— (Phenyl)

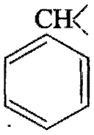

C_6H_4< (*o*-Phenylene)



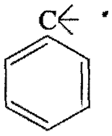
$CH_3C_6H_4$— (*o*-Tolyl)



$C_6H_5CH_2$— (Benzyl or Phenyl methyl)



C_6H_5CH< (Benzal or Benzylidene)



C_6H_5C< (Benzo or Benzylidyne)

II. IUPAC System

The first rational system of naming organic compounds was evolved in 1892 by the International Chemical Congress at Geneva under the name of **Geneva system of nomenclature.** However, the system could not be successfully applied to complicated and multifunctional organic compounds. This system was partially revised in 1931 and the revised system was referred to IUC system. Modifications in this system have been made from time to time by the **International Union of Pure and Applied Chemistry** and in its present form, the system is known as IUPAC system (pronounced as eye-you-pack). It is the most modern and largely used system. This system has been evolved in 1957 and some additions and subtractions were done in 1967. The IUPAC system has set rules for naming organic compounds on the basis of their structures. These rules underwent further modifications in 1979 and later revised in 1993 **(A Guide to IUPAC Nomenclature of Organic Chemistry by R. Panico, W.H. Powell and J.C. Richer)**. The name assigned on the basis of latest IUPAC rules to an organic compound is known as its systematic name.

Salient Features of IUPAC System

1. A given compound can be assigned only one name.
2. A given name can clearly direct in writing of one and only one molecular structure.
3. The system can be applied in naming complex organic compounds.
4. The system can be applied in naming multifunctional organic compounds.
5. This is a simple, systematic and scientific method for nomenclature of organic compounds.

Basic rules of nomenclature : For naming simple aliphatic compounds, the normal saturated hydrocarbons have been considered as the parent compounds and the other compounds as their derivatives obtained by the replacement of one or more hydrogen atoms with various functional groups. Each systematic name has two or three of the following parts:

(i) Root word, (ii) Primary suffix and (iii) Secondary suffix.

(i) Root words : The basic unit is a series of root words which indicate linear or continuous chains of carbon atoms. Chains containing one to four carbon atoms are known by special root words while chains from C_5 onwards are known by Greek number roots.

Chain length	Root word	Chain length	Root word
C_1	Meth-	C_{11}	Undec-
C_2	Eth-	C_{12}	Dodec-
C_3	Prop-	C_{13}	Tridec-
C_4	But-	C_{14}	Tetradec-
C_5	Pent-	C_{15}	Pentadec-
C_6	Hex-	C_{16}	Hexadec-
C_7	Hept-	C_{20}	Eicos-
C_8	Oct-	C_{30}	Triacont-
C_9	Non-	C_{40}	Tetracont-
C_{10}	Dec-	C_{50}	Pentacont-

In general, the root word for any carbon chain is alk-.

(ii) Primary suffixes : Primary suffixes are added to the root words to show saturation or unsaturation in a carbon chain.

Nature of carbon chain	Primary suffix	IUPAC name
Saturated (C—C)	-ane	Alkane
Unsaturated (C=C) with one double bond	-ene	Alkene
Unsaturated (C≡C) with one triple bond	-yne	Alkyne
Unsaturated with two (C=C) bonds	-adiene	Alkadiene
Unsaturated with two (C≡C) bonds	-adiyne	Alkadiyne
Unsaturated with three (C=C) bonds	-atriene	Alkatriene

(iii) Secondary suffixes : Suffixes added after the primary suffix to indicate the presence of a particular functional group in the carbon chain are known as secondary suffixes.

Functional group	Secondary suffix
Alcohol (—OH)	-ol
Aldehyde (—CHO)	-al
Ketone (>CO)	-one
Carboxylic acid (—COOH)	-oic acid
Sulphonic (—SO_3H)	-sulphonic acid
Amine (—NH_2)	-amine
Thioalcohol (—SH)	-thiol
Cyanide (—CN)	-nitrile
Ester (—COO*R*)	-oate
Amide (—$CONH_2$)	-amide
Acid halide (—CO*X*)	-oyl halide

The terminal '*e*' of the primary suffix is usually removed before attaching the secondary suffix. To illustrate the application of above basic rules, the IUPAC names of few classes of organic compounds are given below:

Homologous series	Root word	Primary suffix	Secondary suffix	IUPAC name
Alcohols (saturated)	Alk	-ane	-ol	Alkanol
Alcohols (unsaturated) one double bond	Alk	-ene	-ol	Alkenol
Alcohols (unsaturated) one triple bond	Alk	-yne	-ol	Alkynol
Aldehydes (saturated)	Alk	-ane	-al	Alkanal
Ketones (saturated)	Alk	-ane	-one	Alkanone
Carboxylic acids (saturated)	Alk	-ane	-oic acid	Alkanoic acid
Acid chlorides (saturated)	Alk	-ane	-oyl chloride	Alkanoyl chloride

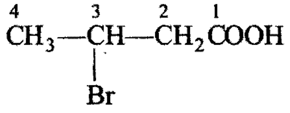
Prefix : It should always be kept in mind that alkyl groups forming branches of the parent chain are considered as side-chains. Atoms or groups of atoms such as fluoro (—F), chloro (—Cl), bromo (—Br), iodo (—I), nitro (—NO_2) and nitroso (—NO) are referred to as substituents. Root words are prefixed with the name of the substituent or side chain.

Arrangement of Prefixes, Root word and Suffixes

These are arranged as follows while writing the name.

Prefix (es) + *Root word* + *Primary suffix* + *Secondary suffix*

For example,



$$\overset{4}{\mathrm{CH_3}}-\underset{\underset{\mathrm{Br}}{|}}{\overset{3}{\mathrm{CH}}}-\overset{2}{\mathrm{CH_2}}\overset{1}{\mathrm{COOH}}$$

Prefix = Bromo (at position 3)

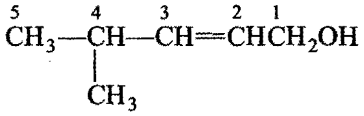
Root word = But,

Primary suffix = -ane,

Secondary suffix = -oic acid

Hence, the name of the compound is,

3-Bromo butanoic acid



$$\overset{5}{\mathrm{CH_3}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{4}{\mathrm{CH}}}-\overset{3}{\mathrm{CH}}=\overset{2}{\mathrm{CH}}\overset{1}{\mathrm{CH_2OH}}$$

Prefix = Methyl (at position 4),

Root word = Pent,

Primary suffix = - ene (at position 2),

Secondary suffix = - ol

Hence, the name of the compound is,

4-Methylpent-2-en-1-ol

The names of simple aliphatic organic compounds containing only straight chains of carbon atoms of various homologous series are described in tables (pages 76-77) as to explain the basic rules of IUPAC system. In case of compounds, other than hydrocarbons, only the saturated compounds have been considered.

S. No.	Homologous series (1)	Structural formula (2)	Root word (3)	Primary suffix (4)	Secondary suffix (5)	IUPAC name (6)
1.	Paraffins or Alkanes (C_nH_{2n+2})	$\overset{1}{C}H_4$	Meth	-ane	—	Methane
		$\overset{2}{C}H_3\overset{1}{C}H_3$	Eth	-ane	—	Ethane
		$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_3$	Prop	-ane	—	Propane
		$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_3$	But	-ane	—	Butane
2.	Olefins or Alkenes (C_nH_{2n})	$H_2\overset{2}{C}{=}\overset{1}{C}H_2$	Eth	-ene	—	Ethene
		$\overset{3}{C}H_3\overset{2}{C}H{=}\overset{1}{C}H_2$	Prop	-ene	—	Propene
		$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H{=}\overset{1}{C}H_2$	But	-ene	—	But-1-ene
		$\overset{4}{C}H_3\overset{3}{C}H{=}\overset{2}{C}H\overset{1}{C}H_3$	But	-ene	—	But-2-ene
3.	Acetylenes or Alkynes (C_nH_{2n-2})	$H\overset{2}{C}{\equiv}\overset{1}{C}H$	Eth	-yne	—	Ethyne
		$\overset{3}{C}H_3{-}\overset{2}{C}{\equiv}\overset{1}{C}H$	Prop	-yne	—	Propyne
		$\overset{4}{C}H_3\overset{3}{C}H_2{-}\overset{2}{C}{\equiv}\overset{1}{C}H$	But	-yne	—	But-1-yne
		$\overset{4}{C}H_3{-}\overset{3}{C}{\equiv}\overset{2}{C}{-}\overset{1}{C}H_3$	But	-yne	—	But-2-yne
4.	Monohydric Alcohols ($C_nH_{2n+1}OH$)	$\overset{1}{C}H_3OH$	Meth	-ane	-ol	Methanol
		$\overset{2}{C}H_3\overset{1}{C}H_2OH$	Eth	-ane	-ol	Ethanol
		$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2OH$	Prop	-ane	-ol	Propan-1-ol
		$\overset{3}{C}H_3\overset{2}{C}HOH\overset{1}{C}H_3$	Prop	-ane	-ol	Propan-2-ol
		$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2OH$	But	-ane	-ol	Butan-1-ol
		$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}HOH\overset{1}{C}H_3$	But	-ane	-ol	Butan-2-ol
5.	Aldehydes ($C_nH_{2n}O$)	$H\overset{1}{C}HO$	Meth	-ane	-al	Methanal
		$\overset{2}{C}H_3\overset{1}{C}HO$	Eth	-ane	-al	Ethanal
		$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}HO$	Prop	-ane	-al	Propanal
		$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}HO$	But	-ane	-al	Butanal
6.	Ketones ($C_nH_{2n}O$)	$\overset{3}{C}H_3\overset{2}{C}O\overset{1}{C}H_3$	Prop	-ane	-one	Propanone
		$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}O\overset{1}{C}H_3$	But	-ane	-one	Butanone
		$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}O\overset{1}{C}H_3$	Pent	-ane	-one	Pentan-2-one
		$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}O\overset{2}{C}H_2\overset{1}{C}H_3$	Pent	-ane	-one	Pentan-3-one
7.	Carboxylic acids (Mono) ($C_nH_{2n}O_2$)	$H\overset{1}{C}OOH$	Meth	-ane	-oic acid	Methanoic acid
		$\overset{2}{C}H_3\overset{1}{C}OOH$	Eth	-ane	-oic acid	Ethanoic acid
		$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}OOH$	Prop	-ane	-oic acid	Propanoic acid
		$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH$	But	-ane	-oic acid	Butanoic acid
8.	Acid chlorides (*R*COCl)	$\overset{2}{C}H_3\overset{1}{C}OCl$	Eth	-ane	-oyl chloride	Ethanoyl chloride
		$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}OCl$	Prop	-ane	-oyl chloride	Propanoyl chloride
		$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OCl$	But	-ane	-oyl chloride	Butanoyl chloride

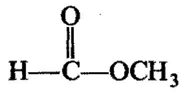
Contd.

S. No.	Homologous series (1)	Structural formula (2)	Root word (3)	Primary suffix (4)	Secondary suffix (5)	IUPAC name (6)
9.	Acid amides ($RCONH_2$)	$\overset{2}{C}H_3\overset{1}{C}ONH_2$	Eth	-ane	amide	Ethanamide
		$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}ONH_2$	Prop	-ane	amide	Propanamide
		$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}ONH_2$	But	-ane	amide	Butanamide
10.	Amines (R—NH_2) Primary	$\overset{1}{C}H_3NH_2$	Meth	-ane	amine	Methanamine
		$\overset{2}{C}H_3\overset{1}{C}H_2NH_2$	Eth	-ane	amine	Ethanamine
		$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2NH_2$	Prop	-ane	amine	Propan-1-amine
		$\overset{3}{C}H_3\overset{2}{C}HNH_2\overset{1}{C}H_3$	Prop	-ane	amine	Propan-2-amine
11.	Cyanides or nitriles (R—CN)	$\overset{2}{C}H_3\overset{1}{C}N$	Eth	-ane*	nitrile	Ethane nitrile
		$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}N$	Prop	-ane*	nitrile	Propane nitrile
		$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}N$	But	-ane*	nitrile	Butane nitrile
12.	Alkyl halides ($C_nH_{2n+1}X$)	$\overset{1}{C}H_3Cl$	Meth	-ane	Chloro	Chloromethane
		$\overset{2}{C}H_3\overset{1}{C}H_2Cl$	Eth	-ane	Chloro	Chloroethane
		$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2Br$	Prop	-ane	Bromo	1-Bromopropane
		$\overset{3}{C}H_3\overset{2}{C}HBr\overset{1}{C}H_3$	Prop	-ane	Bromo	2-Bromopropane
13.	Ethers	$\overset{1}{C}H_3OCH_3$†	Meth	-ane	Methoxy	Methoxymethane
		$\overset{2}{C}H_3\overset{1}{C}H_2OCH_3$†	Eth	-ane	Methoxy } Prefix	Methoxyethane
		$\overset{2}{C}H_3\overset{1}{C}H_2OC_2H_5$†	Eth	-ane	Ethoxy	Ethoxyethane
14.	Nitro compounds	$\overset{1}{C}H_3NO_2$	Meth	-ane	Nitro	Nitromethane
		$\overset{2}{C}H_3\overset{1}{C}H_2NO_2$	Eth	-ane	Nitro	Nitroethane
		$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2NO_2$	Prop	-ane	Nitro	1-Nitropropane
		$\overset{3}{C}H_3\overset{2}{C}HNO_2\overset{1}{C}H_3$	Prop	-ane	Nitro	2-Nitropropane

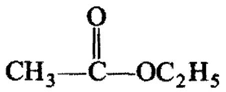
(15) **Esters :** The esters are formed when the hydrogen atom in the carboxyl group is replaced by an alkyl group.

$$\underset{\text{Carboxylic acid}}{RCOOH} \xrightarrow[+R']{-H} \underset{\text{Ester}}{RCOOR'},\quad \underset{\text{Functional group}}{[\text{—}COOR']}$$

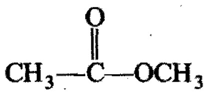
These are named as the alkyl salts of the parent acid. Their names consist of two words. The first word is the name of the alkyl group attached to oxygen atom. The second word is derived from the carboxylic acid name with -ic acid changed to -ate.


$H-\overset{\overset{O}{\|}}{C}-OCH_3$

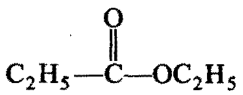
Methyl methanoate


$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$

Ethyl ethanoate

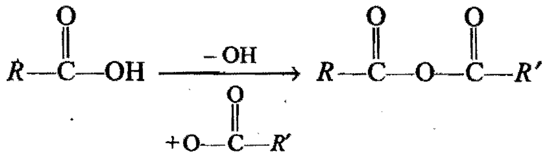

$CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$

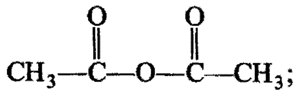
Methyl ethanoate


$C_2H_5-\overset{\overset{O}{\|}}{C}-OC_2H_5$

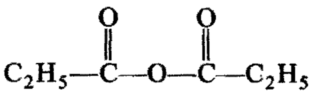
Ethyl propanoate

(16) **Anhydrides :** Anhydrides are derived from acids by replacing OH with OCOR. Anhydrides are named by changing the suffix acid of the parent acid to anhydride.

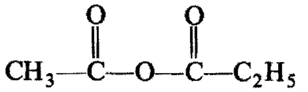

$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[+O-\overset{\overset{O}{\|}}{C}-R']{-OH} R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$$


$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$;

Ethanoic anhydride


$C_2H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-C_2H_5$

Propanoic anhydride


$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-C_2H_5$

Ethanoic propanoic anhydride

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* 'e' of the primary suffix -ane is not removed.

† Carbon of the alkoxy group is not counted in the chain.

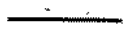
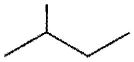
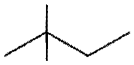
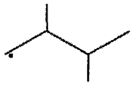
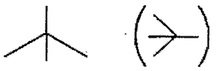
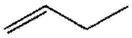
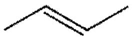
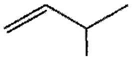
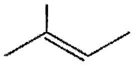
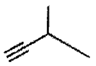
Bond Line Notations of Organic Molecules

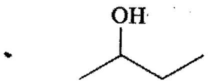
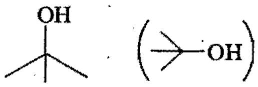
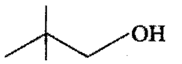
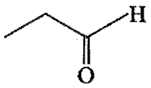
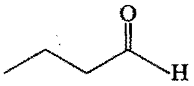
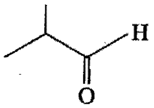
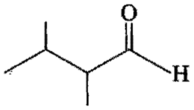
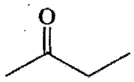
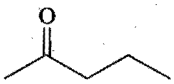
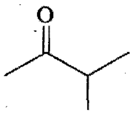
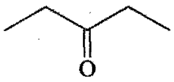
It is a simple, short and convenient method of representing organic molecules. The main points of this notation are as follows:

(i) The bonds (C—C) are shown by lines: Single bond by a single line (—), double bond by two parallel lines (=) and a triple bond by three parallel lines (≡).

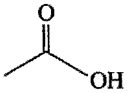
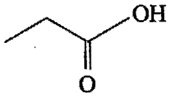
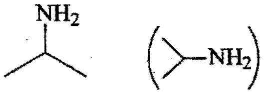
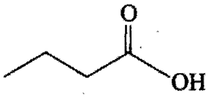
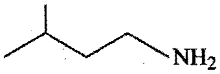
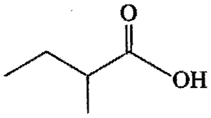
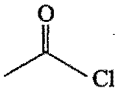
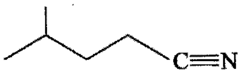
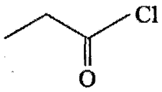
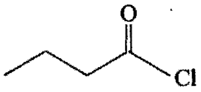
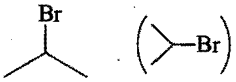
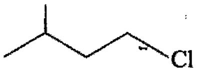
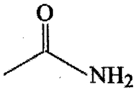
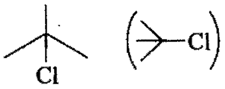
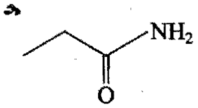
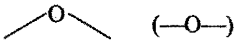
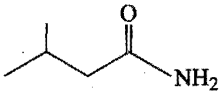
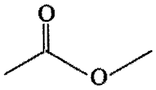
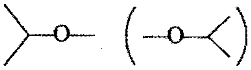
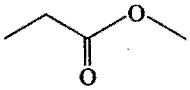
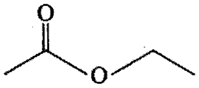
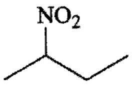
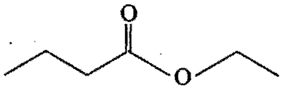
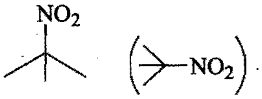
(ii) Carbon atoms are represented by lines drawn in a zig-zag fashion and carbon atoms by line ends and intersections. It is assumed that required number of hydrogen atoms are present wherever they are necessary to satisfy the tetravalency of carbon. Terminal denotes CH_3 groups and unsubstituted intersection, a CH_2 group.

IUPAC Nomenclature of Organic Compounds in Bond Line Structures

Series	Name	Structural formula
1. Alkanes	Ethane	
	Propane	
	Butane	
	Pentane	
	2-Methyl butane	
	2, 2-Dimethyl butane	
	2, 3-Dimethyl butane	
	2, 2-Dimethyl propane	
2. Alkenes	Ethene	
	Propene	
	But-1-ene	
	But-2-ene	
	3-Methyl but-1-ene	
	2-Methyl but-2-ene	
	3-Methyl pent-1-ene	
3. Alkynes	Ethyne	
	Prop-1-yne	
	But-1-yne	
	But-2-yne	
	Pent-1-yne	
	3-Methyl but-1-yne	

Series	Name	Structural formula
4. Alcohols (Mono)	Propan-1-ol (1-Propanol)	
	Propan-2-ol (2-Propanol)	
	Butan-1-ol (1-Butanol)	
	Butan-2-ol (2-Butanol)	
	2-Methyl propan-2-ol (2-Methyl-2-propanol)	
	2,2-Dimethyl propan-1-ol (2, 2-Dimethyl-1-propanol)	
5. Aldehydes	Propanal	
	Butanal	
	2-Methyl propanal	
	2, 3-Dimethyl butanal	
6. Ketones	Butan-2-one (2-Butanone)	
	Pentan-2-one (2-Pentanone)	
	3-Methyl butan-2-one (3-Methyl-2-butanone)	
	Pentan-3-one (3-Pentanone)	

Contd.

Series	**Name**	**Structural formula**	**Series**	**Name**	**Structural formula**
7. Carboxylic acids (Mono)	Ethanoic acid		11. Amines (Primary)	Ethanamine	
				Propan-1-amine (1-Propanamine)	
	Propanoic acid			Propan-2-amine (2-Propanamine)	
	Butanoic acid			3-Methyl butan-1-amine	
			12. Cyanides	Ethane nitrile	—C≡N
	2-Methyl butanoic acid			Propane nitrile	
				Butane nitrile	
8. Acid chlorides	Ethanoyl chloride			4-Methyl pentane nitrile	
	Propanoyl chloride		13. Alkyl halides	Chloroethane	
	Butanoyl chloride			2-Bromo propane	
				3-Methyl 1-chlorobutane	
9. Acid amides	Ethanamide			2-Chloro 2-methyl propane	
	Propanamide		14. Ethers	Methoxy methane	
	3-Methyl butanamide			Methoxy ethane	
				Ethoxy ethane	
10. Esters	Methyl ethanoate			2-Methoxy propane	
			15. Nitro alkanes	Nitro ethane	
	Methyl propanoate			1-Nitro propane	
	Ethyl ethanoate			2-Nitro butane	
	Ethyl butanoate			2-Methyl-2-nitro propane	

3.4 IUPAC SYSTEM OF NOMENCLATURE OF COMPLEX COMPOUNDS

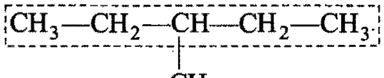
IUPAC system has framed a set of rules for various types of organic compounds.

[A] Rules for Naming Complex Aliphatic Compounds when no Functional Group is Present (Saturated Hydrocarbons or Paraffins or Alkanes)

1. Longest chain rule : The first step in naming an organic compound is to select the longest continuous chain of carbon atoms which may or may not be horizontal (straight). This continuous chain is called **parent chain** or **main chain** and other carbon chains attached to it are known as side chains (substituents). On the basis of number of carbon atoms present in the parent chain, the parent normal hydrocarbon is named (Root word + ane). The groups attached to this chain are identified and named accordingly.

Examples :

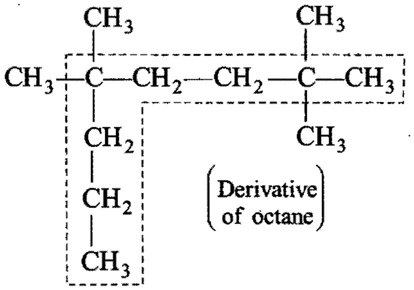
(a) The longest chain is of five carbon atoms. Hence, it is a derivative of pentane. The substituent is a methyl group.



$CH_3—CH_2—\underset{CH_3}{\underset{|}{CH}}—CH_2—CH_3$

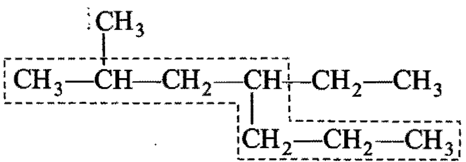
(Derivative of pentane)

(b) The horizontal straight chain consists six carbon atoms while the longest zig-zag chain consists eight carbon atoms. Hence, the longest chain consists eight carbon atoms and the compound is a derivative of octane. The various substituents are methyl groups.



(Derivative of octane)

(c) The horizontal chain consists six carbon atoms while the longest zig-zag chain consists seven carbon atoms. It is, thus, derivative of heptane. The substituents are ethyl and methyl groups.

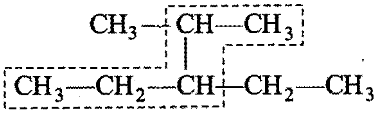


(Derivative of heptane)

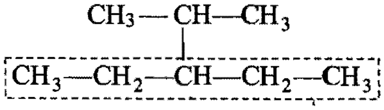
Note : It is possible that sometimes there may be two or more carbon chains of equal lengths in the molecule. In such a case the selected chain should (a) contain maximum number of side chains (substituents) or (b) have the least branched side chains.

Example :

(a)



(I)
Two substituents

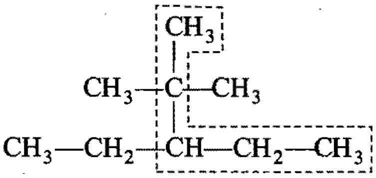


(II)
One substituent

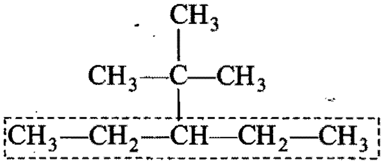
The chain of (I) is chosen as the parent chain because it has two substituents.

Example :

(b)



(I)
Three substituents

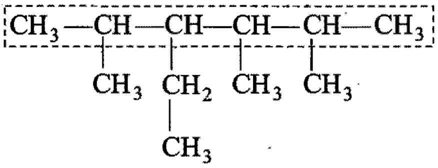


(II)
One substituent

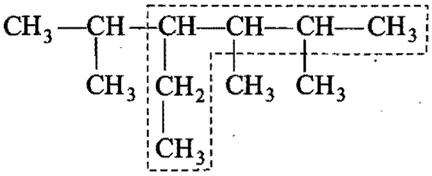
The chain of (I) is chosen as the parent chain because it has three substituents.

Example :

(c)



(I)
Four substituents



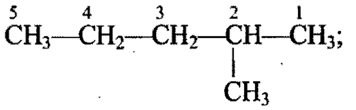
(II)
Three substituents

The chain of (I) is chosen as the parent chain because it has four substituents.

2. Numbering of the carbon atoms of the longest chain : The carbon atoms of the longest continuous chain (Parent chain) are numbered by arabic numerals 1, 2, 3, 4 . . .

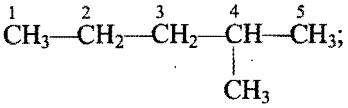
etc., from one end to the other. The number that locates the position of the substituent is known as **Locant**.

(a) The carbon atoms carrying the first substituent get the lowest possible number **(lowest individual number rule or lowest locant rule).** The positions of the substituents (side chains) are indicated by the number assigned to the carbon atom to which it is attached.



$CH_3-CH_2-CH_2-CH(CH_3)-CH_3$

2-Methylpentane
(Correct)

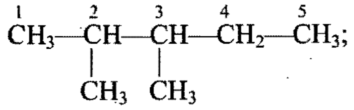


$CH_3-CH_2-CH_2-CH(CH_3)-CH_3$

4-Methylpentane
(Wrong)

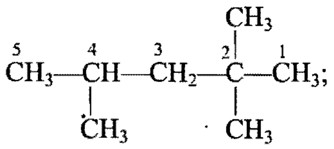
(b) In case, there are two or more similar substituents attached to the parent chain, their positions are indicated separately by the prefixes such as di, tri, tetra, etc.

(Lowest set of locants rule).



$CH_3-CH(CH_3)-CH(CH_3)-CH_2-CH_3$

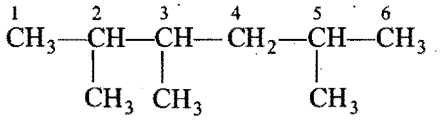
2,3-Dimethylpentane (Correct)
3,4-Dimethylpentane (Wrong)



$CH_3-CH(CH_3)-CH_2-C(CH_3)_2-CH_3$

2,2,4-Trimethylpentane (Correct)
2,4,4-Trimethylpentane (Wrong)

(c) When many substituents are present, the numbering is done from the end where upon the sum of locants is the lowest **(Lowest sum rule).**



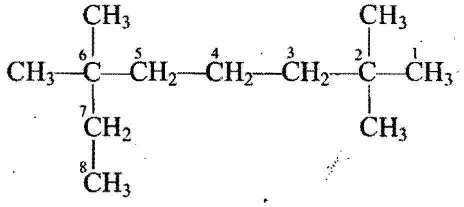
$CH_3-CH(CH_3)-CH(CH_3)-CH_2-CH(CH_3)-CH_3$

2,3,5-Trimethylhexane (Correct)

Sum of locants $= 2+3+5=10$

2,4,5-Trimethylhexane (Wrong)

Sum of locants $= 2+4+5=11$



$CH_3-C(CH_3)(CH_2CH_3)-CH_2-CH_2-CH_2-C(CH_3)_2-CH_3$

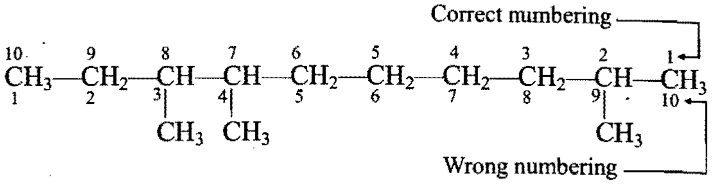
2,2,6,6-Tetramethyloctane (Correct)

Sum of locants $=2+2+6+6=16$

3,3,7,7-Tetramethyloctane (Wrong)

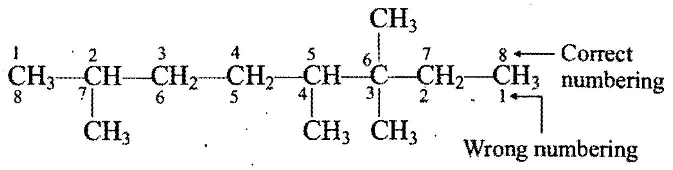
Sum of locants $=3+3+7+7=20$

Thus, it is evident from the above examples that both the lowest set of locants rule and lowest sum rule give the same results when the length of the carbon chain is not very long. However, when the length of the carbon chain is long, the two rules often give different results. Hence, that set of locants is preferred which has a lower number at the first point of difference even, if it violates the lowest sum rule **(First point of difference rule).**



$CH_3-CH_2-CH(CH_3)-CH(CH_3)-CH_2-CH_2-CH_2-CH_2-CH(CH_3)-CH_3$

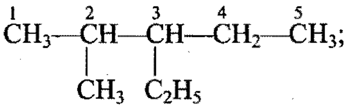
The correct name is 2,7,8-trimethyldecane and not 3,4,9-trimethyldecane, because at the first point of difference 2 is less than 3. Thus, the lowest set of locants rule is more general and preferred over the lowest sum rule. Other example is,



$CH_3-CH(CH_3)-CH_2-CH_2-CH(CH_3)-C(CH_3)_2-CH_2-CH_3$

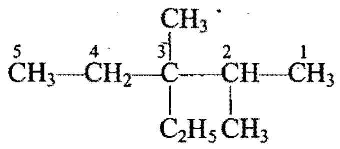
The correct name is 2,5,6,6-tetramethyloctane and not 3,3,4,7-tetramethyloctane, because 2 is lower than 3 when we compare the locants in the two names term by term.

(d) If there are different alkyl substituents attached to the parent chain, their names are written in the alphabetical order **(Alphabetical order of simple substituents).** It may be noted that prefixes such as di, tri, etc., are not considered while arranging the substituent alphabetically.



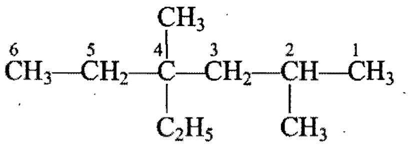
$CH_3-CH(CH_3)-CH(C_2H_5)-CH_2-CH_3$

3-Ethyl-2-methylpentane



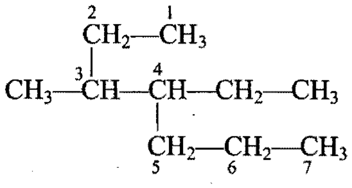
$CH_3-CH_2-C(CH_3)(C_2H_5)-CH(CH_3)-CH_3$

3-Ethyl-2,3-dimethylpentane



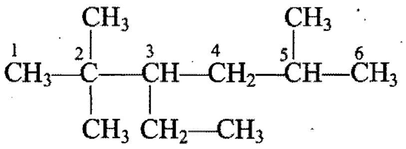
$CH_3-CH_2-C(CH_3)(C_2H_5)-CH_2-CH(CH_3)-CH_3$

4-Ethyl-2,4-dimethylhexane



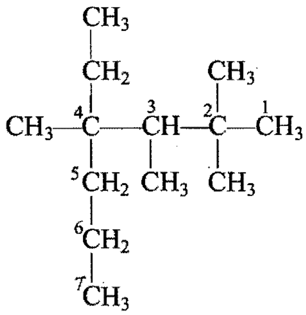
$CH_3-CH(CH_2CH_3)-CH(CH_2CH_2CH_3)-CH_2-CH_3$

4-Ethyl-3-methylheptane



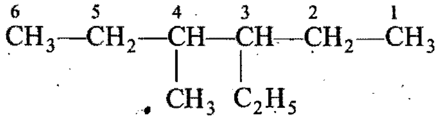
$CH_3-C(CH_3)_2-CH(CH_2CH_3)-CH_2-CH(CH_3)-CH_3$

3-Ethyl-2,2,5-trimethylhexane



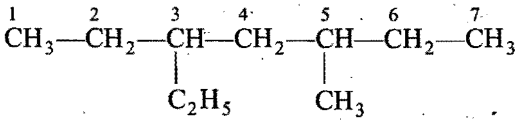
4-Ethyl-2,2,3,4-tetramethylheptane

(e) In case, there are **different alkyl substituents at equivalent positions,** then numbering of the parent chain is done in such a way that the alkyl group which comes first in the alphabetical order gets the lower number.



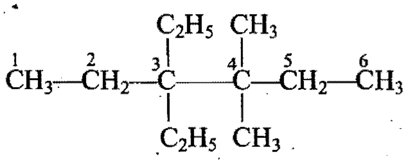
$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{\underset{CH_3}{C}}H-\overset{3}{\underset{C_2H_5}{C}}H-\overset{2}{C}H_2-\overset{1}{C}H_3$

3-Ethyl-4-methylhexane



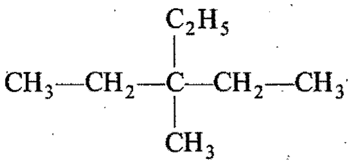
$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{\underset{C_2H_5}{C}}H-\overset{4}{C}H_2-\overset{5}{\underset{CH_3}{C}}H-\overset{6}{C}H_2-\overset{7}{C}H_3$

3-Ethyl-5-methylheptane



$\overset{1}{C}H_3-\overset{2}{C}H_2-\underset{C_2H_5}{\overset{C_2H_5}{\overset{3}{C}}}-\underset{CH_3}{\overset{CH_3}{\overset{4}{C}}}-\overset{5}{C}H_2-\overset{6}{C}H_3$

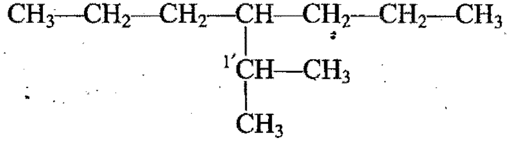
3,3-Diethyl-4,4-dimethylhexane



$CH_3-CH_2-\underset{CH_3}{\overset{C_2H_5}{C}}-CH_2-CH_3$

3-Ethyl-3-methylpentane

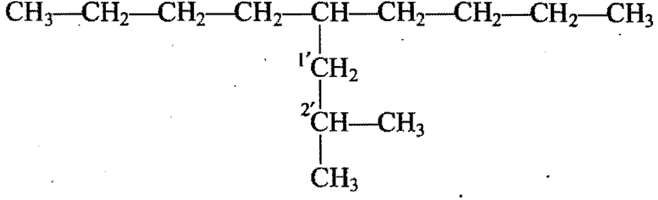
(f) **Naming the complex alkyl substituents :** When the substituents on the parent chain has itself branched chain, it is named as substituted alkyl group and its carbon chain is separately numbered in such a way, that the carbon atom directly attached to the parent chain is given number 1′. The name of this complex substituent is written in brackets to avoid confusion with the number of carbon atoms of the parent chain.



4-(1′-Methyl ethyl) heptane or 4-Isopropyl heptane

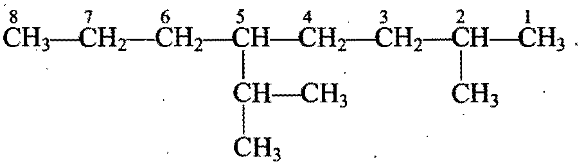
Note : According to IUPAC system of nomenclature, certain trivial or semi-systematic names may be used for unsubstituted radicals. For example, the following names may be used:

$(CH_3)_2CH-$	Isopropyl
$(CH_3)_2CHCH_2-$	Isobutyl
$CH_3CH_2\underset{\vert}{C}HCH_3$	*Sec.* butyl
$(CH_3)_3C-$	*Tert.* butyl
$(CH_3)_2CHCH_2CH_2-$	Isopentyl
$(CH_3)_3C-CH_2-$	Neopentyl
$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-$	*Tert.* pentyl
$(CH_3)_2CH-CH_2CH_2CH_2-$	Isohexyl



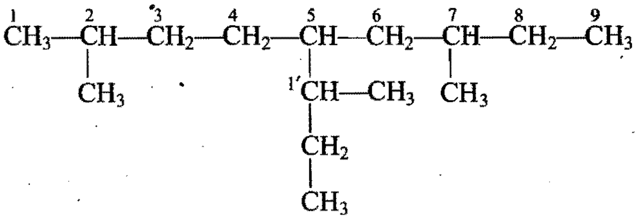
5-(2′-Methyl propyl)nonane or 5-Isobutyl nonane

The preffixes *iso*, *neo* and cyclo are considered in alphabetising substituent groups.



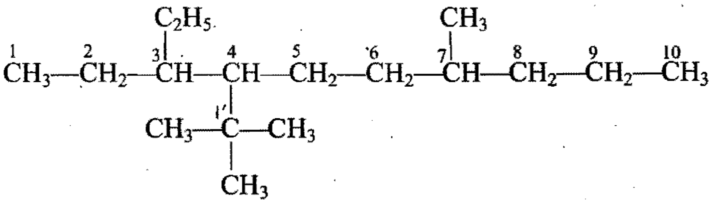
5-Isopropyl-2-methyloctane

While deciding the alphabetical order of the various substituents, the name of the complex substituent is considered to begin with the first letter of its complete name.



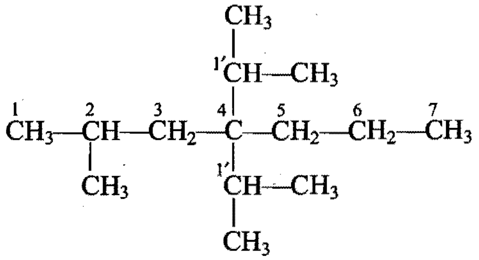
2,7-Dimethyl-5-(1′-Methyl propyl)nonane
or 2,7-Dimethyl-5-*Sec.* butyl nonane

Alphabet '*d*' of dimethyl group as a complete substituent comes before '*m*' of methyl propyl group.



4-(1′,1′-Dimethyl ethyl)-3-ethyl-7-methyldecane

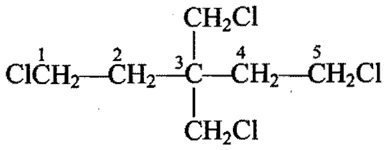
The numerical prefixes '*bis*-' (for two), '*tris*-' (for three), etc., are used to indicate a multiplicity of substituted substituent.



$$\overset{1}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\underset{\underset{\underset{CH_3}{|}}{\overset{1'}{C}H-CH_3}}{|}}{\overset{\overset{\overset{CH_3}{|}}{\overset{1'}{C}H-CH_3}}{|}}{\overset{4}{C}}}-\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H_3$$

2-Methyl-4,4-*bis*(1′-methyl ethyl)heptane

(*Bis* is used for two same complex substituents.)

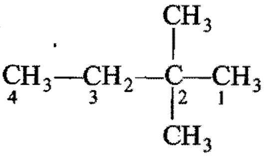


$$Cl\overset{1}{C}H_2-\overset{2}{C}H_2-\underset{\underset{CH_2Cl}{|}}{\overset{\overset{CH_2Cl}{|}}{\overset{3}{C}}}-\overset{4}{C}H_2-\overset{5}{C}H_2Cl$$

3,3-*Bis*-(chloro methyl)-1,5-dichloropentane

SOME WORKED EXAMPLES

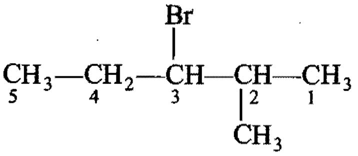
Example 1.



$$\underset{4}{CH_3}-\underset{3}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\underset{2}{C}}}-\underset{1}{CH_3}$$

The name of the compound is :
2,2-Dimethylbutane

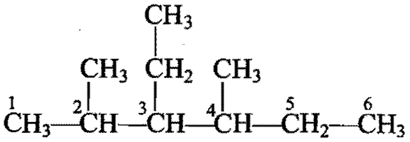
Example 2.



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\overset{\overset{Br}{|}}{\underset{3}{CH}}-\underset{\underset{CH_3}{|}}{\underset{2}{CH}}-\underset{1}{CH_3}$$

The name of the compound is :
3-Bromo-2-methylpentane

Example 3.



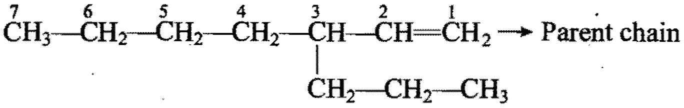
$$\overset{1}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{2}{C}H}-\overset{\overset{\overset{CH_3}{|}}{\overset{CH_2}{|}}}{\overset{3}{C}H}-\overset{\overset{CH_3}{|}}{\overset{4}{C}H}-\overset{5}{C}H_2-\overset{6}{C}H_3$$

The name of the compound is:

3-Ethyl-2,4-dimethylhexane.

[B] Rules for Naming Complex Unsaturated Aliphatic Hydrocarbons

(1) Longest chain : In the case of unsaturated hydrocarbons, the longest chain of carbon atoms (parent chain) is so selected as to include the double or triple bond even if it is not the actual longest chain of carbon atoms.

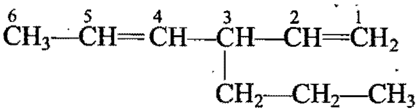


$$\overset{7}{C}H_3-\overset{6}{C}H_2-\overset{5}{C}H_2-\overset{4}{C}H_2-\underset{\underset{CH_2-CH_2-CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H=\overset{1}{C}H_2 \rightarrow \text{Parent chain}$$

The name of the compound is:

3-Propylhept-1-ene

When more than one double or triple bond is present in the molecule, the longest chain of carbon atoms is so selected that it includes maximum number of such bonds even if it is not the actual longest chain.



$$\overset{6}{C}H_3-\overset{5}{C}H=\overset{4}{C}H-\underset{\underset{CH_2-CH_2-CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H=\overset{1}{C}H_2$$

The name of the compound is:

3-Propylhexa-1,4-diene

(2) A primary suffix is added to the root word to indicate the presence of double or triple bond in the parent chain.

For one double bond = Root word + locant + ene

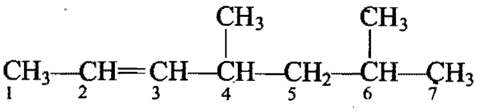
For one triple bond = Root word + locant + yne

In case the parent chains contain two or more double bonds (two or more triple bonds), the prefixes di-, tri-, tetra-, etc., are used before primary suffix.

For two double bonds = Root word + locant + diene

For two triple bonds = Root word + locant + diyne

(3) Numbering of carbon chain : The parent carbon chain is numbered in a manner so as to give lowest number to that carbon atom linked by double or triple bond even if it violates the rules of saturated hydrocarbons.



$$\underset{1}{CH_3}-\underset{2}{CH}=\underset{3}{CH}-\overset{\overset{CH_3}{|}}{\underset{4}{CH}}-\underset{5}{CH_2}-\overset{\overset{CH_3}{|}}{\underset{6}{CH}}-\underset{7}{CH_3}$$

(*A*)

The name of the compound is: 4,6-Dimethylhept-2-ene.

The position of the multiple bond (double or triple) is placed immediately before the suffix **ene** or the **yne** and not before the root word as was the practice being followed earlier. For example,

$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2$$

But-1-ene
(Formerly 1-butene)

$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_3$$

Pent-2-ene
(Formerly 2-Pentene)

$$\overset{1}{C}H_3-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$$

Hex-2-yne
(Formerly 2-Hexyne)

Note : Whenever the word formerly has been used, it implies that this name is still being used but the one given outside the bracket is preferred.

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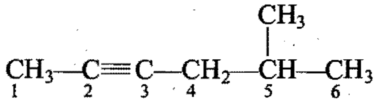
(4) Alkyl groups or other substituents are numbered, named and placed as prefixes in alphabetical order.

Examples :

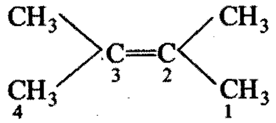
(a)



$$\underset{1}{CH_3}-\underset{2}{C}\equiv\underset{3}{C}-\underset{4}{CH_2}-\overset{\overset{CH_3}{|}}{\underset{5}{CH}}-\underset{6}{CH_3}$$

5-Methylhex-2-yne

(b)

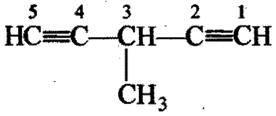


2,3-Dimethylbut-2-ene

(c)

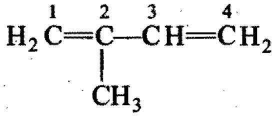
$\overset{6}{CH_3}-\overset{\overset{CH_3}{|}}{\overset{5}{C}H}-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}H=\overset{1}{C}H_2$

5-Methylhexa-1,3-diene



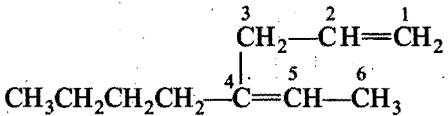
$\overset{5}{H}C\equiv\overset{4}{C}-\underset{\underset{CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}\equiv\overset{1}{C}H$

3-Methylpenta-1,4-diyne



$H_2\overset{1}{C}=\underset{\underset{CH_3}{|}}{\overset{2}{C}}-\overset{3}{C}H=\overset{4}{C}H_2$

2-Methylbuta-1,3-diene

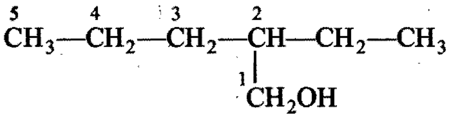


$CH_3CH_2CH_2CH_2-\overset{\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2}{\overset{|}{\overset{4}{C}}}=\overset{5}{C}H-\overset{6}{C}H_3$

4-Butylhexa-1,4-diene

[C] Rules for Naming Complex Aliphatic Compounds Containing One Functional Group

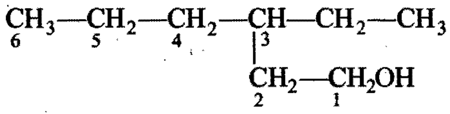
(1) Longest chain : The parent carbon chain is so chosen as to include the functional group even if it is not the actual longest continuous chain.



$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\underset{\underset{\overset{1}{C}H_2OH}{|}}{\overset{2}{C}H}-CH_2-CH_3$

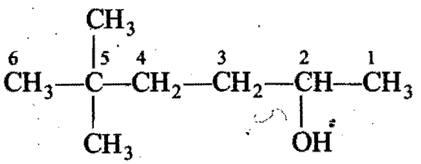
2-Ethylpentan-1-ol

(2) Numbering of parent chain : The numbering of the parent carbon chain is done in such a way that the carbon linking to functional group gets the lowest number even if there is violation of saturated hydrocarbon rules.



$\underset{6}{C}H_3-\underset{5}{C}H_2-\underset{4}{C}H_2-\underset{\underset{\underset{2}{C}H_2-\underset{1}{C}H_2OH}{|}}{\overset{}{\underset{3}{C}H}}-CH_2-CH_3$

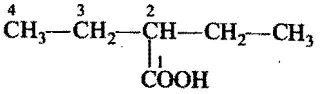
3-Ethylhexan-1-ol



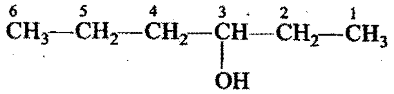
$\overset{6}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{5}{C}}}-\overset{4}{C}H_2-\overset{3}{C}H_2-\underset{\underset{OH}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$

5,5-Dimethylhexan-2-ol

Note : When a chain terminating group such as —CHO, —COOH, —COO*R*, —$CONH_2$,—C≡N, etc., is present as the functional group, it must be assigned number 1. This does not apply to non-terminal groups such as >CO, —NH_2 and —OH which may or may not be assigned 1.



$\overset{4}{C}H_3-\overset{3}{C}H_2-\underset{\underset{\overset{1}{C}OOH}{|}}{\overset{2}{C}H}-CH_2-CH_3$



$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H_2-\underset{\underset{OH}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_3$

(3) The last 'e' of the primary suffix is dropped and the secondary suffix representing the functional group is added.

The number giving the position of the functional group is inserted in the name.

The compound $\overset{6}{CH_3}\overset{5}{CH_2}\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{CO}\overset{1}{CH_3}$ is named as: Hexan-2-one

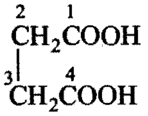
Similarly, the compound $\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CHOH}\overset{4}{CH_2}\overset{5}{CH_3}$ may be named as: Pentan-3-ol.

(4) The names of the substituents are prefixed to the parent hydrocarbon according to IUPAC rules with alphabetical order without considering the presence of functional group. Halo and nitro groups are considered as substituents.

(5) Numerical prefixes di-, tri-, tetra-, etc., are attached before the designations of functional group if two or more identical groups are present, *e.g.*,

(i) $\overset{1}{CH_2OH}-\overset{2}{CH_2OH}$ is named ethane-1,2-diol.

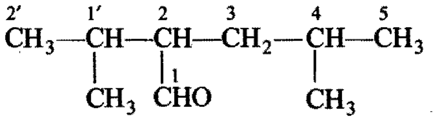
(ii)



$\begin{array}{l}\overset{2}{C}H_2\overset{1}{C}OOH\\ {}^{3}|\ \ {}^{4}\\ CH_2COOH\end{array}$

is named butane-1,4-dioic acid.

(iii)



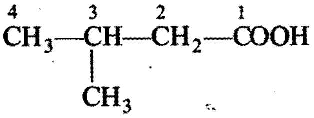
$CH_3-\underset{\underset{CH_3}{|}}{\overset{1'}{C}H}-\underset{\underset{\overset{1}{C}HO}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{4}{C}H}-\overset{5}{C}H_3$ (2′ over the first CH_3)

2(1′-Methyl ethyl)-4-methylpentanal
or 2-Isopropyl-4-methylpentanal

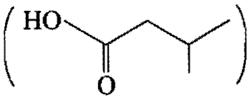
SOME MORE WORKED EXAMPLES

Example 1. $(CH_3)_2CH-CH_2-COOH$

Rewriting the structure of the compound,



$\overset{4}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}OOH$

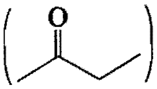


The name of the compound is :

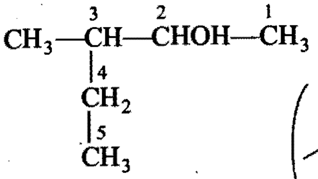
3-Methylbutanoic acid.

Example 2. $\overset{1}{CH_3}\overset{2}{CO}\overset{3}{CH_2}\overset{4}{CH_3}$

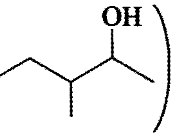
The name of the compound is :
Butan-2-one



Example 3.



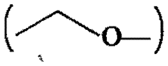
$$\begin{array}{l} CH_3-\overset{3}{C}H-\overset{2}{C}HOH-\overset{1}{C}H_3 \\ \qquad\quad |_{4} \\ \qquad\quad CH_2 \\ \qquad\quad |_{5} \\ \qquad\quad CH_3 \end{array}$$



The name of the compound is:

3-Methylpentan-2-ol

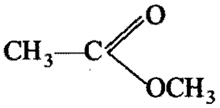
Example 4. $CH_3-CH_2-O-CH_3$



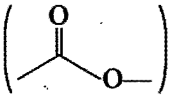
The name of the compound is:

Methoxyethane

Example 5.



$$CH_3-C\begin{array}{l} /\!\!/ O \\ \diagdown OCH_3 \end{array}$$

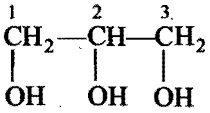


The name of the compound is:

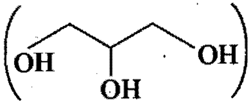
Methylethanoate

Example 6. $CH_2OHCHOHCH_2OH$

Rewriting the structure of the compound.



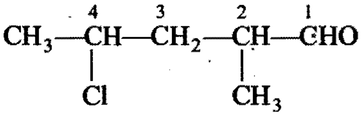
$$\begin{array}{ccccc} \overset{1}{CH_2} & - & \overset{2}{CH} & - & \overset{3}{CH_2} \\ | & & | & & | \\ OH & & OH & & OH \end{array}$$



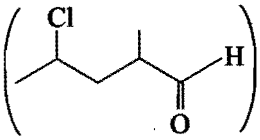
The name of the compound is:

Propane-1,2,3-triol

Example 7.



$$\begin{array}{ccccccccc} CH_3 & - & \overset{4}{CH} & - & \overset{3}{CH_2} & - & \overset{2}{CH} & - & \overset{1}{CHO} \\ & & | & & & & | & & \\ & & Cl & & & & CH_3 & & \end{array}$$



The name of the compound is:

4-Chloro-2-methylpentanal

[D] Rules for Naming Aliphatic Compounds Having Polyfunctional Groups

· A compound is said to be polyfunctional compound if it contains more than one functional group. The multiple bond ($>C=C<$ or $-C\equiv C-$) is also considered as a functional group. In IUPAC system, one of the functional groups is chosen as the **principal functional group** (secondary suffix) and the remaining functional groups (secondary functional groups) are treated as **substituents** and indicated by prefixes. For example, in the following structure:

$$\begin{array}{l} \;\;OH \leftarrow \text{Substituent} \\ \;\;| \\ CH_3-CH-CH_2-CH_2-COOH \leftarrow \text{Principal functional group} \end{array}$$

The —COOH group is the principal functional group, while the —OH group is a substituent. The principal functional group is mentioned with its suffix name while secondary functional groups are mentioned only with their prefix name.

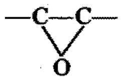
The carboxylic and sulphonic acid groups are always chosen as principal functions, and the choice of the principal functional group is made on the basis of the following order of preference.

Sulphonic acids > carboxylic acids > acid anhydrides > esters > acid chlorides > acid amides > cyanides > aldehydes > ketones > alcohols, phenols, thiols > amines > ethers > alkenes, alkynes.

Alkyl ($R-$), phenyl (C_6H_5-), Cl, Br, NO_2, etc., are prefix substituents.

The order of seniority among the principal groups is given according to the following table along with their prefix and suffix names. The functional group which occurs higher up in the table is the principal functional group.

Seniority Table for Principal Groups
(Highest Priority Group at the Top)

Group	Prefix name	Suffix name
$-SO_3H$	Sulpho	sulphonic acid
$-COOH$	Carboxy	-oic acid
$-COOR$	Alkoxy carbonyl or carbalkoxy	alkyl oate
$-COX$	Haloformyl or halocarbonyl	-oyl halide
$-CONH_2$	Carbamoyl	amide
$-CN$	Cyano	nitrile
$-NC$	Isocyano	carbylamine
$-CHO$	Formyl or aldo	-al
$>C=O$	Keto or oxo	-one
$-OH$	Hydroxy	-ol
$-SH$	Mercapto	thiol
$-NH_2$	Amino	amine
$-OR$	Alkoxy	—
	Epoxy	—
$>C=C<$	—	-ene
$-C\equiv C-$	—	-yne
$-N=N-$	Azo	—
$-NO_2$	Nitro	—
$-NO$	Nitroso	—
$-X$	Halo (Chloro, bromo, iodo)	—

1. The first step in the naming of polyfunctional compounds is the selection of principal functional group. The principal functional group gives the class name of the structure.

2. The second step is the selection of parent chain. The parent chain is so selected that it includes the maximum number of functional groups including the principal group.

3. The third step is the numbering of parent chain. The parent chain is numbered from the side of principal functional group, *i.e.*, it gets lowest number. The following decreasing order of preference for giving the lowest numbers is followed.

Principal functional group > Double bond
or Triple bond > Substituents

Note : (a) If a molecule contains both carbon-carbon double or triple bonds, the two are treated at par in seeking the lowest number combination. However, if the sum of numbers turns out to be the same starting from either of the carbon chain, then lowest number is given to the C=C double bond. Such compounds are named as **alkenynes** (a derivative of alkynes rather than alkenes) with numbering as low as possible given to the multiple bonds.

$\overset{5}{C}H_3-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}\equiv\overset{1}{C}H$

Pent-3-en-1-yne

$\overset{5}{C}H_3-\overset{4}{C}\equiv\overset{3}{C}-\overset{2}{C}H=\overset{1}{C}H_2$

Pent-1-en-3-yne

$H\overset{5}{C}\equiv\overset{4}{C}-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$

Pent-1-en-4-yne

$H\overset{6}{C}\equiv\overset{5}{C}-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}H=\overset{1}{C}H_2$

Hexa-1,3-dien-5-yne

So, in the parent chain containing both double and triple bonds, the terminal 'e' in the name is dropped when it is followed by the suffix beginning with 'a', 'i', 'o', 'u' or 'y'. Therefore, the terminal 'e' of ene in *en-yne* and *a dien-yne* is dropped because it comes before 'y' (of-yne). However, 'e' is **not dropped** in case of *enediyne* because it comes before 'd' of -diyne.

(b) In case two substituents of same seniority occupy identical positions in relation to the end of the chain, the lowest number should be given to the substituent in alphabetical order.

$Cl\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2Br$	$Cl\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2Br$
1-Bromo-3-chloropropane (Right)	3-Bromo-1-chloropropane (Wrong)

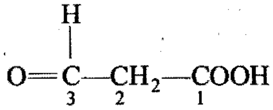
---

4. Substituents, side chains and secondary functional groups are named in alphabetical order.

Some Specific Rules for IUPAC Nomenclature

1. If the substituent group is named as an oxygen derivative of CH_3— or CH_2 group, the carbon atom of the substituent group is also counted towards parent chain.

For example:

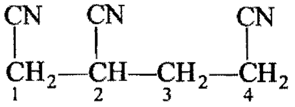


$O=\underset{3}{\overset{\overset{H}{|}}{C}}-\underset{2}{C}H_2-\underset{1}{C}OOH$ 3-Formylpropanoic acid

2. Nomenclature of polyfunctional compounds containing more than two like functional groups.

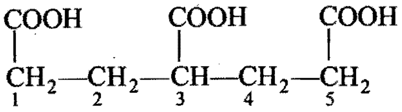
According to IUPAC convention 1993, if an unbranched carbon chain is directly linked to more than two like functional groups, the organic compound is named as a derivative of parent alkane which does not include the carbon atom of the functional groups. These are named by use of suffix such as **tricarboxylic acid** (for three —COOH groups), **tricarboaldehyde** (for three —CHO groups) or **tricarbonitrile** (for three —CN groups).

e.g.,



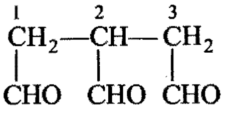
$\underset{1}{\overset{\overset{CN}{|}}{CH_2}}-\underset{2}{\overset{\overset{CN}{|}}{CH}}-\underset{3}{CH_2}-\underset{4}{\overset{\overset{CN}{|}}{CH_2}}$

Butane-1,2,4-tricarbonitrile
(formerly 3-cyanohexane-1,6-dinitrile)



$\underset{1}{\overset{\overset{COOH}{|}}{CH_2}}-\underset{2}{CH_2}-\underset{3}{\overset{\overset{COOH}{|}}{CH}}-\underset{4}{CH_2}-\underset{5}{\overset{\overset{COOH}{|}}{CH_2}}$

Pentane-1,3,5-tricarboxylic acid .
(formerly 4-carboxy heptane-1,7-dioic acid)



$\overset{1}{\underset{\underset{CHO}{|}}{CH_2}}-\overset{2}{\underset{\underset{CHO}{|}}{CH}}-\overset{3}{\underset{\underset{CHO}{|}}{CH_2}}$

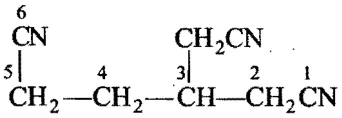
Propane-1,2,3-tricarboaldehyde
(formerly 3-formyl pentane-1,5-dial)

Note: If all the three like groups are not directly linked to the unbranched carbon chain, the carbon atoms of the two like groups are included in the parent chain while the third which forms the side chain is considered as a substituent group.

---

e.g.,

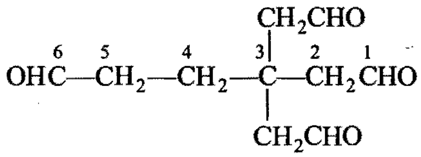
(i)



$\underset{5}{\overset{\overset{\overset{6}{CN}}{|}}{CH_2}}-\underset{4}{CH_2}-\underset{3}{\overset{\overset{CH_2CN}{|}}{CH}}-\underset{2}{C}H_2\underset{1}{C}N$

3-(Cyano methyl) hexane-1,6-dinitrile

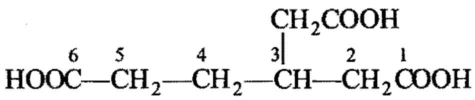
(ii)



$OH\underset{6}{C}-\underset{5}{CH_2}-\underset{4}{CH_2}-\underset{\underset{CH_2CHO}{|}}{\overset{\overset{CH_2CHO}{|}}{\overset{3}{C}}}-\underset{2}{C}H_2\underset{1}{C}HO$

3,3-*Bis* (formyl methyl) hexane-1,6-dial

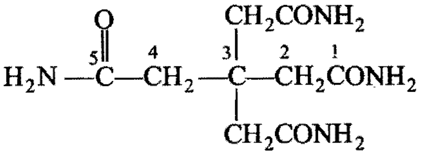
(iii)



$HOO\underset{6}{C}-\underset{5}{CH_2}-\underset{4}{CH_2}-\overset{\overset{CH_2COOH}{|}}{\underset{3}{CH}}-\underset{2}{C}H_2\underset{1}{C}OOH$

3-(Carboxy methyl) hexane-1,6-dioic acid

(iv)



$H_2N-\overset{\overset{O}{\|}}{\underset{5}{C}}-\underset{4}{CH_2}-\underset{\underset{CH_2CONH_2}{|}}{\overset{\overset{CH_2CONH_2}{|}}{\overset{3}{C}}}-\underset{2}{C}H_2\underset{1}{C}ONH_2$

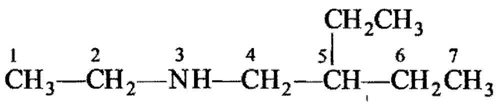
3,3-*Bis* (carbamoyl methyl) pentane-1,5-diamide

3. Replacement Nomenclature: In this system, ethers, sulphides, selenides and amines are named as oxa, thia, selena and aza derivatives of alkane corresponding to the total number of carbon and oxygen or sulphur or selenium or nitrogen atoms.

The location of these hetero atoms on the carbon chain are indicated by numerals in accordance with *lowest set of locant rule*.

e.g.,

(a)



$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{N}H-\overset{4}{C}H_2-\overset{\overset{CH_2CH_3}{|}}{\overset{5}{C}H}-\overset{6}{C}H_2\overset{7}{C}H_3$

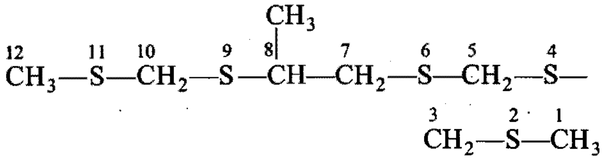
5-Ethyl-3-azaheptane

(b) $\overset{1}{H_2N}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{NH}-\overset{5}{CH_2}-\overset{6}{CH_3}$

1,4-Diazahexane

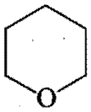
(c) $\overset{1}{CH_3}-\overset{2}{O}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{O}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{O}-\overset{9}{CH_3}$

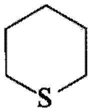
2,5,8-Trioxanonane

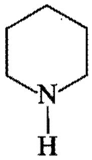
(d) 

$\overset{12}{CH_3}-\overset{11}{S}-\overset{10}{CH_2}-\overset{9}{S}-\overset{CH_3}{\overset{8}{CH}}-\overset{7}{CH_2}-\overset{6}{S}-\overset{5}{CH_2}-\overset{4}{S}-\overset{3}{CH_2}-\overset{2}{S}-\overset{1}{CH_3}$

8-Methyl-2,4,6,9,11-pentathiadodecane

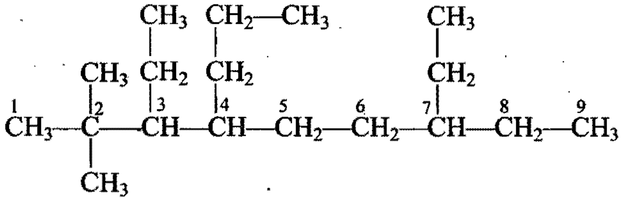
(e)  Oxacyclohexane

(f)  Thiacyclohexane

(g)  Azacyclohexane

MISCELLANEOUS WORKED EXAMPLES

Example 8.

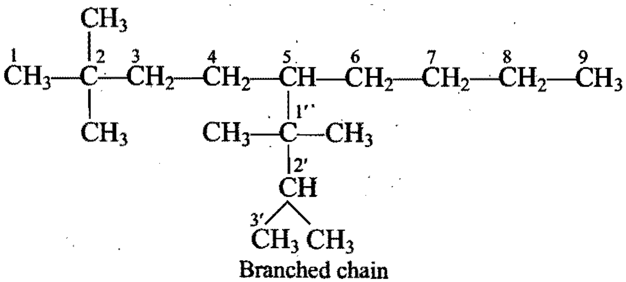


$\overset{1}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{CH_2-CH_3}{\overset{3}{CH}}-\overset{CH_2-CH_2-CH_3}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{CH_2-CH_3}{\overset{7}{CH}}-\overset{8}{CH_2}-\overset{9}{CH_3}$

The name of the compound is:

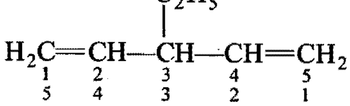
3,7-Diethyl-2,2-dimethyl-4-propylnonane

Example 9.



$\overset{1}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\underset{CH_3-\underset{CH(CH_3)_2}{C}-CH_3}{\overset{5}{CH}}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH_2}-\overset{9}{CH_3}$

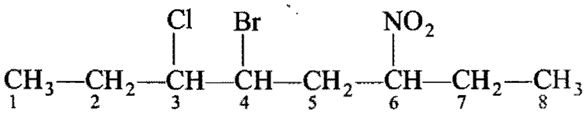
2,2-Dimethyl-5-(1′,1′,2′-trimethylpropyl)nonane

Example 10. 

$H_2C=CH-\overset{C_2H_5}{CH}-CH=CH_2$

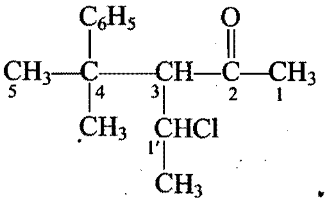
3-Ethylpenta-1,4-diene

Example 11.



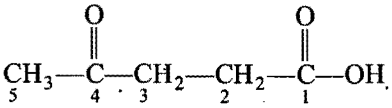
$\underset{1}{CH_3}-\underset{2}{CH_2}-\overset{Cl}{\underset{3}{CH}}-\overset{Br}{\underset{4}{CH}}-\underset{5}{CH_2}-\overset{NO_2}{\underset{6}{CH}}-\underset{7}{CH_2}-\underset{8}{CH_3}$

4-Bromo-3-chloro-6-nitro octane

Example 12. 

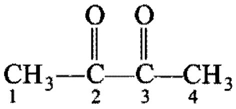
$\underset{5}{CH_3}-\underset{CH_3}{\overset{C_6H_5}{\underset{4}{C}}}-\underset{\underset{CH_3}{\underset{1'}{CHCl}}}{\underset{3}{CH}}-\overset{O}{\overset{\|}{\underset{2}{C}}}-\underset{1}{CH_3}$

3-(1′-Chloroethyl)-4-methyl-4-phenylpentan-2-one

Example 13. 

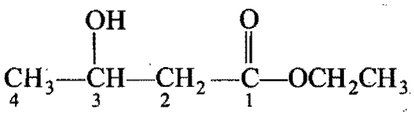
$\underset{5}{CH_3}-\overset{O}{\overset{\|}{\underset{4}{C}}}-\underset{3}{CH_2}-\underset{2}{CH_2}-\overset{O}{\overset{\|}{\underset{1}{C}}}-OH$

4-Oxopentanoic acid

Example 14. 

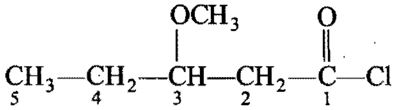
$\underset{1}{CH_3}-\overset{O}{\overset{\|}{\underset{2}{C}}}-\overset{O}{\overset{\|}{\underset{3}{C}}}-\underset{4}{CH_3}$

Butane-2,3-dione

Example 15. 

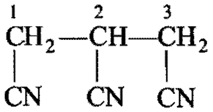
$\underset{4}{CH_3}-\overset{OH}{\underset{3}{CH}}-\underset{2}{CH_2}-\overset{O}{\overset{\|}{\underset{1}{C}}}-OCH_2CH_3$

Ethyl-3-hydroxybutanoate

Example 16. 

$\underset{5}{CH_3}-\underset{4}{CH_2}-\overset{OCH_3}{\underset{3}{CH}}-\underset{2}{CH_2}-\overset{O}{\overset{\|}{\underset{1}{C}}}-Cl$

3-Methoxypentanoylchloride

Example 17. 

$\underset{CN}{\overset{1}{CH_2}}-\underset{CN}{\overset{2}{CH}}-\underset{CN}{\overset{3}{CH_2}}$

In this case a special suffix carbonitrile is used and all functional groups having highest priority should be treated as principal functional groups. Thus, these are named as carbonitrile derivatives of the parent chain.

Thus, the name of the compound* is:

Propane-1,2,3-tricarbonitrile

(*Formerly named as 3-cyanopentane-1,5-dinitrile)

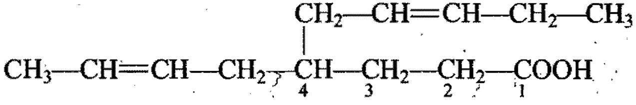
Example 18. $\overset{5}{CH_3}-\overset{4}{CH}=\overset{3}{CH}-\overset{2}{C}\equiv\overset{1}{CH}$

Pent-3-en-1-yne

Example 19. $\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{C}\equiv\overset{4}{CH}$

But-1-en-3-yne

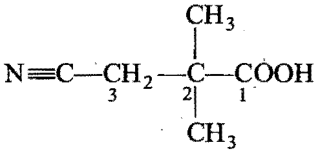
Example 20.



$CH_3-CH=CH-CH_2-\underset{4}{\overset{\overset{5}{CH_2}-\overset{6}{CH}=\overset{7}{CH}-\overset{8}{CH_2}-\overset{9}{CH_3}}{CH}}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{COOH}$

4-(2′-Butenyl)-non-6-enoic acid

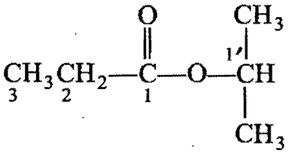
Example 21.



$$N\equiv\underset{3}{C}-CH_2-\underset{\underset{CH_3}{2|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{1}{C}OOH$$

3-Cyano-2,2-dimethylpropanoic acid

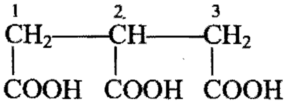
Example 22.



$$\underset{3}{CH_3}\underset{2}{CH_2}-\underset{1}{\overset{\overset{O}{\|}}{C}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{1'|}}{CH}}$$

(1′-Methylethyl) propanoate or Isopropylpropanoate

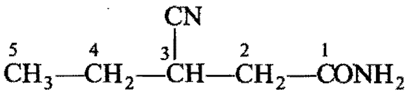
Example 23.



$$\underset{\underset{COOH}{|}}{\overset{1}{CH_2}}-\underset{\underset{COOH}{|}}{\overset{2}{CH}}-\underset{\underset{COOH}{|}}{\overset{3}{CH_2}}$$

Propane-1,2,3-tricarboxylic acid
(Formerly named as 3-carboxy pentane-1,5-dioic acid)

Example 24.

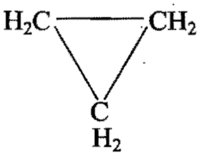


$$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{\overset{CN}{3|}}{CH}-\overset{2}{CH_2}-\overset{1}{C}ONH_2$$

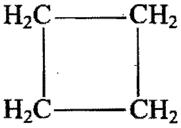
3-Cyanopentanamide

3.5 IUPAC NOMENCLATURE OF ALICYCLIC COMPOUNDS

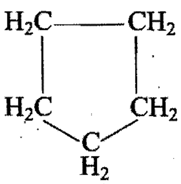
(1) Cycloalkanes : Cycloalkanes are alkanes in which carbon atoms are arranged in a ring. These are named by adding the prefix **cyclo-** to the name of alkane having the same number of carbon atoms as in the rings.



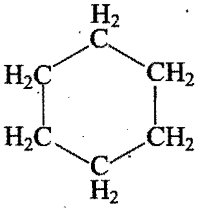
Cyclopropane



Cyclobutane

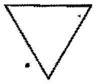


Cyclopentane

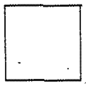


Cyclohexane

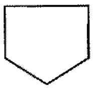
These are also represented by simple geometrical figures.



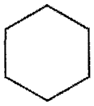
Cyclopropane



Cyclobutane

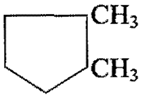


Cyclopentane

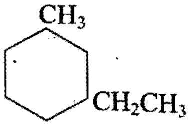


Cyclohexane

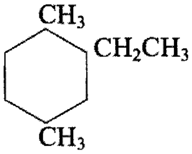
Substituted cycloalkanes are named as **alkyl cycloalkanes.** The numbering of the carbon atoms in the ring is done in such a way that the substituent which comes first in the alphabetical order is given the lowest possible number provided it does not violate the lowest set of locants rule.



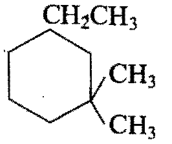
1,2-Dimethyl cyclopentane



1-Ethyl-3-methyl cyclohexane

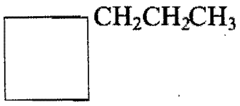


2-Ethyl-1, 4-dimethyl-cyclohexane

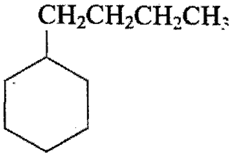


3-Ethyl-1, 1-dimethyl-cyclohexane

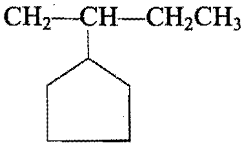
When the ring contains more or equal number of carbon atoms than the alkyl group attached to it, then it is named as a derivative of cycloalkane and the alkyl group is treated as substituent.



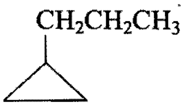
Propylcyclobutane



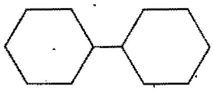
Butylcyclohexane



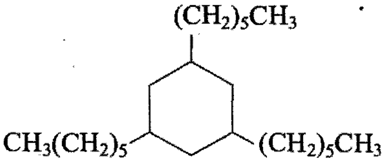
(2-Butyl) cyclopentane



Propylcyclopropane

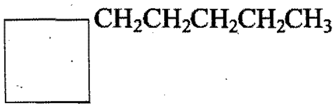


Cyclohexyl Cyclohexane

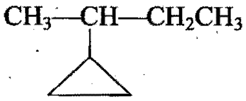


1,3,5-*Tris* (hexyl) Cyclohexane

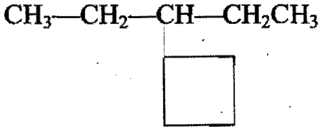
Note : In case, the alkane chain contains greater number of carbon atoms than present in the ring, the compound is considered as the derivative of alkane and the ring is designated as substituent.



1-Cyclobutylpentane



2-Cyclopropylbutane



3-Cyclobutylpentane

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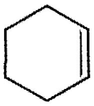
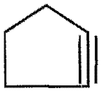
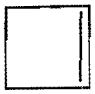
(2) Cycloalkenes and cycloalkynes : The word cyclo is prefixed before the name of alkene and alkyne having the same number of carbon atoms as in the ring.



Cyclohexene

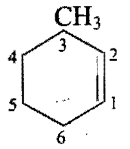


Cyclopentyne

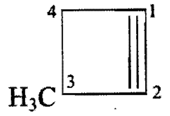


Cyclobutene

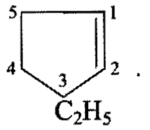
In the case of substituted cycloalkenes and cycloalkynes, the numbering of double or triple bond is done as 1 and 2, the direction is so chosen as to give lowest numbers to the substituents.



3-Methylcyclohexene

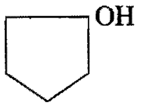


3-Methylcyclobutyne

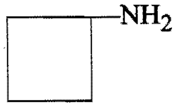


3-Ethylcyclopentene

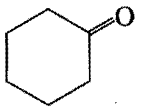
(3) Alicyclic compounds containing functional group : Alicyclic alcohols, amines, aldehydes, ketones, acids, etc. are named in the same fashion as corresponding aliphatic compounds by prefixing the word cyclo before the name.



Cyclopentanol

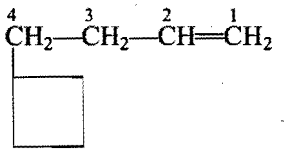


Cyclobutane-amine

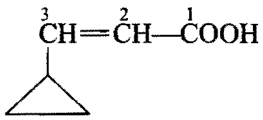


Cyclohexanone

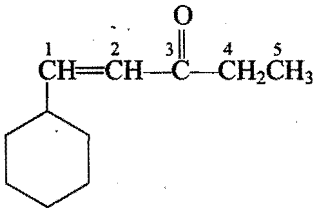
If however, the side chain contains a multiple bond or a functional group, the alicyclic ring is treated as substituent irrespective of the size of the ring.



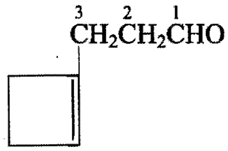
4-Cyclobutylbut-1-ene



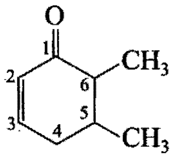
3-Cyclopropyl prop-2-en-1-oic acid



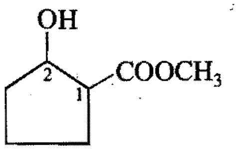
1-Cyclohexyl pent-1-en-3-one



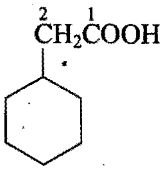
3-Cyclobut-1-enylpropanal



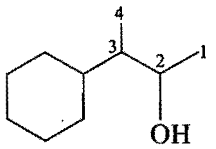
5,6-Dimethyl cyclo hex-2-en-1-one



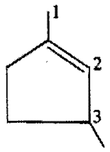
Methyl (2-hydroxy cyclopentane) carboxylate



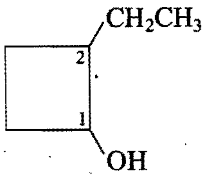
2-Cyclohexyl ethanoic acid



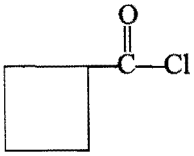
3-Cyclohexyl butan-2-ol



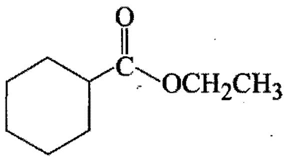
1,3-Dimethyl cyclopent-1-ene



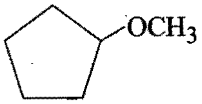
2-Ethyl cyclobutan-1-ol



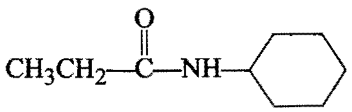
Cyclobutane carbonyl chloride



Ethyl cyclohexyl methanoate

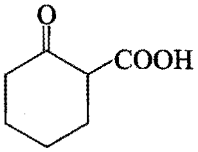


Methoxy cyclopentane

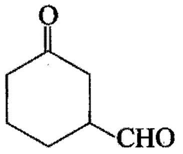


N-Cyclohexyl propanamide

In case of cyclic ketones any functional group present in the ring is treated as substituents (even —CHO, —COOH etc.) and keto group is always treated as principal functional group. This is because carbon of the keto group is a part of the ring. This rule is applicable till the number of carbon atoms in substituent is less or equal to the number of carbon atoms present in the ring *e.g.*,

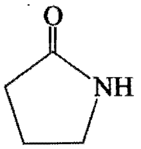


2-Carboxy cyclohexanone

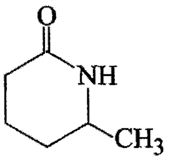


3-Formylcyclohexanone

Cyclic amides are called **Lactams.** The IUPAC name of these compounds are **Azacycloalkanone.**

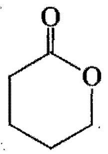


2-Aza cyclopentanone

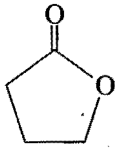


2-Aza-3-methyl cyclohexanone

Cyclic esters are called **Lactones.** The IUPAC name of these compounds are **Oxacycloalkanone.**



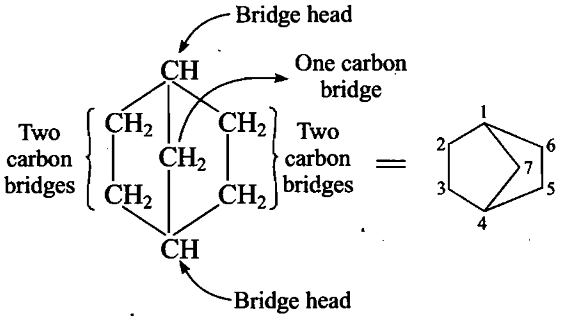
2-Oxa cyclohexanone



2-Oxa cyclopentanone

Nomenclature of Bicyclo and Spiro Compounds

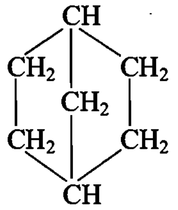
Bicyclo compounds contain two fused rings with the help of a bridge. We use the name of the alkane corresponding to the total number of carbon atoms as the base name. The carbon atoms common to both the rings are called bridge heads, and each bond or chain of atoms connecting the bridge head atoms, is called a bridge.



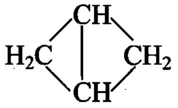
(Bicycloheptane)

- While naming the bicycloalkane we write an expression between the word bicyclo and alkane (in square bracket), that denotes the number of carbon atoms in each bridge. The numerals are written in descending order and the numbers are separated by full stops.

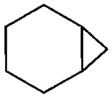
Examples of Bicyclo Compounds

(1)


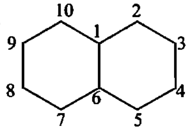
Bicyclo [2.2.1] heptane. It's common name is norbornane

(2)


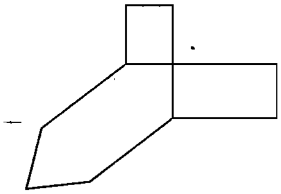
Bicyclo [1.1.0] butane

(3)


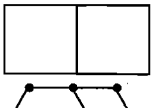
Bicyclo [4.1.0] heptane

(4)


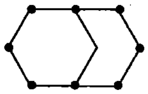
Bicyclo [4.4.0] decane (Decalin)

(5)


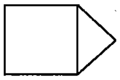
Bicyclo [3.2.2] nonane

(6)


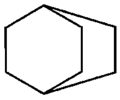
Bicyclo [2.2.0] hexane

(7)


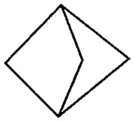
Bicyclo [3.3.1] nonane

(8)


Bicyclo [2.1.0] pentane

(9)


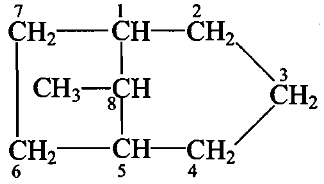
Bicyclo [2.2.2] octane

(10)


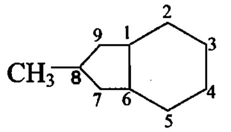
Bicyclo [1.1.1] pentane

If substituents are present, we number the bridged ring system beginning at one bridge head, proceeding first along the longest bridge to the other bridge head, then along the next longest bridge back to the first bridge head. The shortest bridge is named the last.

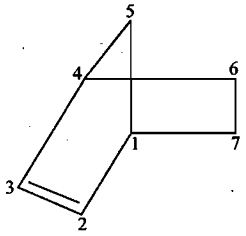
e.g.,

(1)


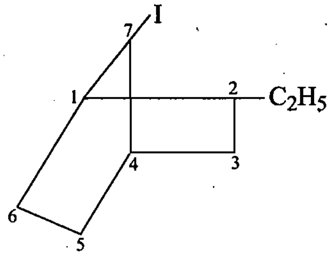
8-Methyl bicyclo [3.2.1] octane

(2)


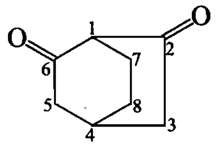
8-Methyl bicyclo [4.3.0] nonane

(3)


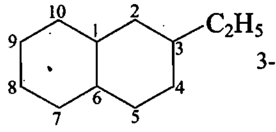
Bicyclo [2.2.1] hept-2-ene

(4)


2-Ethyl-7-iodo bicyclo [2.2.1] heptane

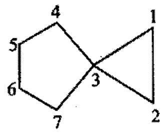
(5)


Bicyclo [2.2.2] octa-2,6-dione

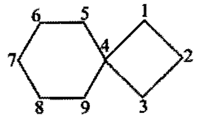
(6)


3-Ethyl bicyclo [4.4.0] decane

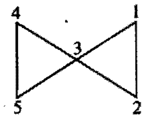
Spiro compounds: If two rings are joined by quaternary carbon at the apex, then they are prefixed by the word **spiro** followed by brackets containing the number of carbon atoms in each ring in ascending order and then by the name of parent hydrocarbon containing total number of carbon atoms in the two rings. The numbering starts from the atom next to the spiro atom and proceeds through the smaller ring first.

(1) 

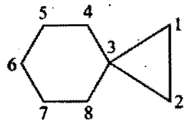
Spiro [2.4] heptane

(2) 

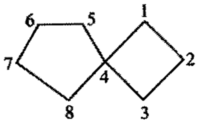
Spiro [3.5] nonane

(3) 

Spiro [2.2] pentane

(4) 

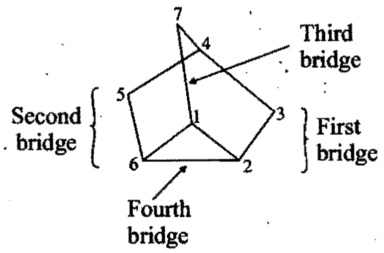
Spiro [2.5] octane

(5) 

Spiro [3.4] octane

Nomenclature of Tricyclic Compounds: The nomenclature of tricyclic compounds is similar to bicyclo compounds. Tricyclic compounds have four bridges. The largest ring and the longest bridge make the bicyclic system whose numbering is done as per rules of the bicyclic systems. The location of the fourth bridge (secondary bridge) is shown by superscripts following the number indicating the number of carbon atoms in the fourth bridge. While the superscripts denote the lowest set of locants of the carbon atoms holding that bridge.

e.g.,

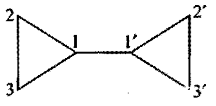


Tricyclo [2,2,1 $O^{2,6}$] heptane

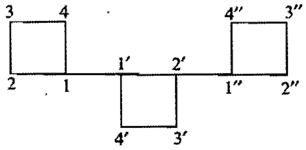
IUPAC Nomenclature of unbranched identical hydrocarbon units joined by a single bond.

These systems are named by placing a suitable numeral prefix as bi, ter, quater, quinque for two, three, four, five respectively before the name of hydrocarbon unit. Starting from either end, the carbon atoms of each repetitive hydrocarbon unit are numbered with unprimed and primed arabic numerals such as 1, 2, 3..., 1′, 2′, 3′......, 1″, 2″, 3″......, etc. The connecting points of hydrocarbon units are indicated by placing the appropriate locants before the name.

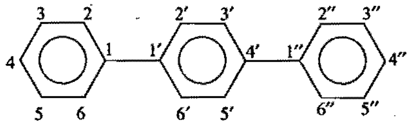
e.g.,

(1) 

1,1′-Bicyclopropane

(2) 

1,1′,2′,1″-Tercyclobutane

(3) 

1,1′,4′,1″-Terphenyl

3.6 WRITING THE STRUCTURAL FORMULA FROM THE GIVEN IUPAC NAME

The IUPAC name of an organic compound consists two, three or all the following parts:

(a) Root word, (b) Primary suffix, (c) Secondary suffix, (d) Prefixes.

(a) Root word indicates the longest carbon chain. Thus, the first step is to locate the longest chain from the root word. Write the number of carbon atoms in a straight chain and number them from one end.

(b) Primary suffix (-ane, -ene or -yne) indicates the nature of the chain. In case multiple bonds are present, place them at proper places in the chain and rest by single bonds.

(c) Secondary suffix indicates the principal functional group. Place it at proper place in the chain. In case the principal functional group is the chain terminating group, put it at carbon-1. (If the functional group does not carry any numerical number, it is assumed that it is located at carbon-1.)

(d) Prefixes are the substituents or secondary functional groups. Place them at the proper places with the help of locants.

(e) Skeleton formula is obtained by considering the above steps. Now add hydrogen atoms to satisfy four valencies of each carbon atom to get the structural formula.

Example 1. Write the structural formula of 2-methyl pentan-1-ol.

Root word = Pent, Primary suffix = an(e)

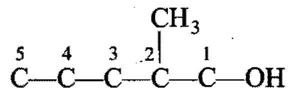
Thus, the chain consists five carbon atoms, all linked by single bonds.

$$\overset{5}{C}-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$

Functional group = -ol = —OH at carbon-1

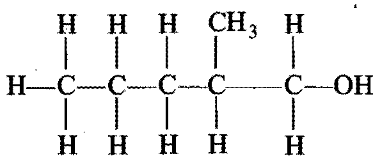
$$\overset{5}{C}-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}-OH$$

Substituent = methyl group at carbon-2

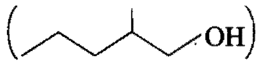


$$\overset{5}{C}-\overset{4}{C}-\overset{3}{C}-\overset{\overset{CH_3}{|}}{\overset{2}{C}}-\overset{1}{C}-OH$$

Satisfying four valencies of carbon atoms, the structural formula obtained is:



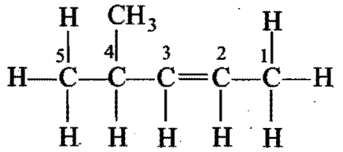
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-OH$$



Example 2. Write the structural formula of the compound

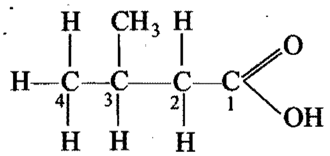
4-methyl pent-2-ene

4-methyl (Substituent with locant)
Pent (Root word)
2-ene (Double bond at carbon-2)

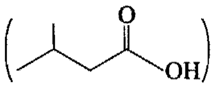


$$H-\underset{H}{\overset{\overset{H}{|}}{\overset{5}{C}}}-\underset{H}{\overset{\overset{CH_3}{|}}{\overset{4}{C}}}-\underset{H}{\overset{3}{C}}=\underset{H}{\overset{2}{C}}-\underset{H}{\overset{\overset{H}{|}}{\overset{1}{C}}}-H$$

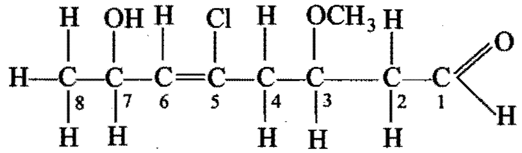
Example 3. Write the structural formula of the compound 3-methylbutanoic acid.



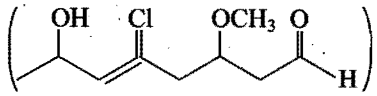
$$H-\underset{\underset{H}{4|}}{\overset{H}{C}}-\underset{\underset{H}{3|}}{\overset{CH_3}{C}}-\underset{\underset{H}{2|}}{\overset{H}{C}}-\underset{1}{\overset{O}{\overset{\|}{C}}}-OH$$



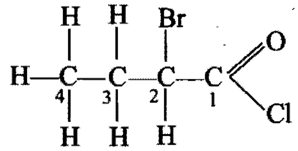
Example 4. Write the structural formula of the compound 5-chloro-7-hydroxy-3-methoxyoct-5-enal.



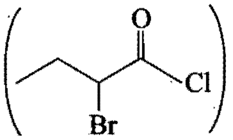
$$H-\underset{\underset{H}{8}}{\overset{H}{C}}-\underset{\underset{H}{7}}{\overset{OH}{C}}-\underset{6}{\overset{H}{C}}=\underset{5}{\overset{Cl}{C}}-\underset{\underset{H}{4}}{\overset{H}{C}}-\underset{\underset{H}{3}}{\overset{OCH_3}{C}}-\underset{\underset{H}{2}}{\overset{H}{C}}-\underset{1}{\overset{O}{\overset{\|}{C}}}-H$$



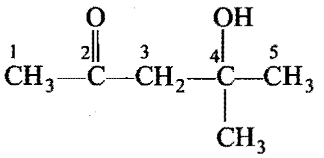
Example 5. Write the structural formula of the compound 2-bromo butanoylchloride.



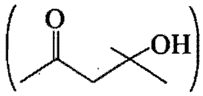
$$H-\underset{\underset{H}{4|}}{\overset{H}{C}}-\underset{\underset{H}{3|}}{\overset{H}{C}}-\underset{\underset{H}{2|}}{\overset{Br}{C}}-\underset{1}{\overset{O}{\overset{\|}{C}}}-Cl$$



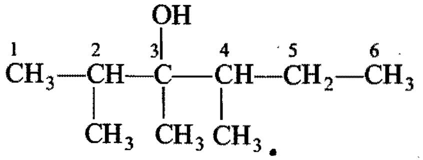
Example 6. Write the structural formula of the compound 4-hydroxy-4-methyl-2-pentanone.



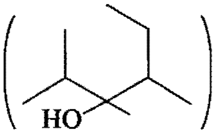
$$\overset{1}{CH_3}-\overset{\overset{O}{\|}}{\overset{2}{C}}-\overset{3}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{\overset{4}{C}}}-\overset{5}{CH_3}$$



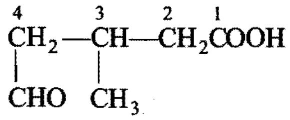
Example 7. Write the structural formula of the compound 2,3,4-trimethylhexan-3-ol.



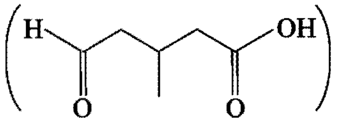
$$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{\overset{3}{C}}}-\underset{\underset{CH_3}{|}}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_3}$$



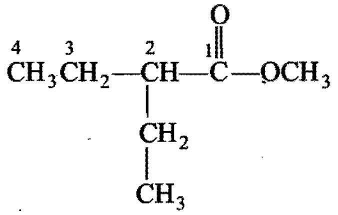
Example 8. Write the structural formula of the compound 4-formyl-3-methylbutanoic acid.



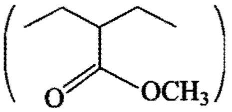
$$\underset{\underset{CHO}{|}}{\overset{4}{CH_2}}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{2}{CH_2}\overset{1}{COOH}$$



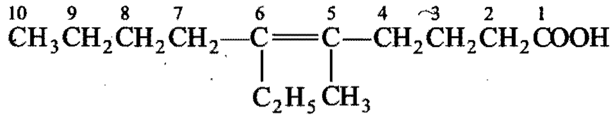
Example 9. Write the structural formula of the compound methyl-2-ethylbutanoate.



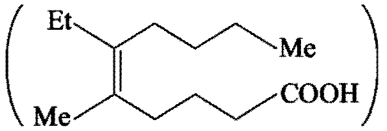
$$\overset{4}{CH_3}\overset{3}{CH_2}-\underset{\underset{\underset{CH_3}{|}}{CH_2}}{\overset{2}{CH}}-\overset{\overset{O}{\|}}{\overset{1}{C}}-OCH_3$$



Example 10. Write the structural formula of the compound 6-ethyl-5-methyl dec-5-enoic acid.

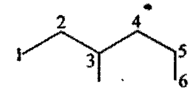


$$\overset{10}{CH_3}\overset{9}{CH_2}\overset{8}{CH_2}\overset{7}{CH_2}-\underset{\underset{C_2H_5}{|}}{\overset{6}{C}}=\underset{\underset{CH_3}{|}}{\overset{5}{C}}-\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{COOH}$$

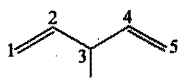


SOME MORE WORKED EXAMPLES

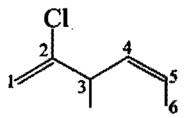
(a) 3-Methylhexane



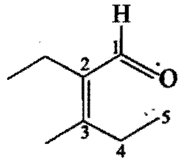
(b) 3-Methyl penta-1,4-diene



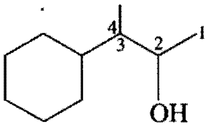
(c) 2-Chloro-3-methyl hexa-1,4-diene



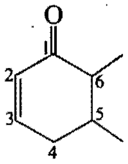
(d) 2-Ethyl-3-methyl pent-2-en-1-al



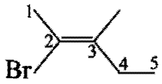
(e) 3-Cyclohexyl butan-2-ol



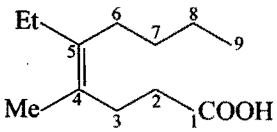
(f) 5,6-Dimethyl cyclohex-2-en-1-one



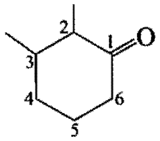
(g) 2-Bromo-3-methyl pent-2-ene



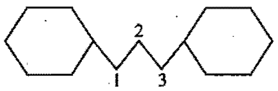
(h) 5-Ethyl-4-methyl non-4-enoic acid



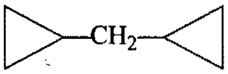
(i) 2,3-Dimethyl cyclohexanone



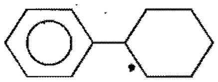
(j) 1,3-Dicyclohexylpropane



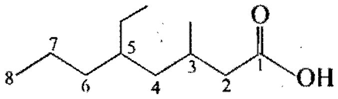
(k) Dicyclopropyl methane



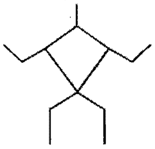
(l) Cyclohexyl benzene



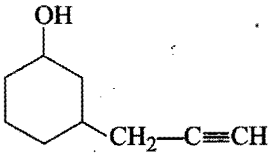
(m) 5-Ethyl-3-methyl octanoic acid



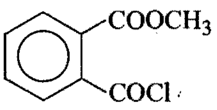
(n) 1,1,2,4-tetraethyl-3-methyl cyclobutane



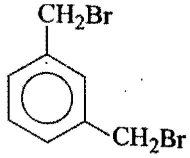
(o) 3-(2-propynyl) cyclohexanol



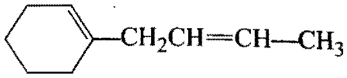
(p) Methyl-2(chlorocarbonyl) benzoate



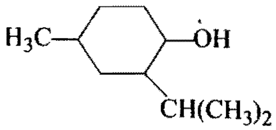
(q) 1,3-*bis* (bromomethyl) benzene



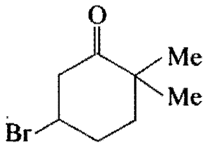
(r) 1-(2-butenyl) cyclohexene



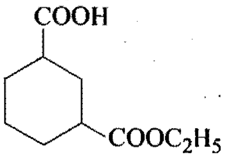
(s) 2-Isopropyl-4-methyl cyclohexanol



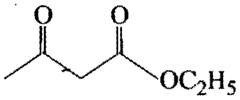
(t) 5-Bromo-2,2-dimethyl cyclohexanone



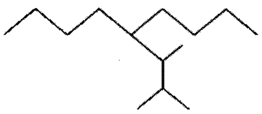
(u) 3-Ethoxy carbonyl cyclohexane carboxylic acid



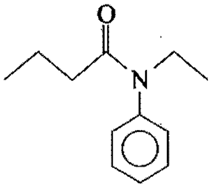
(v) Ethyl-3-oxobutanoate



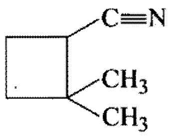
(w) 5-(1,2-dimethyl propyl) nonane



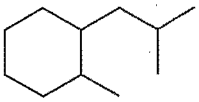
(x) *N*-Ethyl-*N*-phenyl butanamide



(y) 2,2-Dimethyl cyclobutane carbonitrile



(z) 1-Isobutyl-2-methyl cyclohexane



IMPORTANT POINTS TO REMEMBER (SUMMARY)

☐ Organic compounds have been classified on the basis of carbon skeleton (structure) or functional group or the concept of homology.

☐ **Acyclic or open-chain compounds (Aliphatic compounds)** may be straight or branched chains.

☐ **Cyclic or closed-chain compounds (Ring compounds)** contain one or more closed-chains or rings of atoms in their molecules.

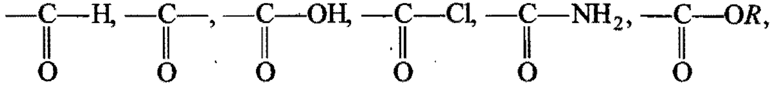
☐ Homocyclic or carbocyclic compounds contain a ring or rings of carbon atom only in the molecule.

☐ **Alicyclic compounds (Cycloalkanes)** are carbocyclic compounds which resemble aliphatic compounds in most of their properties. Examples are cyclopropane, cyclobutane, cyclopentane and cyclohexane, etc.

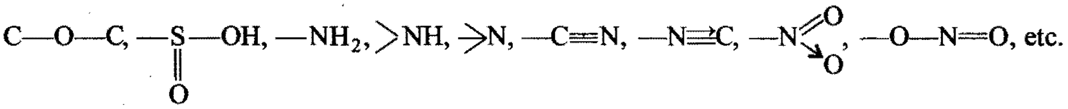
☐ **Aromatic compounds** consist of at least one benzene ring, *i.e.*, a six-membered carbocyclic ring having alternate single and double bonds.

☐ **Heterocyclic compounds** are cyclic compounds containing one or more hetero atoms (O, N, S, etc.) in the ring. Examples are furan, thiophene, pyrrole, pyridine, indole and quinoline, etc.

☐ **Functional group** is an atom or group of atoms present in a molecule which largely determines its chemical properties. For example, $C{=}C$, $C{\equiv}C$, X(Cl, Br, I), —OH, —SH,



$-\underset{\underset{O}{\|}}{C}-H$, $-\underset{\underset{O}{\|}}{C}-$, $-\underset{\underset{O}{\|}}{C}-OH$, $-\underset{\underset{O}{\|}}{C}-Cl$, $-\underset{\underset{O}{\|}}{C}-NH_2$, $-\underset{\underset{O}{\|}}{C}-OR$,



$C-O-C$, $-\underset{\underset{O}{\|}}{S}-OH$, $-NH_2$, $>NH$, $\geqslant N$, $-C{\equiv}N$, $-N{\equiv}C$, $-N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$, $-O-N{=}O$, etc.

☐ **Homologous series** is a group of compounds in which the various members have the similar structural features and similar chemical properties and the two successive members differ in their molecular formula by CH_2 (molecular mass 14).

☐ **Nomenclature of organic compounds:** Their **common names (Trivial system)** are generally based on the source from which they were obtained.

☐ **IUPAC System:** The complete IUPAC name of an organic compound consists of the following parts:

Secondary prefix + Primary prefix + Root word + Primary suffix + Secondary suffix.

The IUPAC names of some simple aliphatic organic compounds are as follows :
Alkane, Alkene, Alkyne, Haloalkane, Alkanol, Alkanal, Alkanone, Alkanoic acid, Alkanoyl chloride, Alkanamide, Alkylalkanoate, Alkanoic anhydride, Alkanamine, Alkane nitrile, Alkane isonitrile, Alkoxy alkane, Nitroalkane and Alkanethiol etc.

IUPAC system has framed a **set of rules** for nomenclature of various types of organic compounds such as :

☐ Nomenclature of complex branched chain alkanes.

☐ Nomenclature of complex unsaturated aliphatic hydrocarbons.

☐ Nomenclature of complex aliphatic compounds containing one functional group, multiple bonds and substituents.

☐ Nomenclature of aliphatic compounds having polyfunctional groups. The order of preference for the choice of principal functional group is:

Sulphonic acids > carboxylic acids > acid anhydrides > esters > acid chlorides > acid amides > cyanides > aldehydes > ketones > alcohols, phenols, thiols > amines > ethers > alkenes, alkynes > halo, nitro, alkyl.

☐ Nomenclature of polyfunctional compounds containing more than two like functional groups.

☐ Nomenclature of organic compounds in bond Line structures.

☐ Nomenclature of alicyclic compounds.

☐ Nomenclature of bicyclo and spiro compounds.

☐ Nomenclature of simple aromatic compounds.

☐ Nomenclature of di and poly functional aromatic compounds.

QUESTIONS

❖ Very Short Answer Type

1. Fill in the blanks:

(i) Cyclohexane is an ...... while benzene is an......

(ii) Organic compounds are broadly classified as ...... chain and ...... chain compounds.

(iii) The organic compounds containing carbon and ...... only are called hydrocarbons. These are ...... and unsaturated.

(iv) Each member of a homologous series differs from its preceding member by a common difference of......

(v) Open chain compounds are also called ......

(vi) The two types of aliphatic unsaturated hydrocarbons are ...... and ......

(vii) A functional group is an atom or ...... in a molecule that gives the molecule its characteristic ......

(viii) All members of homologous series are composed of ...... elements and contain the same ...... group.

(ix) The general formula of the alkenes is ......

(x) Thiophene is a ...... compound.

(xi) The trivial names of organic compounds are called ......

(xii) Wood spirit was named ......

(xiii) Systematic names of organic compounds are obtained from ...... system.

(xiv) Full form of IUPAC system is ......

(xv) ...... system of nomenclature of organic compounds is universally accepted system.

(xvi) The functional group in an alcohol is ...... and its suffix in IUPAC system is ......

(xvii) Paraffins are ...... aliphatic hydrocarbons.

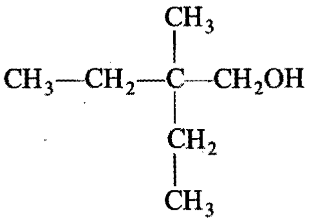
(xviii) The systematic names of the alkanes are based on ...... of carbon atoms in the ...... continuous chain of carbon atoms.

(xix) Maximum number of functional groups must be included in the carbon atoms chain selected, even if it does not satisfy the ......

(xx) In the case of compounds containing more than one functional group, the most important functional group is considered as ...... and the rest are considered as ......

(xxi) In case a carbon compound consists two functional groups one of which is —COOH group, the numbering of the chain should start from carbon atom linked to ......

(xxii) The name of compound with the structural formula,



$$CH_3—CH_2—\underset{\underset{CH_3}{|}{CH_2}}{\overset{CH_3}{\overset{|}{C}}}—CH_2OH$$ is .....

(xxiii) IUPAC name of succinic acid is ......

(xxiv) IUPAC name of $CH_3CHClCH_2CHO$ is ......

(xxv) The common name of $CH_2{=}CHCN$ is ......

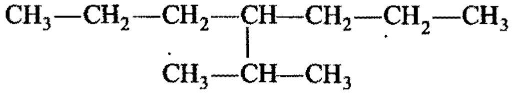
(xxvi) 1-Hydroxy-2-propanone has the structural formula ......

(xxvii) The structural formula of 3-Ethyl-2-methyl hexane is ......

(xxviii) The IUPAC name of the compound $HC{\equiv}C—CH_2—CH_2—CH_3$ is ......

(xxix) The IUPAC name of tertiary butyl bromide is .....

(xxx) The IUPAC name of the organic compound having structure,



$$CH_3—CH_2—CH_2—\underset{CH_3—CH—CH_3}{\underset{|}{CH}}—CH_2—CH_2—CH_3$$

is ......

State, whether the following statements are **True** or **False** :

(i) Homologous series can be represented by a general formula.

(ii) Chemical properties of an organic compound depend on the functional group.

(iii) In homologous series, all members have the same physical properties.

(iv) C_nH_{2n} is the general formula of alkanes.

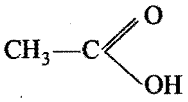
(v) Groups obtained by the removal of one hydrogen atom from the alkanes are called as alkyl radicals.

(vi) IUPAC means International Union of Physics and Chemistry.

(vii) Propane consists two primary carbon atoms and one secondary carbon atom.

(viii) Alkynes consist of one double bond in their molecules.

(ix) Acetic acid is the systematic name of vinegar.

(x)  is an unsaturated compound.

(xi) Prefixes like *n*-, iso-, *sec*-, *tert*-, neo-, etc., are used in IUPAC system.

(xii) The systematic names of the acids are formed by dropping the -e of the name of parent alkane and adding suffix -oic acid.

(xiii) Primary suffixes are added to the root word to show saturation or unsaturation in a carbon chain.

(xiv) Neohydrocarbons contain a tertiary carbon atom.

(xv) The common name of 2-propanol is isopropyl alcohol.

(xvi) The IUPAC name of CH_3COOCH_3 is methyl acetate.

(xvii) The IUPAC name of HCHO is methanal.

(xviii) The IUPAC name of CH_3CN is methyl cyanide.

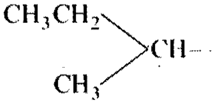
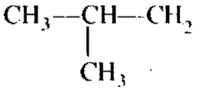
(xix) Methane was named as firedamp as it formed explosive mixture with air.

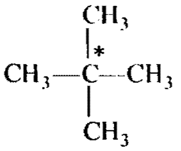
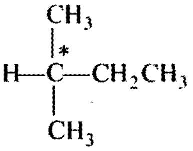
(xx) The IUPAC name of dimethyl ketone is propanone.

3. Match the following:

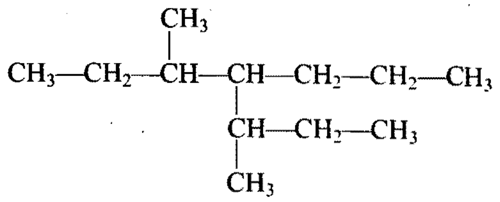
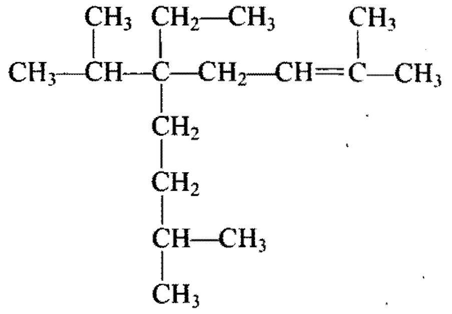
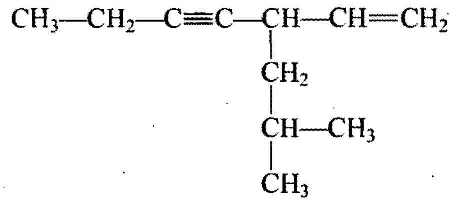
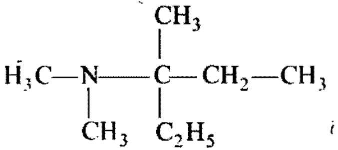
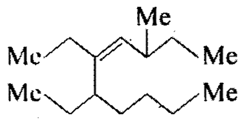
[A]	(a) Benzene	(1) Alicyclic
	(b) Pyridine	(2) Aliphatic
	(c) Cycloalkane	(3) C_2H_5CHO
	(d) Anthracene	(4) Aromatic (Monocyclic)
	(e) Glycerol	(5) Aromatic (Tricyclic)
	(f) Next homologue of CH_3CHO	(6) Heterocyclic
[B]	(a) Acetic acid	(1) 2-Butyne
	(b) Wood spirit	(2) Trichloromethane
	(c) Acetone	(3) Ethanoic acid
	(d) Dimethyl acetylene	(4) Dichlorodifluoro methane
	(e) Chloroform	(5) Methanol
	(f) Freon	(6) Propanone
[C]	(a) C_nH_{2n+2}	(1) Alkynes
	(b) C_nH_{2n}	(2) Nitriles
	(c) C_nH_{2n-2}	(3) Carboxylic group
	(d) $C_nH_{2n+1}CN$	(4) Alkenes
	(e) Principal functional group	(5) Cyclohexane
	(f) C_6H_{12}	(6) Paraffins or alkanes

4. Select the principal functional group when the following groups are present in the molecule:
   (a) OH, COOH, $-NO_2$
   (b) NO_2, NH_2, $-CONH_2$
   (c) Br, CH_3, $-CHO$
   (d) Cl, CH_3, $-OH$.

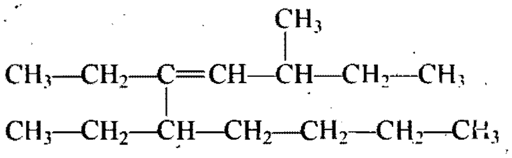
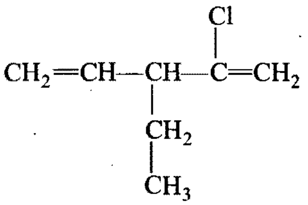
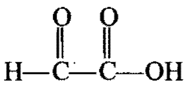
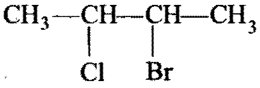
5. Name the following alkyl groups:
   (a) CH_3CH_2-
   (b) $(CH_3)_3C$
   (c) $(CH_3)_2CH$
   (d) $CH_3CH_2CH_2$
   (e) 
   (f) 
   $CH_3{-}\underset{\substack{|\\ CH_3}}{CH}{-}CH_2$

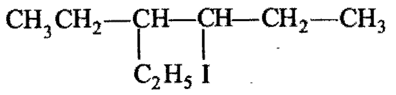
6. What is the nature of carbon atom marked with asterisk(*) sign in the following compounds?
   (a) 
   $CH_3{-}\overset{\substack{CH_3\\ |*}}{\underset{\substack{|\\ CH_3}}{C}}{-}CH_3$
   (b) 
   $H{-}\overset{\substack{CH_3\\ |*}}{\underset{\substack{|\\ CH_3}}{C}}{-}CH_2CH_3$
   (c) $CH_3{-}CH_2{-}\overset{*}{C}H_2{-}CH_3$
   (d) $CH_3{-}CH_2{-}CH_2{-}\overset{*}{C}H_3$

7. Answer the following:
   (i) What would be the molecular formula for a straight chain hydrocarbon having 8 carbon atoms with (a) all C—C single bonds, (b) One C—C double bond, (c) One C—C triple bond?
   (ii) What is the structural unit that is added to one normal alkane in order to form the next member in the homologous series?
   (iii) What is the minimum number of carbon atoms in, (a) a branched alkane, (b) cyclo-alkane?
   (iv) Name the isoradical that does not have a corresponding isoalkane.
   (v) What system of nomenclature of organic compounds are universally accepted?

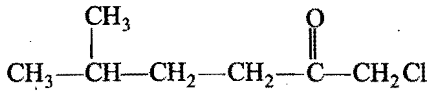
8. Give the IUPAC names of the following compounds:
   (i) 
   (ii) 
   (iii) 
   (iv) $CH_2{=}CH{-}CH(CH_3)_2$
   (v) 
   $H_3C{-}\underset{\substack{|\\ CH_3}}{N}{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ C_2H_5}}{C}}{-}CH_2{-}CH_3$
   (vi) 
   [PMT (Kerala) 2006]

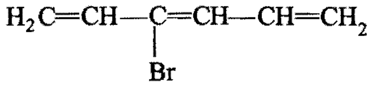
   or

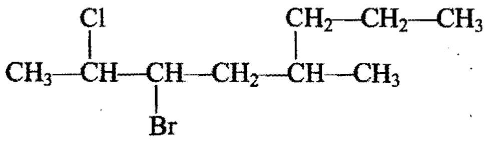
   
   (vii) 
   $CH_2{=}CH{-}\underset{\substack{|\\ CH_2\\ |\\ CH_3}}{CH}{-}\overset{\substack{Cl\\ |}}{C}{=}CH_2$
   (viii) $(CH_3)_3COH$
   (ix) $CH_3HC{=}CHCH_2NH_2$
   (x) 
   $H{-}\overset{\substack{O\\ \|}}{C}{-}\overset{\substack{O\\ \|}}{C}{-}OH$
   (xi) 
   $CH_3{-}\underset{\substack{|\\ Cl}}{CH}{-}\underset{\substack{|\\ Br}}{CH}{-}CH_3$

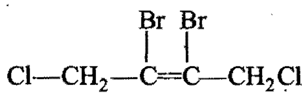
(xii) 
$CH_3CH_2-\underset{C_2H_5}{CH}-\underset{I}{CH}-CH_2-CH_3$

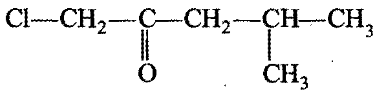
9. Write the IUPAC names of the following compounds:

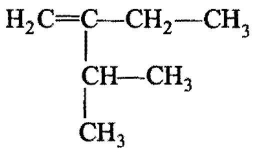
(a) 
$CH_3-\overset{CH_3}{CH}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2Cl$

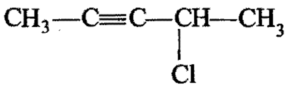
(b) 
$H_2C=CH-\underset{Br}{C}=CH-CH=CH_2$

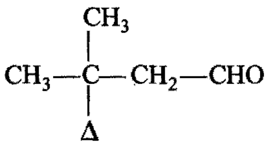
(c) 
$CH_3-\overset{Cl}{CH}-\underset{Br}{CH}-CH_2-\overset{CH_2-CH_2-CH_3}{CH}-CH_3$

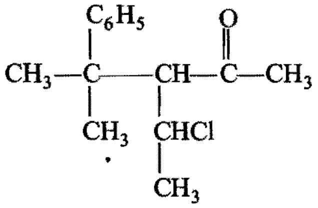
(d) 
$Cl-CH_2-\overset{Br}{C}=\overset{Br}{C}-CH_2Cl$

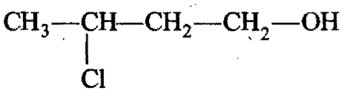
(e) 
$Cl-CH_2-\underset{O}{\underset{\|}{C}}-CH_2-\underset{CH_3}{CH}-CH_3$

(f) 
$H_2C=\underset{\underset{CH_3}{CH-CH_3}}{C}-CH_2-CH_3$

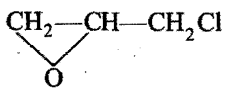
(g) 
$CH_3-C\equiv C-\underset{Cl}{CH}-CH_3$

(h) 
$CH_3-\overset{CH_3}{\underset{\Delta}{C}}-CH_2-CHO$

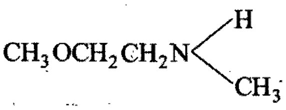
(i) 
$CH_3-\overset{C_6H_5}{\underset{CH_3}{C}}-\underset{\underset{CH_3}{CHCl}}{CH}-\overset{O}{\overset{\|}{C}}-CH_3$

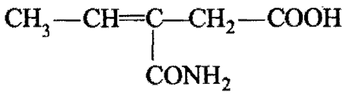
(j) 
$CH_3-\underset{Cl}{CH}-CH_2-CH_2-OH$

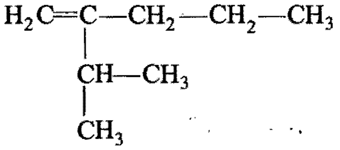
(k) $CH_3CH_2CH=CHCOOH$

(l) 

(m) $CH_2(COOH)_2$

(n) 

(o) 
$CH_3-CH=\underset{CONH_2}{C}-CH_2-COOH$

(p) 
$H_2C=\underset{\underset{CH_3}{CH-CH_3}}{C}-CH_2-CH_2-CH_3$

10. Write the structures of the following compounds whose IUPAC names are given as under:
(a) But-2-ene (b) 1,2,3-propantriol
(c) Ethanoyl chloride (d) 2,3-pentadione
(e) Octa-3,5-diene
(f) 4-hydroxy-3-pentenoic acid
(g) 2,3-dimethylbutan-2-ol (h) 2,2-dimethylpentanal
(i) 2,7-dimethylocta-2,4,6-triene

11. Give the IUPAC names of the following compounds:
(a) Glycerol (b) Acetone
(c) Formic acid (d) Oxalic acid
(e) Isopropyl alcohol (f) Acetaldehyde
(g) Acetylene (h) Ethyl alcohol
(i) Acetic acid (j) Ethylene
(k) Vinyl cyanide

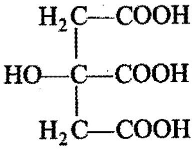
12. Give the common names of the following compounds which have been named according to the IUPAC system of nomenclature:
(a) Ethanoyl chloride (b) Methanol
(c) Ethanol (d) Ethanoic acid
(e) Propane-1,2,3-tricarboxylic acid (f) 1,2,3-Propanetriol
(g) Butanal (h) Methyl ethanoate
(i) Ethyl carbylamine

13. Explain why the given names in the following are wrong. Give a correct name in each case:
(a) 1-methylpentane
(b) 2-ethylbutane
(c) 2,3-dichloropropane
(d) 1,1,3-trimethyl propane
(e) 3-bromo-2-methylpropane
(f) 1-chloro-1-methylpropan-2-ol
(g) 3-propyl-4-methylbutan-1-oic acid
(h) 4,4-dimethylbut-2-en-1-ol
(i) 1,1,2,2-tetramethylethane
(j) 1,4-dihydroxybut-2-yne
(k) 2-keto-pentan-5-oic acid
(l) 1-aminobutan-3-one.

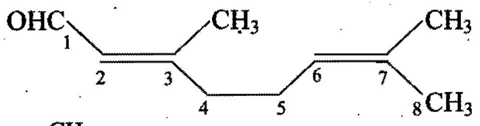
14. Are the following names correct according to IUPAC system of nomenclature ? If not, give the correct names:
(a) Pent-3-yne (b) *Tert.* butanol
(c) Hexa-1,6-diene (d) 4,4,3-Trimethylhex-1-yne
(e) 2-Keto-*n*-propanol (f) 1-Methoxyethan-2-ol
(g) 3-Methylhexa-1,5-diyne (h) 4,4,5-Trimethylhex-1-yne

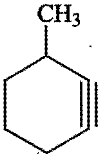
15. Give the correct IUPAC names of the following:
(a) 2-Vinyl propane (b) Isoprene
(c) Succinic acid (d) Tartaric acid
(e) Chloropicrin (f) Neopentane
(g) Methyl cyanide (h) Dimethyl ether
(i) Acetamide (j) Ethyl chloride

16. Assign the IUPAC names for the following compounds:

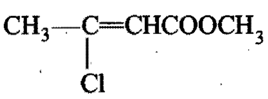
(a) 

$$\begin{array}{c} H_2C{-}COOH \\ | \\ HO{-}C{-}COOH \\ | \\ H_2C{-}COOH \end{array}$$

(b) 

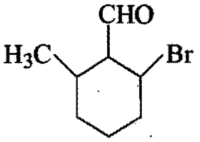
(c) 

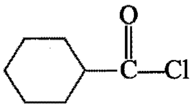
[CBSE (Med.) 2005]

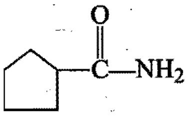
(d) 

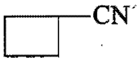
$CH_3{-}\underset{\underset{Cl}{|}}{C}{=}CHCOOCH_3$

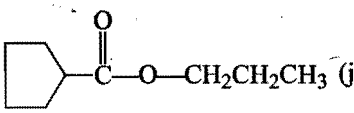
[CBSE (Med.) 2005]

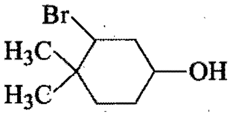
(e) 

(f) 

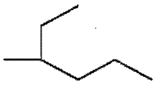
(g) 

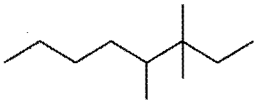
(h) 

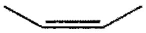
(i) 

(j) 

17. Write the IUPAC names of the following compounds:

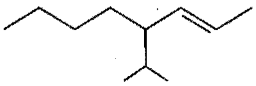
(a) 

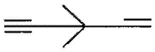
(b) 

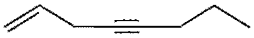
(c) 

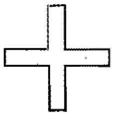
(d) 

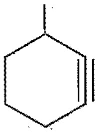
(e) 

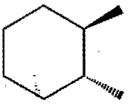
(f) 

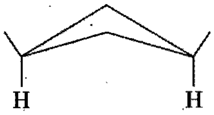
(g) 

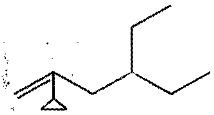
(h) 

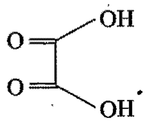
(i) 

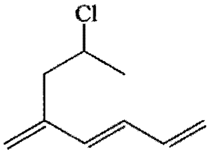
(j) 

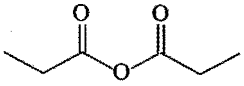
(k) 

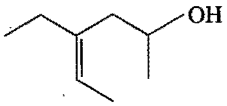
(l) 

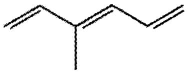
(m) 

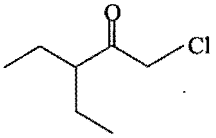
(n) 

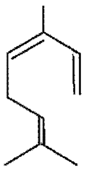
(o) 

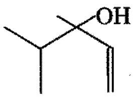
(p) 

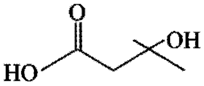
(q) 

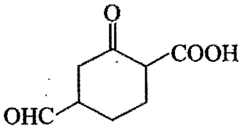
(r) 

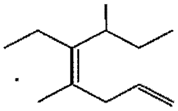
(s) 

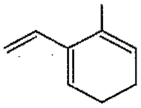
(t) 

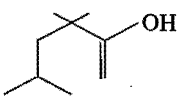
(u) 

(v) 

(w) 

(x) 

(y) 

(z) 

18. Draw the bond line structures of the following compounds whose IUPAC names are given as under:

(a) 4-Methylpent-1-ene;
(b) Hex-1-yne;
(c) 2,3-Dimethyl but-2-ene;
(d) 3-Isobutylhept-1-ene;
(e) 3-Ethyl-5-methylhex-1-ene;
(f) Penta-1,4-diyne;
(g) Pent-1-en-4-yne;
(h) *Trans*-1,3-dichlorocyclopentane;
(i) 3,4-Dipropylhepta-1,3,5-triene;
(j) 4,4-Dimethylpentanal;
(k) Ethyl-2-cyanopropanoate;
(l) *N*-Methylpropan-1-amine;
(m) *N*-Ethyl-*N*-methyl-2-aminopropane;
(n) Pentanalimine;
(o) *N*-*N*-Dimethylbutanamide;
(p) 4-Phenylbutanal;
(q) 3-Ethenylpenta-1,3-diene;
(r) 4-Hydroxy-4-methyl-2-pentanone;
(s) 2,6-Dimethylhepta-2,5-dienoic acid;
(t) 1-Cyclopropyl-3-methylpent-1-ene;
(u) 2,2,6,6-Tetramethyloctane;
(v) 3-Cyclobutylbut-1-ene;
(w) 5,6-Dimethylcyclohex-2-en-1-one;
(x) 3-Ethyl-4-methylhex-4-en-2-one;
(y) 3-Phenylprop-2-en-1-oic acid;
(z) 1,1,1-Trichloro-2,2-diphenylethane.

❖ Short Answer Type

19. Draw polygon formulae for $C_5H_{10}O$.

20. Define the following terms:
   (a) Paraffins
   (b) Alkyl group
   (c) Carbocyclic compounds
   (d) Heterocyclic compounds
   (e) Unsaturated compounds
   (f) Saturated compounds

21. Write the structural formulae of (a) a dibasic acid, (b) a polyhydric alcohol and (c) an acid chloride. Name them according to IUPAC system.

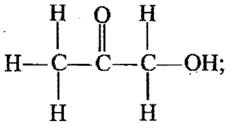
22. Explain the lowest sum rule in IUPAC system with an example.

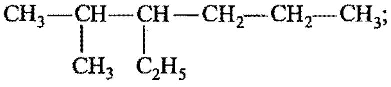
23. What is the meaning of primary, secondary and tertiary carbon atom?

24. Mention four characteristics of homologous series.

ANSWERS

1. (i) alicyclic, aromatic; (ii) open, closed; (iii) hydrogen, saturated; (iv) CH_2; (v) acyclic or aliphatic compounds; (vi) alkenes or olefins, alkynes or acetylenes; (vii) group of atoms, chemical properties; (viii) same, functional; (ix) C_nH_{2n}; (x) heterocyclic; (xi) common names; (xii) methyl alcohol or methanol; (xiii) IUPAC; (xiv) International union of pure and applied chemistry; (xv) IUPAC; (xvi) —OH, -ol; (xvii) saturated; (xviii) number, longest; (xix) longest chain rule; (xx) principal functional group, substituents; (xxi) —COOH group; (xxii) 2-ethyl-2-methyl-1-butanol; (xxiii) 1,4-butanedioic acid; (xxiv) 3-chloro-butanal; (xxv) vinyl cyanide;

(xxvi) 
$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH$;

(xxvii) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-CH_2-CH_3$;

(xxviii) pent-1-yne; (xxix) 2-bromo-2-methyl propane; (xxx) 4(1′-methyl ethyl)-heptane.

2. (i) True; (ii) True; (iii) False—In homologous series, there is a gradual change in the physical properties from member to member; (iv) False—C_nH_{2n} is the general formula of alkenes; (v) True; (vi) False—International union of pure and applied chemistry; (vii) True; (viii) False—Alkynes consist of one triple bond in their molecules; (ix) False—Acetic acid is the common name of vinegar; (x) False—Is a saturated compound; (xi) False—used in trivial system; (xii) True; (xiii) True; (xiv) False—having one quaternary carbon atom; (xv) True; (xvi) False— methyl ethanoate; (xvii) True; (xviii) False—ethane nitrile; (xix) True; (xx) True.

3. [A] (a—4); (b —6); (c—1); (d—5); (e—2); (f—3)
[B] (a—3); (b —5); (c—6); (d—1); (e—2); (f— 4)
[C] (a—6); (b — 4); (c—1); (d—2); (e—3); (f—5)

4. (a) Carboxylic, —COOH; (b) Amide, —$CONH_2$; (c) Aldehyde, —CHO; (d) Alcoholic, —OH.

5. (a) Ethyl; (b) *Tert.* butyl; (c) Isopropyl; (d) *n*-Propyl; (e) *Sec.* butyl; (f) Isobutyl.

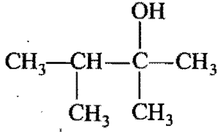
6. (a) Quaternary; (b) Tertiary; (c) Secondary; (d) Primary.

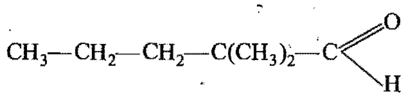
7. (i) (a) C_8H_{18}; (b) C_8H_{16}; (c) C_8H_{14}; (ii) CH_2; (iii) (a) 4; (b) 3; (iv) Isopropyl $(CH_3)_2CH$—; (v) IUPAC.

8. (i) 3,5-Dimethyl-4-propylheptane; (ii) 5-Ethyl-2,8-dimethyl-5-(1′-methylethyl) non-2-ene; (iii) 3-(2′-Methyl propyl) hept-1-en-4-yne; (iv) 3-Methylbut-1-ene; (v) 3-(*N*, *N*-Dimethylamino)-3-methyl pentane; (vi) 5,6-Diethyl-3-methyldec-4-ene; (vii) 2-Chloro-3-ethylpenta-1-4-diene; (viii) 2-Methylpropan-2-ol; (ix) But-2-en-1-amine; (x) 2-Oxoethanoic acid. (xi) 2-Bromo-3-chlorobutane; (xii) 3-Ethyl-4-iodohexane.

9. (a) 1-Chloro-5-methylhexan-2-one; (b) 3-Bromohexa-1,3,5-triene; (c) 3-Bromo-2-chloro-5-methyloctane; (d) 2,3-Dibromo-1,4-dichlorobut-2-ene; (e) 1-Chloro-4-methylpentan-2-one; (f) 2-Ethyl-3-methylbut-1-ene; (g) 4-Chloropent-2-yne; (h) 3-Cyclopropyl-3-methylbutanal; (i) 3-(1′-Chloroethyl)-4-methyl-4-phenylpentan-2-one; (j) 3-Chlorobutan-1-ol; (k) Pent-2-enoic acid; (l) 3-Chloro-1,2-epoxypropane; (m) Propan-1,3-dioic acid; (n) 2-Methoxy-1-*N*-methylethanamine; (o) 3-carbamoyl pent-3-enoicacid; (p) 2-(1′-methyl ethyl)pent-1-ene.

10. (a) $CH_3-CH=CH-CH_3$
(b) $CH_2OH\cdot CHOH\cdot CH_2OH$
(c) CH_3COCl
(d) $CH_3COCOCH_2CH_3$
(e) $CH_3CH_2CH=CH-CH=CH-CH_2-CH_3$
(f) $HOOC-CH_2-CH=C(OH)CH_3$

(g) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

(h) 

(i) $(CH_3)_2-C=CH-CH=CH-CH=C(CH_3)_2$

11. (a) Propane-1,2,3-triol; (b) Propanone; (c) Methanoic acid; (d) Ethanedioic acid; (e) Propan-2-ol; (f) Ethanal; (g) Ethyne; (h) Ethanol; (i) Ethanoic acid; (j) Ethene; (k) Prop-2-en-1-nitrile.

12. (a) Acetyl chloride; (b) Methyl alcohol; (c) Ethyl alcohol; (d) Acetic acid; (e) Tricarballylic acid; (f) Glycerol; (g) Butyraldehyde; (h) Methyl acetate; (i) Ethyl isocyanide.

13. (a) The longest chain is of six carbon atoms. The correct name is hexane.
(b) The longest chain consists of five carbon atoms. The correct name is 3-methylpentane.
(c) The numbering has been done wrongly. The correct name is 1,2-dichloro propane.
(d) The longest chain consists of five carbon atoms. The correct name is 2-methyl pentane.
(e) The numbering has been done wrongly. The correct name is 1-bromo-2-methylpropane.
(f) The longest chain has not been selected properly. The correct name is 3-chloro butan-2-ol.
(g) The longest chain consists of 6 carbon atoms. The correct name is 3-ethylhexanoic acid.
(h) The longest chain consists of five carbon atoms. The correct name is 4-methyl pent-2-en-1-ol.
(i) The longest chain consists of four carbon atoms. The correct name is 2,3-dimethyl butane.
(j) —OH is a primary functional group and not substituent. The correct name is but-2-yne-1,4-diol.
(k) Carboxylic group is a principal functional group and numbering should be done from this end. The correct name of the compound is 4-ketopentanoic acid.

(l) Keto is a principal functional group and lowest number should be given to it. The correct name of the compound is 4-aminobutan-2-one.

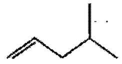
14. (a) No, it should be pent-2-yne; (b) No, *Tert.* word is not used in IUPAC system. It is 2-methylpropan-2-ol; (c) No, it should be hexa-1,5-diene; (d) No, it should be 3,4,4-trimethylhex-1-yne; (e) No, Keto is not used. It is the principal functional group. It is 1-hydroxy propan-2-one; (f) No, it should be 2-methoxy ethan-1-ol; (g) Yes; (h) Yes.

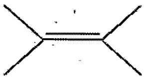
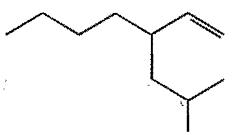
15.

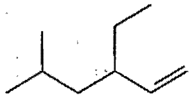
(a) 3-Methylbut-1-ene	(b) 2-Methylbuta-1,3-diene
(c) Butane-1,4-dioic acid	(d) 2,3-Dihydroxybutane-1,4-dioic acid
(e) Trichloro nitro methane	(f) 2,2-Dimethyl propane
(g) Ethane nitrile	(h) Methoxy methane
(i) Ethanamide	(j) Chloroethane

16. (a) 2-Hydroxy-1,2,3-propane tricarboxylic acid;
(b) 3,7-Dimethylocta-2,6-dienal;
(c) 3-Methyl cyclohexyne;
(d) Methyl-3-chlorobut-2-enoate.
(e) 2-Bromo-6-methyl cyclohexane carbaldehyde.
(f) Cyclohexane carbonylchloride.
(g) Cyclopentane carboxamide.
(h) Cyclobutane carbonitrile.
(i) Propyl cyclopentyl methanoate.
(j) 3-Bromo-4,4-dimethyl cyclohexanol.

17. (a) 3-Methyl hexane; (b) 3,3,4-Trimethyl octane;
(c) *Cis*-2-butene; (d) *Trans*-2-butene;
(e) Hexa-2,4-diyne; (f) 4-Isopropyl-oct-2-ene;
(g) 3,3-Dimethyl pent-1-en-4-yne; (h) Octa-1-en-4-yne;
(i) Cyclo dodecane; (j) 3-Methyl-1-cyclohexyne;
(k) *Trans*-1,2-dimethyl cyclohexane;
(l) *Cis*-1,3-dimethyl cyclobutane;
(m) 4-Ethyl-2-cyclopropyl-hex-1-ene;
(n) 1,2-Ethanedioic acid;
(o) 2-(2′-Chloropropyl)hexa-1,3,5-triene;
(p) Propanoic anhydride;
(q) 4-Ethyl hex-4-en-2-ol;
(r) 3-Methyl hexa-1,3,5-triene;
(s) 1-Chloro-3-ethyl-2-pentanone;
(t) 3,7-Dimethyl octa-1,3,6-triene;
(u) 3,4-Dimethyl pent-1-en-3-ol;
(v) 3-Hydroxy-3-methyl butanoic acid;
(w) 2-Carboxy-5-formyl cyclohexanone;
(x) 5-Ethyl-4,6-dimethyl octa-1,4-diene;
(y) 2-Ethenyl-3-methyl cyclohexa-1,3-diene;
(z) 3,3,5-Trimethyl hex-1-en-2-ol.

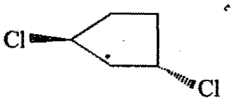
18. (a)  ; (b)  ;

(c)  ; (d)  ;

(e)  ; (f) 

;

(g) 

; (h) 

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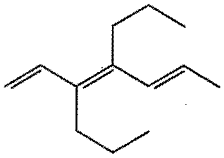
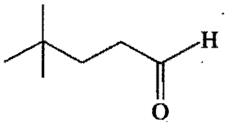
(i)  ; (j) 

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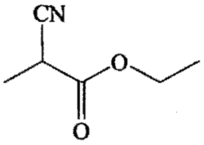
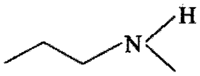
(k) 

; (l) 

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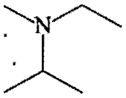
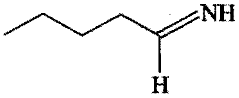
(m) 

; (n) 

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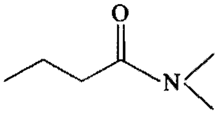
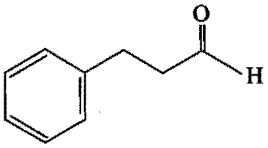
(o) 

; (p) 

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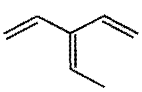
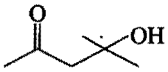
(q)  ; (r) 

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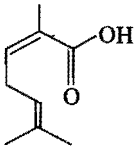
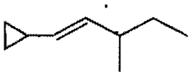
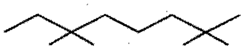
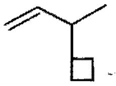
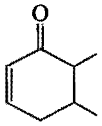
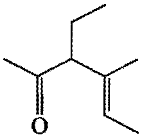
(s) 

; (t)  ;

(u)  ; (v)  ;

(w) 

; (x) 

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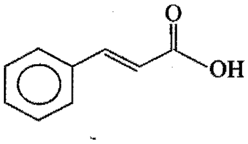
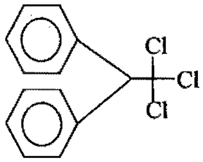
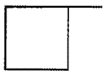
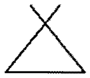
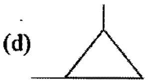
(y) 

; (z) 

19. (a)  (b)  (c) 

(d)  (e) 

OBJECTIVE QUESTIONS

SET I : This set contains questions with single correct answer.

1. Alicyclic compounds are:
(a) aromatic compounds ☐
(b) aliphatic cyclic compounds ☐
(c) heterocyclic compounds ☐
(d) none of the above ☐

2. Which one of the following is the heterocyclic compound?
(a) Pyrene ☐ (b) Thiophene ☐
(c) Phenol ☐ (d) Aniline ☐

3. A group closely related compounds which can be expressed by a general formula and in which two consecutive members differ by 14 in their molecular masses is called:
(a) a homologous series ☐
(b) a homogeneous series ☐
(c) a heterogeneous series ☐
(d) an electrochemical series ☐

4. Which one is not correct for a homologous series?
(a) All members have a general formula ☐
(b) All members have same chemical properties ☐
(c) All members have same physical properties ☐
(d) All members have same functional group ☐

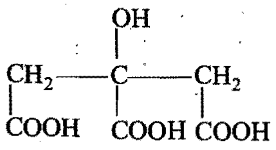
5. The correct decreasing order of preference of functional groups during the IUPAC nomenclature of polyfunctional compounds is: **[AIEEE 2008]**
(a) $-COOH, -SO_3H, -CONH_2, -CHO$ ☐
(b) $-SO_3H, -COOH, -CONH_2, -CHO$ ☐
(c) $-CHO, -COOH, -SO_3H, -CONH_2$ ☐
(d) $-CONH_2, -CHO, -SO_3H, -COOH$ ☐

6. The IUPAC name of $(CH_3)_2CHCH_3$ is: **[BHU(S) 2008]**
(a) isopropyl methane ☐ (b) 2-methyl propane ☐
(c) trimethyl methane ☐ (d) dimethyl ethane ☐

7. The IUPAC name of $CH_3OC_2H_5$ is:
(a) ethoxy methane ☐ (b) methoxy ethane ☐
(c) ethyl methyl ether ☐ (d) methyl ethyl ether ☐

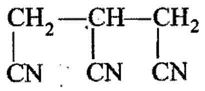
8. The IUPAC name of $CH_3CH(OH)CH_2CH_2COOH$ is:
(a) 4-hydroxy pentanoic acid ☐
(b) 1-carboxybutan-3-ol ☐
(c) 1-carboxybutan-4-ol ☐
(d) 4-carboxybutan-2-ol ☐

9. The name(s) of the following compound is:


$$\underset{COOH}{CH_2}-\underset{COOH}{\overset{OH}{C}}-\underset{COOH}{CH_2}$$

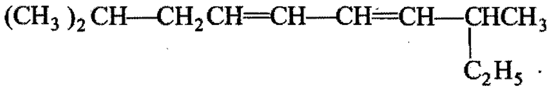
(a) 2-hydroxypropane-1,2,3-tricarboxylic acid ☐
(b) 3-carboxy-3-hydroxy-1,5-pentanedioic acid ☐
(c) citric acid ☐
(d) all of the above ☐

10. The IUPAC name of the following compound is:


$$\underset{CN}{CH_2}-\underset{CN}{CH}-\underset{CN}{CH_2}$$

(a) 1,2,3-tricyano propane ☐
(b) propane tricarbylamine ☐
(c) 1,2,3-propane tricarbonitrile ☐
(d) 3-cyanopropane-1,5-dinitrile ☐

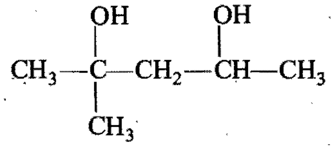
11. The IUPAC name of the following compound is:


$$(CH_3)_2CH-CH_2CH=CH-CH=CH-\underset{C_2H_5}{CHCH_3}$$

[PET (Kerala) 2010]
(a) 1,1,7,7-tetramethyl-2,5-octadiene ☐
(b) 2,8-dimethyl-3,6-decadiene ☐
(c) 1,5-di-isopropyl-1,4-hexadiene ☐
(d) 3,9-dimethyl-4,6-decadiene ☐
(e) 2,8-dimethyl-4,6-decadiene ☐

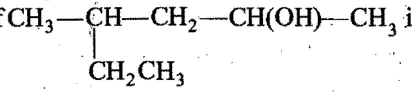
12. The structure of 4-methylpent-2-en-1-ol is:
(a) $(CH_3)_2C=CHCH_2CH_2OH$ ☐
(b) $(CH_3)_2CHCH=CHCH_2OH$ ☐
(c) $CH_3CH_2CH=CHCH_2OH$ ☐
(d) $CH_3CHOHCH=C(CH_3)_2$ ☐

13. The IUPAC name for the following compound is:


$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{OH}{CH}-CH_3$$

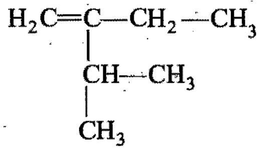
(a) 1,1-dimethyl-1,3-butandiol ☐
(b) 2-methyl-2,4-pentandiol ☐
(c) 4-methyl-2,4-pentandiol ☐
(d) 1,3,3-trimethyl-1,3-propandiol ☐

14. The IUPAC name of $CH_3-\underset{CH_2CH_3}{CH}-CH_2-CH(OH)-CH_3$ is:



(a) 2-ethylpentan-4-ol ☐
(b) 4-ethylpentan-2-ol ☐
(c) 4-methylhexan-2-ol ☐
(d) 4-methylpentan-2-ol ☐

15. The IUPAC name of the following compound is:


$$H_2C=\underset{\underset{CH_3}{CH-CH_3}}{C}-CH_2-CH_3$$

(a) 2-ethyl-3-methylbut-1-ene ☐
(b) 2-isopropylbut-1-ene ☐
(c) 2-methyl-3-ethylbut-3-ene ☐
(d) ethyl isopropyl ethene ☐

16. The IUPAC name of Cl_3CCH_2CHO is:
(a) chloral ☐
(b) 3,3,3-trichloropropanal ☐
(c) 1,1,1-trichloropropanal ☐
(d) 2,2,2-trichloropropanal ☐

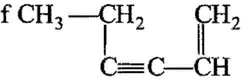
17. The IUPAC name of the compound having the formula $CH_2{=}CHCH_2Cl$ is:
(a) allyl chloride ☐ (b) 1-chloroprop-3-ene ☐
(c) 3-chloropropylene ☐ (d) 3-chloroprop-1-ene ☐

18. The IUPAC name of the following compound is:
$CH_3-CH=CH-C\equiv CH$ **[AIPMT 2010]**
(a) Pent-4-yn-2-ene ☐ (b) Pent-2-en-4-yne ☐
(c) Pent-3-en-1-yne ☐ (d) Pent-1-yn-3-ene ☐

19. The formula of propanenitrile is:
(a) CH_3CN ☐ (b) C_2H_5CN ☐
(c) C_3H_7CN ☐ (d) C_2H_5NC ☐

20. The compound $CH_3COOC_2H_5$ belongs to the class:
(a) alkanals ☐ (b) alkanones ☐
(c) alkyl alkanoates ☐ (d) alkanediols ☐

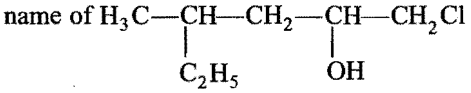
21. The IUPAC name of neopentane is: **[AIEEE 2009]**
(a) 2,2-dimethyl propane ☐ (b) 2-methyl propane ☐
(c) 2,2-dimethyl butane ☐ (d) 2-methyl butane ☐

22. The correct name of  is:

$\overset{CH_3-CH_2}{\overset{|}{C}}\equiv C-\overset{CH_2}{\overset{\|}{CH}}$

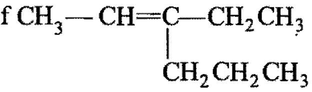
(a) hex-3-yn-5-ene ☐ (b) hex-5-en-3-yne ☐
(c) hex-3-yn-1-ene ☐ (d) hex-1-en-3-yne ☐

23. Which of the following compounds has isopropyl group? **[BHU 2005]**
(a) 2,2,3,3-tetramethylpentane ☐
(b) 2,2-dimethylpentane ☐
(c) 2,2,3-trimethylpentane ☐
(d) 2-methylpentane ☐

24. The IUPAC name of  is:

$H_3C-\underset{C_2H_5}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2Cl$

(a) 1-chloro-4-methylhexan-2-ol ☐
(b) 1-chloro-4-methylhexan-2-al ☐
(c) 1-chloro-4-ethylpentan-2-ol ☐
(d) 1-chloro-2-hydroxy-4-methylhexane ☐

25. The IUPAC name of  is :

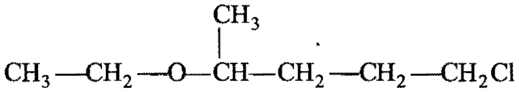
$CH_3-CH=\underset{CH_2CH_2CH_3}{\underset{|}{C}}-CH_2CH_3$

[CPMT 2002]
(a) 3-propylhex-2-ene ☐ (b) 3-propylhex-3-ene ☐
(c) 4-ethylhex-4-ene ☐ (d) 3-ethylhex-2-ene ☐

26. The IUPAC nomenclature of $(CH_3)_3C-CH{=}C(CH_3)_2$ is: **[AFMC 2010]**
(a) 2,4,4-trimethyl pent-3-ene ☐
(b) 2,4,4-trimethyl pent-2-ene ☐
(c) 2,2,4-trimethyl pent-3-ene ☐
(d) 2,2,4-trimethyl pent-2-ene ☐

27. Which one of the following IUPAC names is incorrect?
(a) Ethanoic acid ☐ (b) Ethanal ☐
(c) Pent-3-ene ☐ (d) 3-Methyl-pentan-2-ol ☐

28. The correct IUPAC name for

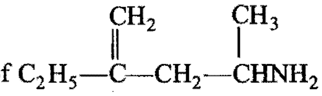


$CH_3-CH_2-O-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_2Cl$

is: **[DCE 2009]**
(a) 2-ethoxy-5-chloropentane ☐
(b) 1-chloro-4-ethoxy-4-methyl butane ☐
(c) 1-chloro-4-ethoxy pentane ☐
(d) ethyl-1-chloropentyl ether ☐

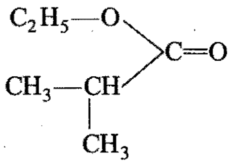
29. Ethanoyl chloride is the IUPAC name of:
(a) CH_3CH_2Cl ☐ (b) CH_3COCl ☐
(c) CCl_3CHO ☐ (d) $CH_2ClCOOH$ ☐

30. The IUPAC name of the compound $CH_3CONHBr$ is:
(a) 1-bromoacetamide ☐ (b) ethanoyl bromide ☐
(c) *N*-bromoethanamide ☐ (d) none of these ☐

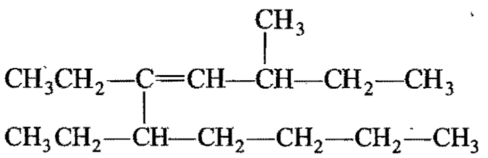
31. The IUPAC name of  is:

$C_2H_5-\overset{CH_2}{\overset{\|}{C}}-CH_2-\overset{CH_3}{\overset{|}{C}}HNH_2$

(a) 4-amino-2-ethylpent-1-ene ☐
(b) 2-ethylpentan-4-amine ☐
(c) aminopent-4-ene ☐
(d) 4-ethylpent-4-en-2-amine ☐

32. The IUPAC name of  is:
(a) ethoxy methanone ☐
(b) ethyl-2-methyl propanoate ☐
(c) ethoxypropanone ☐
(d) 2-methyl ethoxy propanone ☐

33. The correct IUPAC name of the compound,

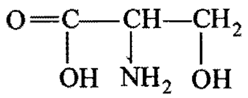


$CH_3CH_2-\underset{CH_3CH_2-CH-CH_2-CH_2-CH_2-CH_3}{\underset{|}{C}}=CH-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$

is:
(a) 5,6-diethyl-3-methyl-dec-4-ene ☐
(b) 5,6-diethyl-8-methyl-dec-6-ene ☐
(c) 6-butyl-5-ethyl-3-methyl-oct-4-ene ☐
(d) 2,4,5-triethyl-3-nonene ☐

34. The IUPAC name of iso-octane is:
(a) 2,2-dimethylpentane ☐
(b) 2,3-dimethylpentane ☐
(c) 2,3,3-trimethylpentane ☐
(d) 2,2,4-trimethylpentane ☐

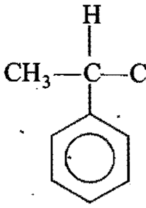
35. The IUPAC name of the following compound is:



$O{=}\underset{OH}{\underset{|}{C}}-\underset{NH_2}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

(a) 3-amino-2-hydroxy propanoic acid ☐
(b) 2-amino-propan-3-ol-1-oic acid ☐
(c) 2-amino-3-hydroxy propanoic acid ☐
(d) amino hydroxy propanoic acid ☐

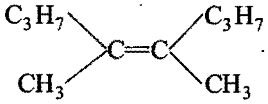
36. The IUPAC name of the compound



$CH_3-C-CH_2CH_3$ is:

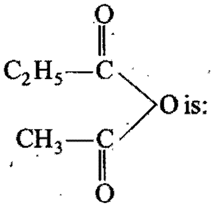
(a) 3-phenylbutane ☐ (b) 3-cyclohexylbutane ☐
(c) 2-cyclohexylbutane ☐ (d) 2-phenylbutane ☐

37. The IUPAC name of the compound



is:
(a) 4,5-dimethyloct-4-ene ☐
(b) 2,3-dipropylbut-2-ene ☐
(c) 4-methyl-5-propylhex-4-ene ☐
(d) none of the above ☐

38. The IUPAC name of the compound

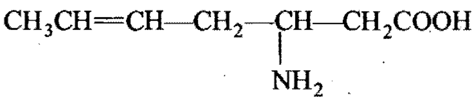


is:

(a) propionic acetic anhydride ☐
(b) ethanoic propanoic anhydride ☐
(c) aceto ethanoate ☐
(d) none of the above ☐

39. The name of citric acid is:
(a) 2-hydroxy propane-1,2,3-tricarboxylic acid ☐
(b) 3-carboxy-3-hydroxy pentane-1,5-dioic acid ☐
(c) both (a) and (b) are correct ☐
(d) both (a) and (b) are wrong ☐

40. The IUPAC name of the following is:



$CH_3CH{=}CH-CH_2-\underset{NH_2}{\underset{|}{CH}}-CH_2COOH$

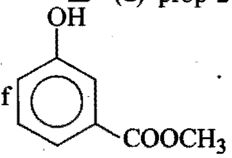
(a) 3-aminohept-5-enoic acid ☐
(b) 5-aminohex-2-ene-carboxylic acid ☐
(c) 3-amino-δ-heptenoic acid ☐
(d) 5-aminohept-2-enoic acid ☐

41. The IUPAC name of $CH_3-C{\equiv}CCH(CH_3)_2$ is:
(a) 4-methylpent-2-yne ☐
(b) 4,4′-dimethylpent-2-yne ☐
(c) methyl isopropyl acetylene ☐
(d) 2-methylpent-4-yne ☐

42. The IUPAC name of $(CH_3)_3C-CH{=}CH_2$ is: **[AMU (Med.) 2005]**
(a) 2,2-dimethylbut-3-ene ☐
(b) 2,2-dimethylpent-4-ene ☐
(c) 3,3-dimethylbut-1-ene ☐
(d) hex-1-ene ☐

43. The IUPAC name of $CH_2{=}CH-CN$ is: **[NSEC 2001]**
(a) ethenenitrile ☐ (b) vinyl cyanide ☐
(c) cyano ethene ☐ (d) prop-2-enenitrile ☐

44. The IUPAC name of

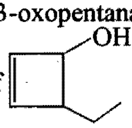


is :

(a) 2-hydroxy methyl benzoate ☐
(b) 2-hydroxy ethyl benzoate ☐
(c) 3-hydroxy methyl benzoate ☐
(d) 1-hydroxy methyl benzoate ☐

45. The IUPAC name of the compound
$BrCH_2-(CONH_2)CH-CO-CH_2-CH_3$ is :
(a) 2-(bromoethyl)-3-oxopentanamide ☐
(b) 2-(bromoethyl)-3-keto pentanamide ☐
(c) 2-(bromomethyl)-3-oxopentanamide ☐
(d) 3-(bromoethyl)-3-oxopentanamide ☐

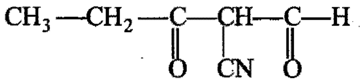
46. The IUPAC name of



is :

(a) 4-ethyl cyclobut-2-en-1-ol ☐
(b) 4-ethyl cyclobut-1-en-3-ol ☐
(c) 3-ethyl cyclobut-1-en-2-ol ☐
(d) 2-ethyl cyclobut-3-en-1-ol ☐

47. The IUPAC name of the given compound



$CH_3-CH_2-\underset{O}{\underset{\|}{C}}-\underset{CN}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-H$ is :

(a) 2-cyano-3-oxopentanal ☐
(b) 2-formyl-3-oxopentanenitrile ☐
(c) 1,3-dioxo-2-cyanopentane ☐
(d) 2-cyano-1,3-pentanedione ☐

48. The IUPAC nomenclature of the given organic compound will be; $(CH_3)_2C(CH_2CH_3)CH_2CH(Cl)CH_3$: **[BCECE 2001]**
(a) 5-chloro 3,3- dimethylhexane ☐
(b) 4-chloro-2-ethyl-2-methylpentane ☐
(c) 2-chloro-4-ethyl-4-methylpentane ☐
(d) 2-chloro-4, 4-dimethylhexane ☐

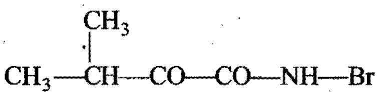
49. The IUPAC name of 4-isopropyl *m*-xylene is: **[DPMT 2001]**
(a) 1-isopropyl 2,4-dimethylbenzene ☐
(b) 4-isopropyl-*m*-xylene ☐
(c) 1-isopropyl-3,5-dimethylbenzene ☐
(d) 4-isopropyl-3,5-dimethylbenzene ☐

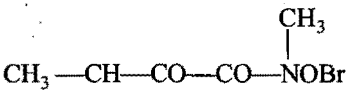
50. The IUPAC name of the given structure **H** is :

(a) 2,2-dimethyl butane ☐ (b) isohexane ☐
(c) 2,3-dimethyl butane ☐ (d) disohexane ☐

51. The structural formula of 2-oxo-3-methyl-(*N*-bromo) butanamide is :

(a) $CH_3CH_2—CO—CO—NH—Br$ ☐

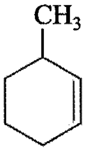
(b) 
$CH_3—\underset{}{\overset{CH_3}{\overset{|}{C}}}H—CO—CO—NH—Br$ ☐

(c) 
$CH_3—CH—CO—CO—\overset{CH_3}{\overset{|}{N}}OBr$ ☐

(d) $(CH_3)_3C—CO—CO—NH—Br$ ☐

52. The IUPAC name of the given structure **A** is :

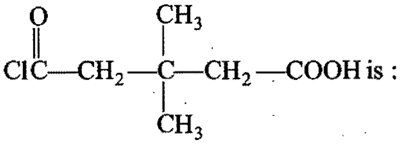
(a) 1,2-dimethyl cyclopropane ☐
(b) cyclopropane-1,2-dimethyl ☐
(c) 1-methyl-1-methyl cyclopropane ☐
(d) cyclopentane ☐

53. The IUPAC name of  is: **[AIIMS 2003]**

(a) 3-methyl cyclohexene ☐
(b) 1-methyl cyclohex-2-ene ☐
(c) 6-methyl cyclohexene ☐
(d) 1-methyl cyclohex-5-ene ☐

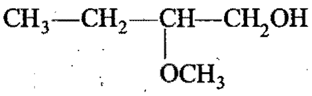
54. The correct IUPAC name for $H_2C{=}CH—C{\equiv}CH$ is: **[CBSE (Med.) 2009]**

(a) but-3-en-1-yne ☐ (b) but-1-en-3-yne ☐
(c) but-1-yn-3-ene ☐ (d) but-3-yn-1-ene ☐

55. The IUPAC name of 
$Cl\overset{O}{\overset{\|}{C}}—CH_2—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—CH_2—COOH$ is :

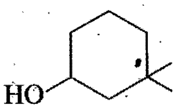
(a) 3,3-dimethyl-5-carboxy pentanoyl chloride ☐
(b) 4-chloroformyl-3,3-dimethyl pentanoic acid ☐
(c) 5-carboxy-3,3-dimethyl pentanoyl chloride ☐
(d) 5-chloroformyl-3,3-dimethyl pentanoic acid ☐

56. The IUPAC name of the compound


$CH_3—CH_2—\underset{OCH_3}{\underset{|}{C}}H—CH_2OH$ is: **[BHU 2004]**

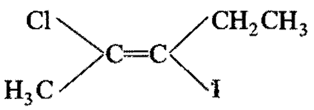
(a) 2-methoxy-1-butanol ☐ (b) 3-methoxy-1-butanol ☐
(c) 1-methoxy-1-butanol ☐ (d) 1, 2-methoxy butanol ☐

57. The IUPAC name of the compound

 is: **[AIEEE 2004]**

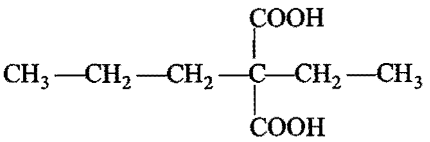
(a) 3,3-dimethyl-1-hydroxy cyclohexane ☐
(b) 1,1-dimethyl-3-hydroxy cyclohexane ☐
(c) 3,3-dimethyl-1-cyclohexanol ☐
(d) 1,1-dimethyl-3-cyclohexanol ☐

58. The IUPAC name of the compound **[DPMT 2004]**

 is:

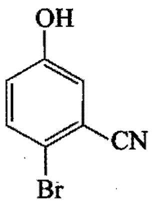
(a) *trans*-2-chloro-3-iodopent-2-ene ☐
(b) *cis*-2-chloro-3-iodopent-2-ene ☐
(c) *trans*-3-iodo-4-chloropent-3-ene ☐
(d) *cis*-3-iodo-4-chloropent-3-ene ☐

59. The IUPAC name of the compound

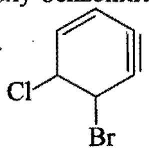

$CH_3—CH_2—CH_2—\underset{COOH}{\underset{|}{\overset{COOH}{\overset{|}{C}}}}—CH_2—CH_3$ is :

(a) 2-propyl-2-ethyl propanedioic acid ☐
(b) 2-ethyl-2-propyl propanedioic acid ☐
(c) 2-ethyl-2-carboxy pentanoic acid ☐
(d) 2-carboxy-2-ethyl pentanoic acid ☐

60. The IUPAC name of the following compound is: **[IIT 2009]**



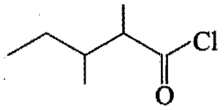
(a) 4-bormo-3-cyanophenol ☐
(b) 2-bromo-5-hydroxy benzonitrile ☐
(c) 2-cyano-4-hydroxy bromobenzene ☐
(d) 6-bromo-3-hydroxy benzonitrile ☐

61. The IUPAC name of  is :

(a) 4-bromo-3-chloro-1-cyclohexen-5-yne ☐
(b) 5-bromo-6-chloro-1-cyclohexen-3-yne ☐
(c) 6-bromo-5-chloro-3-cyclohexen-1-yne ☐
(d) 6-bromo-5-chloro-1-cyclohexen-3-yne ☐

62. The compound which contains all the four 1°, 2°, 3° and 4° carbon atom is: **[CET (J & K) 2005]**

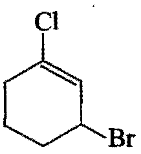
(a) 2,3-dimethylpentane ☐
(b) 3-chloro-2,3-dimethylpentane ☐
(c) 2,3,4-trimethylpentane ☐
(d) 3,3-dimethylpentane ☐

63. The IUPAC name of  is:

[CBSE (Med.) 2006; AIEEE 2006]

(a) 2-ethyl-3-methyl butanoyl chloride ☐
(b) 2,3-dimethyl pentanoyl chloride ☐
(c) 3,4-dimethyl pentanoyl chloride ☐
(d) 1-chloro-1-oxo-2,3-dimethyl pentane ☐

64. The IUPAC name of the compound shown below is:



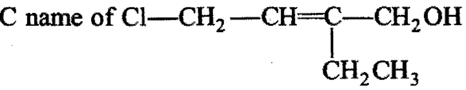
[AIEEE 2006]

(a) 2-bromo-6-chlorocyclohex-1-ene ☐
(b) 6-bromo-2-chlorocyclohexene ☐
(c) 3-bromo-1-chlorocyclohexene ☐
(d) 1-bromo-3-chlorocyclohexene ☐

65. The IUPAC name of C_6H_5COCl is: **[IIT 2006]**

(a) benzoyl chloride ☐
(b) benzene chloroketone ☐
(c) benzene carbonylchloride ☐
(d) chlorophenyl ketone ☐

66. The IUPAC name of

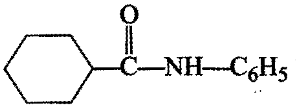


$\mathrm{Cl{-}CH_2{-}CH{=}\underset{\underset{\displaystyle CH_2CH_3}{|}}{C}{-}CH_2OH}$ is:

[DPMT 2006]

(a) 1-chloro-2-ethyl-4-hydroxybut-2-ene ☐
(b) 4-hydroxy-1-chloro-2-ethylbut-2-ene ☐
(c) 4-chloro-2-ethylbut-2-en-1-ol ☐
(d) 2-ethyl-4-chlorobut-2-en-1-ol ☐

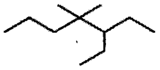
67. The IUPAC name of



is:

(a) *N*-cyclohexyl benzamide ☐
(b) *N*-cyclohexyl-*N*-phenyl methyl amide ☐
(c) *N*-phenyl-*N*-cyclohexyl methanamide ☐
(d) *N*-phenyl cyclohexane carboxamide ☐

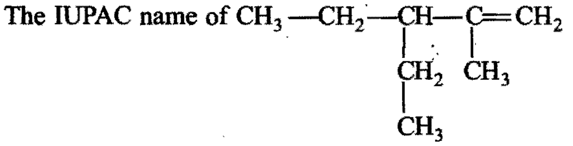
68. The IUPAC name of



is: **[AIEEE 2007]**

(a) 3-ethyl-4,4-dimethylheptane ☐
(b) 1,1-diethyl-2,2-dimethylpentane ☐
(c) 4,4-dimethyl-5,5-diethylpentane ☐
(d) 5,5-diethyl-4,4-dimethylpentane ☐

69. The IUPAC name of

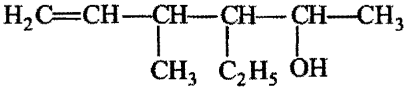


$\mathrm{CH_3{-}CH_2{-}\underset{\underset{\displaystyle \underset{\underset{\displaystyle CH_3}{|}}{CH_2}}{|}}{CH}{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2}$ is:

[Punjab PMET (Med.) 2008; CPMT 2008]

(a) 2-methyl-3-ethyl-1-pentene ☐
(b) 3-ethyl-4-methyl-4-pentene ☐
(c) 3-ethyl-2-methyl-1-pentene ☐
(d) 3-methyl-2-ethyl-1-pentene ☐

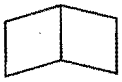
70. The IUPAC name of the compound



$\mathrm{H_2C{=}CH{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}\underset{\underset{\displaystyle C_2H_5}{|}}{CH}{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}CH_3}$ is: **[DPMT 2007]**

(a) 3-ethyl-4-methylhex-5-en-2-ol ☐
(b) 3-methyl-4-ethylhex-1-en-5-ol ☐
(c) 3-ethyl-2-hydroxy-4-methylhex-5-ene ☐
(d) none of the above ☐

71. The IUPAC name of the following compound is: **[UGET (Med.) 2007]**

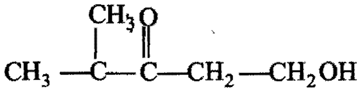


(a) bicyclo [2.2.0] octane ☐
(b) bicyclo [0.2.2] hexane ☐
(c) bicyclo [2.1.1] hexane ☐
(d) bicyclo [2.2.0] hexane ☐

72. The IUPAC name of the compound $(CH_3)_2CH{-}CH{=}CH{-}CHOH{-}CH_3$ is: **[EAMCET (Engg.) 2007]**

(a) 5-methylhex-3-en-2-ol ☐
(b) 2-methylhex-3-en-5-ol ☐
(c) 2-hydroxy-5-methyl-3-hexene ☐
(d) 5-hydroxy-2-methyl-3-hexene ☐

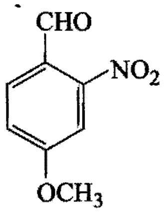
73. The IUPAC name of



$\mathrm{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_2OH}$ is: **[AIIMS 2007]**

(a) 1-hydroxy-4-methylpentan-3-one ☐
(b) 2-methyl-5-hydroxypentan-3-one ☐
(c) 4-methyl-3-oxopentan-1-ol ☐
(d) hexan-1-ol-3-one ☐

74. The correct IUPAC name of the compound



is: **[AFMC 2007]**

(a) 2-formyl-5-methoxynitrobenzene ☐
(b) 4-formyl-3-nitroanisole ☐
(c) 4-methoxy-2-nitrobenzaldehyde ☐
(d) 4-methoxy-6-nitrobenzaldehyde ☐

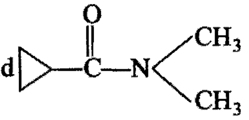
75. The IUPAC name of tertiary butyl iodide is: **[CET (Karnataka) 2008]**

(a) 1-iodo-3-methyl propane ☐
(b) 2-iodo-2-methyl propane ☐
(c) 4-iodobutane ☐
(d) 2-iodobutane ☐

76. The correct structure of 4-bromo-3-methyl but-1-ene is: **[AIIMS 2008]**

(a) $BrCH{=}C(CH_3)_2$ ☐
(b) $H_2C{=}C(CH_3)CH_2CH_2Br$ ☐
(c) $H_2C{=}CH{-}CH(CH_3){-}CH_2Br$ ☐
(d) $CH_3{-}C(CH_3){=}CHCH_2Br$ ☐

77. The IUPAC name of the compound

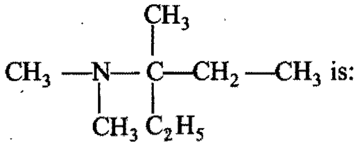


is: **[JIPMER (Med.) 2008]**

(a) cyclopropionamide ☐
(b) *N*-methyl cyclopropanamide ☐

(c) *N,N*-dimethyl cyclopropane carboxamide ☐
(d) none of the above ☐

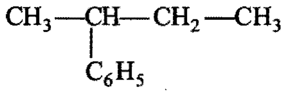
78. The IUPAC name of the following compound



$CH_3-\underset{CH_3}{\underset{|}{N}}-\overset{CH_3}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}-CH_2-CH_3$ is: **[DPMT 2008]**

(a) 3-dimethylamino-3-methyl pentane ☐
(b) 3-(*N,N*-trimethyl)-3-aminopentane ☐
(c) 3-*N,N*-trimethyl pentanimine ☐
(d) 3-(*N,N*-dimethyl) amino-3-methylpentane ☐

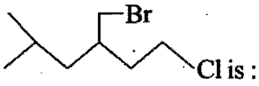
79. The IUPAC name of the following compound is: **[AFMC 2008]**



$CH_3-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-CH_3$

(a) 2-cyclohexyl butane ☐ (b) *sec.*-butyl benzene ☐
(c) 3-cyclohexyl butane ☐ (d) 2-phenyl butane ☐

80. The IUPAC name of the compound



is : **[AMU (Engg.) 2010]**

(a) 3-bromomethyl-1-chloro-5-methyl hexane ☐
(b) 1,1-dimethyl-3-bromoethyl-5-chloropentane ☐
(c) 1-bromomethyl-2-chloroethyl-4-methyl pentane ☐
(d) 4-bromomethyl-1-chloro-6-methyl heptane ☐

81. Match the **List I** and **List II** and select the correct answer using the code given below the lists:

List I	List II
1. C_nH_{2n}	(A) alcohols, ethers
2. C_nH_{2n-2}	(B) alkenes, cycloalkanes
3. $C_nH_{2n+2}O$	(C) aldehydes, ketones
4. $C_nH_{2n}O$	(D) alkynes, alkadienes

Codes:
(a) 1-A, 2-B, 3-C, 4-D ☐ (b) 1-D, 2-C, 3-B, 4-A ☐
(c) 1-B, 2-D, 3-A, 4-C ☐ (d) 1-C, 2-A, 3-D, 4-B ☐

82. Match the following:

1. Dimethyl acetylene	(A) Propanone
2. Methyl acetic acid	(B) Trichloromethane
3. Chloroform	(C) Propanoic acid
4. Acetone	(D) But-2-yne

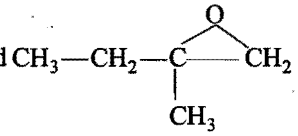
Codes:
(a) 1-D, 2-C, 3-B, 4-A ☐ (b) 1-A, 2-B, 3-C, 4-D ☐
(c) 1-C, 2-D, 3-A, 4-B ☐ (d) 1-B, 2-A, 3-D, 4-C ☐

83. Match the following:

1. Benzene	(A) Aromatic (Bicyclic)
2. Naphthalene	(B) Aromatic (Monocyclic)
3. Anthracene	(C) Alicyclic
4. Pyridine	(D) Heterocyclic
5. Cycloalkane	(E) Aromatic (Tricyclic)

Codes:
(a) 1-A, 2-B, 3-C, 4-E, 5-D ☐
(b) 1-B, 2-A, 3-E, 4-D, 5-C ☐
(c) 1-C, 2-E, 3-D, 4-B, 5-A ☐
(d) 1-D, 2-C, 3-B, 4-A, 5-E ☐
(e) 1-E, 2-D, 3-A, 4-C, 5-B ☐

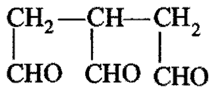
SET II: This set contains the questions with one or more correct answers.



84. The compound may be named as:

(a) 2-ethyl-2-methyl oxirane ☐
(b) 1,2-epoxy-2-methylbutane ☐
(c) 1,2-oxapentane ☐
(d) 2-methyl-2-butoxide ☐

85. Which of the following names are not correct for the given compound?



$\underset{CHO}{\underset{|}{CH_2}}-\underset{CHO}{\underset{|}{CH}}-\underset{CHO}{\underset{|}{CH_2}}$

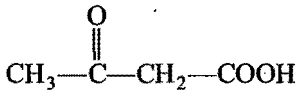
(a) 3-Formyl pentane-1,5-dial ☐
(b) 1,2,3-Triformyl-propane ☐
(c) 2-Formylbutane-1,4-dial ☐
(d) Propane-1,2,3-tricarbaldehyde ☐

86. The name chloromethyl acetylene implies:
(a) $CH_3-CH=CHCl$ ☐ (b) $ClCH_2-CH=CH_2$ ☐
(c) $CH_3-C\equiv C-Cl$ ☐ (d) $ClCH_2-C\equiv CH$ ☐

87. The compound $CH_3-C\equiv C-CH_3$ can be named as:
(a) dimethyl acetylene ☐ (b) crotonylene ☐
(c) but-2-yne ☐ (d) allylene ☐

88. The compound $(CH_3)_2C(OH)CH_2CH_3$ is called:
(a) 2-methyl butan-2-ol ☐
(b) isoamyl alcohol ☐
(c) ethyl dimethyl carbinol ☐
(d) *tert.*-pentyl alcohol ☐

89. Which of the following names are correct for the compound?



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOH$

(a) 3-Keto butan-1-oic acid ☐
(b) 4-Carboxy butan-2-one ☐
(c) 3-Oxo butan-1-oic acid ☐
(d) 3-Carboxy acetone ☐

90. The compound $C_6H_5-CH=CH-COOH$ may be called as:
(a) succinic acid ☐
(b) 3-phenylprop-2-en-1-oic acid ☐
(c) mandelic acid ☐
(d) cinnamic acid ☐

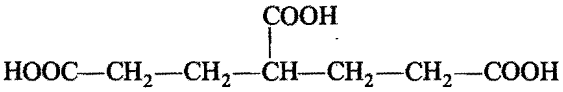
91. Which of the following statements is/are correct?
(a) Spirocompounds contain fused rings at quaternary carbon ☐
(b) Bicyclo compounds contain two rings connected by a bridge ☐

(c) Bicyclo compounds cannot be aromatic ☐
(d) Cyclic alkynes are unstable ☐

92. The IUPAC name for diglyme, *i.e.*, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$ is/are :
(a) 2,5,8-trioxanonane ☐
(b) *bis* (2-methoxy ethyl) ether ☐
(c) β,β'-dimethoxy-diethyl ether ☐
(d) diethylene glycol dimethyl ether ☐

93. Which of the following are the names of cyclic ether?
(a) Oxirane ☐ (b) Epoxyalkane ☐
(c) Alkene oxide ☐ (d) Carbinol ☐

94. Which of the following names are correct for the compound?


$HOOC—CH_2—CH_2—\overset{\overset{\displaystyle COOH}{|}}{C}H—CH_2—CH_2—COOH$

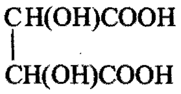
(a) Pentane-1,3,5-tricarboxylic acid ☐
(b) 4-Carboxy heptane-1,7-dioic acid ☐
(c) Heptane-1,4,7-trioic acid ☐
(d) All are correct ☐

95. Which of the following names are correct for the compound?

$(CH_3)_2CHCN$

(a) 2-Methyl propane nitrile ☐
(b) Isobutyro nitrile ☐
(c) Isopropyl cyanide ☐
(d) All are correct ☐

96. The name(s) of the following compound is/are:

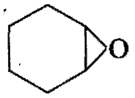

$\begin{array}{l} CH(OH)COOH \\ | \\ CH(OH)COOH \end{array}$

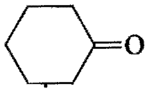
(a) tartaric acid ☐
(b) 2,3-dihydroxy butane-1,4-dioic acid ☐
(c) α,α'-dihydroxy succinic acid ☐
(d) all of the above ☐

ASSERTION-REASON TYPE QUESTIONS

Following questions consist of an **Assertion** (A) and **Reason** (R). Use the following keys to select correct answer:

(a) If both **assertion** and **reason** are correct and **reason** is the correct explanation of the assertion.
(b) If both **assertion** and **reason** are correct but **reason** is not correct explanation of the assertion.
(c) If **assertion** is correct but **reason** is incorrect.
(d) If **assertion** is incorrect but **reason** is correct.

1. (A) The IUPAC name for  is 7-oxabicyclo [4.1.0] heptane.
(R) The prefix oxo is used for >C=O group.

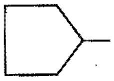
2. (A) The IUPAC name of the compound  is cyclohexylidene methanone.
(R) $CH_2=C=O$ is called ketene.

3. (A)  is called cyclohexanitrile.
(R) It is an aromatic compound.

4. (A) The locant (2.8.7) is preferred over the locant (3.4.9).
(R) Lowest locant number at first difference is preferred.

5. (A) The IUPAC name of $CH_3—CH=CH—C\equiv C—H$ is pent-3-en-1-yne and not pent-2-en-4-yne.
(R) Lowest locant rule for multiple bond is preferred.

6. (A) The IUPAC name for the compound $C_6H_5COOCH_2CH_2COOH$ is 3-benzoyloxy propanoic acid.
(R) $C_6H_5CH_2O$ is called benzoyloxy group.

7. (A) The correct IUPAC name for the compound
 $—CH(CH_3)_2$ is 1-methyl ethyl cyclopentane.
(R) It is named as derivative of cyclopentane because the number of carbon atoms in the ring is more than the side chain.

ANSWERS

OBJECTIVE QUESTIONS

1. (b)	**2.** (b)	**3.** (a)	**4.** (c)	**5.** (b)	**6.** (b)	**7.** (b)	**8.** (a)	**9.** (d)	**10.** (c)
11. (e)	**12.** (b)	**13.** (b)	**14.** (c)	**15.** (a)	**16.** (b)	**17.** (d)	**18.** (c)	**19.** (b)	**20.** (c)
21. (a)	**22.** (d)	**23.** (d)	**24.** (a)	**25.** (d)	**26.** (b)	**27.** (c)	**28.** (a)	**29.** (b)	**30.** (c)
31. (d)	**32.** (b)	**33.** (a)	**34.** (d)	**35.** (c)	**36.** (d)	**37.** (a)	**38.** (b)	**39.** (c)	**40.** (a)
41. (a)	**42.** (c)	**43.** (d)	**44.** (c)	**45.** (c)	**46.** (a)	**47.** (b)	**48.** (d)	**49.** (a)	**50.** (c)
51. (b)	**52.** (a)	**53.** (a)	**54.** (b)	**55.** (d)	**56.** (a)	**57.** (c)	**58.** (a)	**59.** (b)	**60.** (b)
61. (b)	**62.** (b)	**63.** (b)	**64.** (c)	**65.** (c)	**66.** (c)	**67.** (d)	**68.** (a)	**69.** (c)	**70.** (a)
71. (d)	**72.** (a)	**73.** (a)	**74.** (c)	**75.** (b)	**76.** (c)	**77.** (c)	**78.** (d)	**79.** (d)	**80.** (a)
81. (c)	**82.** (a)	**83.** (b)	**84.** (a,b)	**85.** (b,c)	**86.** (c,d)	**87.** (a,b,c)	**88.** (a,c,d)	**89.** (a,c)	**90.** (b,d)
91. (a,b,d)	**92.** (a,b)	**93.** (a,b,c)	**94.** (a,b)	**95.** (d)	**96.** (d)				

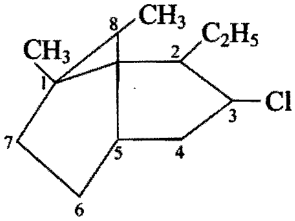
ASSERTION-REASON TYPE QUESTIONS

1. (b)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (a)	**6.** (c)	**7.** (a)

BRAIN STORMING PROBLEMS

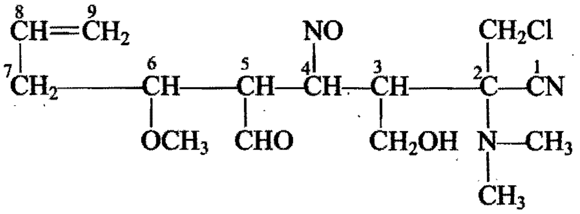
Give the IUPAC names of the following compounds:

1.



Ans. 3-Chloro-2-ethyl-1,8-dimethylbicyclo [3.2.1] octane

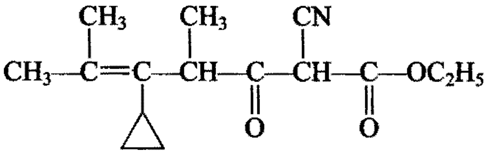
2.



$\overset{\overset{8}{C}H=\overset{9}{C}H_2}{\overset{|}{\overset{7}{C}H_2}}-\underset{\underset{OCH_3}{|}}{\overset{6}{C}H}-\underset{\underset{CHO}{|}}{\overset{5}{C}H}-\overset{\overset{NO}{|}}{\overset{4}{C}H}-\underset{\underset{CH_2OH}{|}}{\overset{3}{C}H}-\overset{\overset{CH_2Cl}{|}}{\underset{\underset{\underset{\underset{CH_3}{|}}{N-CH_3}}{|}}{\overset{2}{C}}}-\overset{1}{C}N$

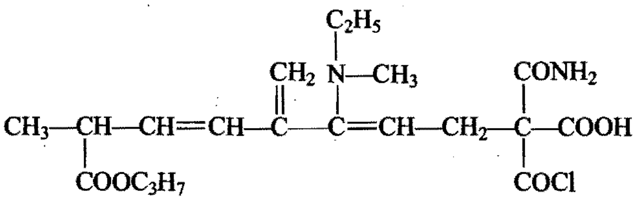
Ans. 2-Chloromethyl-5-formyl-3-hydroxymethyl-2-*N,N*-dimethylamino-6-methoxy-4-nitroso non-8-en-1-nitrile

3.



Ans. Ethyl-2-cyano-3-oxo-4,6-dimethyl-5-cyclopropylhept-5-ene-1-oate

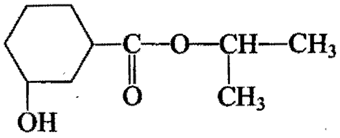
4.



$CH_3-\underset{\underset{COOC_3H_7}{|}}{C}H-CH=CH-\overset{\overset{CH_2}{\|}}{C}-\overset{\overset{\overset{C_2H_5}{|}}{N-CH_3}}{\overset{|}{C}}=CH-CH_2-\overset{\overset{CONH_2}{|}}{\underset{\underset{COCl}{|}}{C}}-COOH$

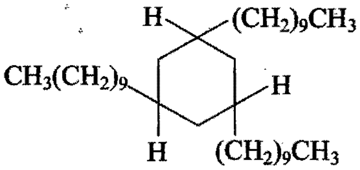
Ans. 2-Amide-2-chlorocarbonyl-5-(*N*-ethyl, *N*-methyl) amino-6-methylene-9-propoxycarbonyldec-4,7-diene-1-oic acid

5.



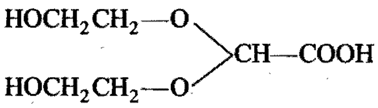
Ans. Isopropyl-3-hydroxycyclohexane carboxylate

6.



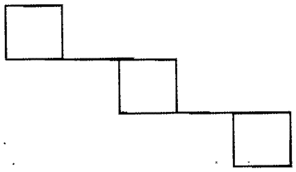
Ans. 1,3,5-Trisdecylcyclohexane

7.



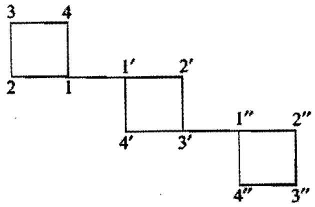
Ans. 2,2-*Bis* (2-hydroxy ethoxy) ethanoic acid

8.



Ans. 1, 1′, 3′, 1″-Tercyclobutane.

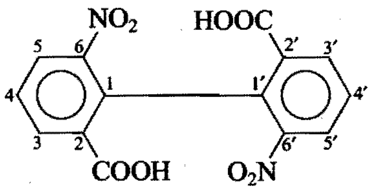
[Hint:



]

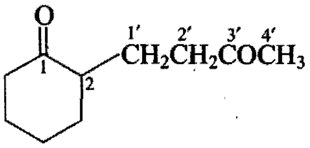
1,1′,3′,1″-Tercyclobutane

9.



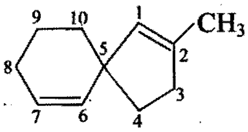
Ans. 6,6′-Dinitrophenyl-2, 2′-dicarboxylic acid

10.



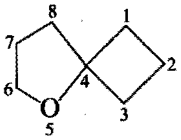
Ans. 2-(3′-Oxobutyl) cyclohexan-1-one

11.



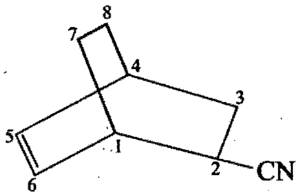
Ans. 2-Methyl spiro [4.5] deca-1,6 diene

12.



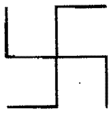
Ans. 5-Oxa-spiro [3.4] octane

13.



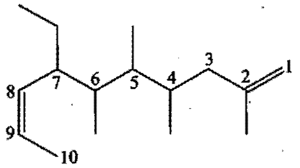
Ans. Bicyclo [2.2.2] oct-5-ene-2-nitrile

14.



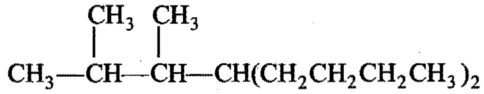
Ans. 3, 3-Diethylpentane

15.



Ans. 7-Ethyl-2,4,5,6-tetramethyldec-1,8-diene

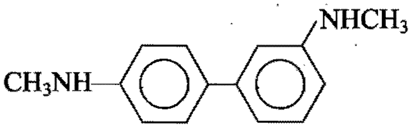
16.



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH(CH_2CH_2CH_2CH_3)_2$$

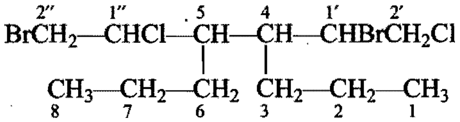
Ans. 5-(1′,2′-dimethyl propyl) nonane

17.



Ans. 3, 4′-*Bis* (*N*-methylamino) biphenyl

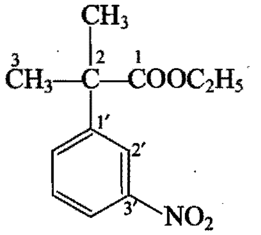
18.



$$\overset{2''}{BrCH_2}-\overset{1''}{CHCl}-\overset{5}{\underset{\underset{\overset{8}{CH_3}-\overset{7}{CH_2}-\overset{6}{CH_2}}{|}}{CH}}-\overset{4}{\underset{\underset{\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_3}}{|}}{CH}}-\overset{1'}{CHBr}\overset{2'}{CH_2Cl}$$

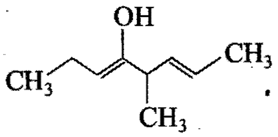
Ans. 4-(1′-Bromo,2′-chloroethyl)-5-(2″-bromo-1″-chloroethyl) octane.

19.



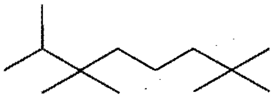
Ans. Ethyl-2-methyl-2-(3′-nitro phenyl) propanoate

20.



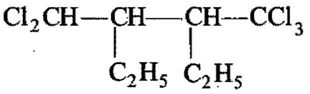
Ans. 5-methyl-3, 6-octadien-4-ol

21.



Ans. 2,3,3,7,7-Pentamethyloctane

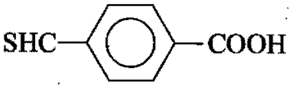
22.



$$Cl_2CH-\underset{C_2H_5}{\underset{|}{CH}}-\underset{C_2H_5}{\underset{|}{CH}}-CCl_3$$

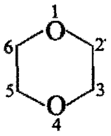
Ans. 3-(Dichloromethyl)-4-(trichloromethyl) hexane

23.



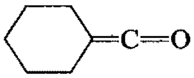
Ans. 4-Thioformyl benzoic acid

24.



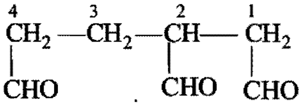
Ans. 1, 4-Dioxacyclohexane

25.



Ans. Cyclohexylidene methanone

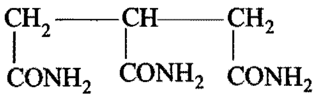
26.



$$\overset{4}{\underset{CHO}{\underset{|}{CH_2}}}-\overset{3}{CH_2}-\overset{2}{\underset{CHO}{\underset{|}{CH}}}-\overset{1}{\underset{CHO}{\underset{|}{CH_2}}}$$

Ans. Butane-1, 2, 4-tricarbaldehyde

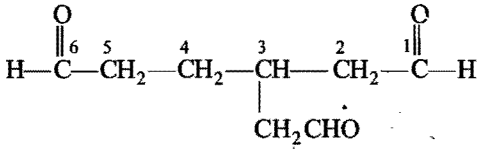
27.



$$\underset{CONH_2}{\underset{|}{CH_2}}-\underset{CONH_2}{\underset{|}{CH}}-\underset{CONH_2}{\underset{|}{CH_2}}$$

Ans. Propane-1, 2, 3-tricarboxamide

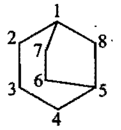
28.



$$H-\overset{O}{\overset{\|\,6}{C}}-\overset{5}{CH_2}-\overset{4}{CH_2}-\overset{3}{\underset{CH_2CHO}{\underset{|}{CH}}}-\overset{2}{CH_2}-\overset{O}{\overset{1\,\|}{C}}-H$$

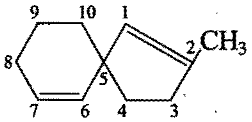
Ans. 3-(Formyl methyl) hexane-1,6-dial

29.



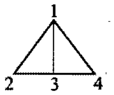
Ans. Bicyclo [3.2.1] octane

30.



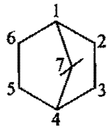
Ans. 2-Methyl spiro [4.5] deca-1, 6-diene

31.



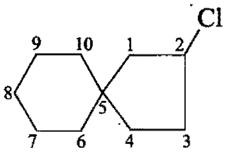
Ans. Bicyclo [1.1.0] butane

32.



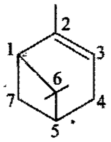
Ans. 7,7-Dimethyl bicyclo [2.2.1] heptane

33.



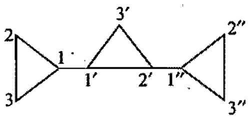
Ans. 2-Chlorospiro [4.5] decane

34.



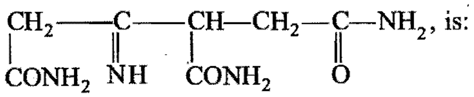
Ans. 2,6,6-Trimethylbicyclo [3.1.1] hept-2-ene

35.



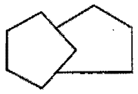
Ans. 1,1′, 2′, 1″-Tercyclopropane.

36. The IUPAC name of



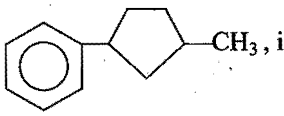
$\underset{CONH_2}{CH_2}—\underset{\overset{\|}{NH}}{C}—\underset{CONH_2}{CH}—CH_2—\underset{\overset{\|}{O}}{C}—NH_2$, is:

(a) 2-iminobutan-1,3,4-tricarboxamide ☐
(b) 3-imino-4-carbamylhexan-1,6-diamide ☐
(c) 6-amino-2-imino-4-carbamylhexanamide ☐
(d) none of the above ☐

37. The IUPAC name of  ,is:

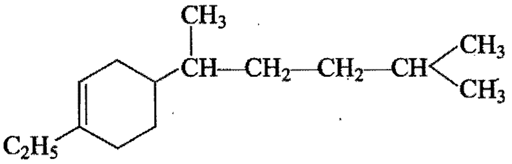
(a) bicyclo [4.3.1] decane ☐
(b) bicyclo [3.2.0] nonane ☐
(c) bicyclo [2.2.2] decane. ☐
(d) bicyclo [3.3.0] nonane. ☐

38. The IUPAC name of the compound



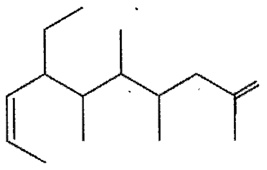
, is :

(a) 3-(3-methylcyclopentyl) benzene ☐
(b) 1-(3′-methylcyclopentyl) benzene ☐
(c) 2-(2-methylcyclopentyl) benzene ☐
(d) none of the above ☐

39. 

The IUPAC name of the above compound will be:
(a) 1-ethyl-4-(5-methylhexyl) cyclohex-1-ene ☐
(b) 1-ethyl-4(1,4-dimethylpentyl) cyclohex-1-ene ☐
(c) 5-(1,4-dimethylpentyl)-2-ethylcyclohex-1-ene ☐
(d) 4-(1,4-dimethylpentyl)-1-ethylcyclohex-1-ene ☐

40. The IUPAC name of the compound

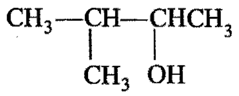


is:

(a) 2,4,5,6-tetramethyl-7-ethyldeca-1,7-diene ☐
(b) 7-ethyl-2,4,5,6-tetramethyldeca-1,8-diene ☐
(c) 4-ethyl-5,6,7,9-tetramethyl deca-2,9-diene ☐
(d) none of the above ☐

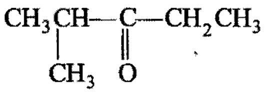
41. Which one of the following compounds has incorrect IUPAC nomenclature?

(a) $CH_3—CH_2CH_2—COOC_2H_5$ ☐
ethylbutanoate

(b)  ☐

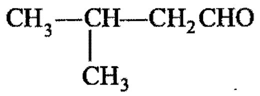
$CH_3—\underset{CH_3}{CH}—\underset{OH}{CH}CH_3$

2-methylbutan-3-ol

(c)  ☐

$CH_3\underset{CH_3}{CH}—\underset{O}{\overset{}{\underset{\|}{C}}}—CH_2CH_3$

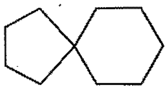
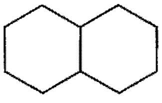
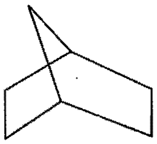
2-methylpentan-3-one

(d)  ☐

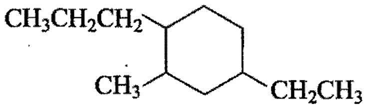
$CH_3—\underset{CH_3}{CH}—CH_2CHO$

3-methylbutanal

42. Match the **List I** and **List II**; select the correct answer from the given code:

	List I	**List II**
A.		1. fused bicycle
B.		2. bridged bicyclic
C.		3. spirocyclic

Codes :
(a) (A–3), (B–1), (C–2) ☐ (b) (A–1), (B–2), (C–3) ☐
(c) (A–3), (B–2), (C–1) ☐ (d) (A–2), (B–1), (C–3) ☐

43. 

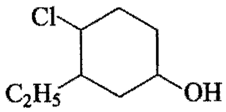
The IUPAC name of the above compound will be:
(a) 5-ethyl-1-methyl-2-propylcyclohexane ☐
(b) 1-ethyl-3-methyl-4-propylcyclohexane ☐
(c) 4-ethyl-2-methyl-1-propylcyclohexane ☐
(d) 1-propyl-3-ethyl-2-methylcyclohexane ☐

44. The IUPAC name of the compound

is :

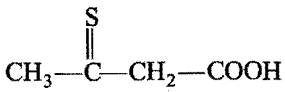
(a) 1-cyclopropyl-4-*tert.* butyl cyclohexane ☐
(b) 4-cyclopropyl-1-*tert.* butyl cyclohexane ☐
(c) 1-cyclopropyl hexyl-2,2-dimethylpropane ☐
(d) 1-dimethyl ethyl-4-cyclopropyl cyclohexane ☐

45. Select the correct IUPAC name of the following compound:



(a) 2-ethyl, 1-chloro, cyclohexanol ☐
(b) 4-chloro, 3-ethylcyclohexanol ☐
(c) 4-chloro, 5-ethylcyclohexanol ☐
(d) 4-hydroxy, 2-ethyl-1-chlorocyclohexane ☐

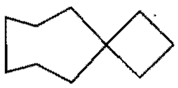
46. Give the IUPAC name of the following compound:



$CH_3—\overset{\overset{S}{\|}}{C}—CH_2—COOH$

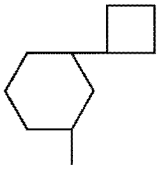
(a) 3-Thiabutanoic acid ☐
(b) 3-Sulphobutanoic acid ☐
(c) 3-Thiobutanoic acid ☐
(d) 3-Thioxobutanoic acid ☐

47. Select the correct IUPAC name of the following compound:



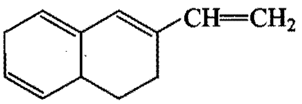
(a) 1,1-cyclobutyl heptane ☐
(b) Bicyclo [6.3.0] nonane ☐
(c) Spiro [3.6] decane ☐
(d) Spiro [6.3] decane ☐

48.



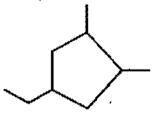
Which of the following is the correct IUPAC name of the above compound?
(a) 3-cyclobutyl-1-methylcyclohexane ☐
(b) 1-methyl-3-cyclobutylcyclohexane ☐
(c) 1-cyclobutyl-5-methylcyclohexane ☐
(d) 1-cyclobutyl-3-methylcyclohexane ☐

49.



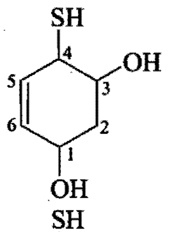
Give the correct IUPAC name of the above compound:
(a) 2-vinyl-3,4,7,10-tetrahydronaphthalene ☐
(b) 1-vinyl-5,8,9,10-tetrahydronaphthalene ☐
(c) 2-ethenylbicyclo [4.4.0] deca-1,5,8-triene ☐
(d) 3-ethenyl bicyclo [4.4.0] deca-3,5,8-triene ☐

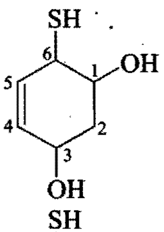
50. Select the correct IUPAC name of the following compound:

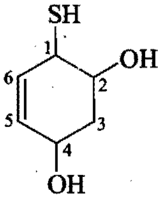


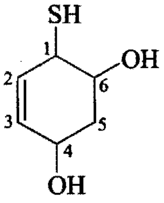
(a) 3-ethyl-1,5-dimethylcyclopentane ☐
(b) 1-ethyl-3,4-dimethylcyclopentane ☐
(c) 4-ethyl-1,2-dimethylcyclopentane ☐
(d) 2-ethyl-4,5-dimethylcyclopentane ☐

51. Select the structure with correct numbering for IUPAC name of the compound:

(a)


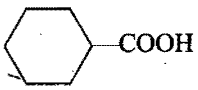
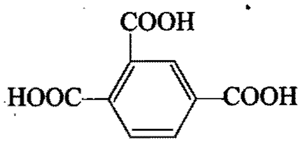
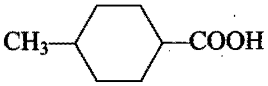
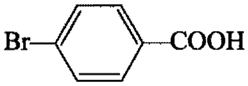
(b)


(c)


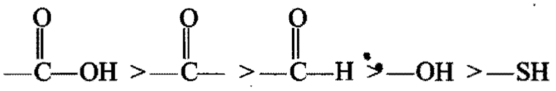
(d)


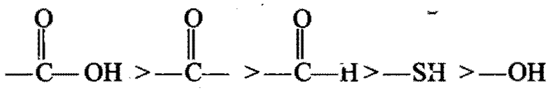
52. Which of the following is the correct IUPAC name for the compound given in above question?
(a) 6-mercapto-4-cyclohexene-1,3-diol ☐
(b) 4-mercapto-5-cyclohexene-1,3-diol ☐
(c) 2,4-dihydroxy-5-cyclohexene-1-mercaptan ☐
(d) 4,6-dihydroxy-2-cyclohexene-1-mercaptan ☐

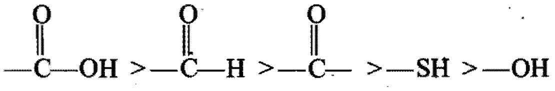
53. The IUPAC name of which of the following compounds is not correct?

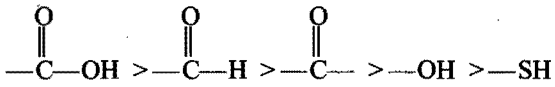
	Compound	**IUPAC name**
(a)		cyclohexanoic acid
(b)		1,2,4-benzene tricarboxylic acid
(c)		4-methylcyclohexane-carboxylic acid
(d)		4-bromobenzoic acid

54. Select the correct priority for citation as principal group:

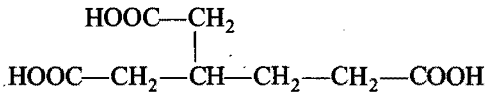
(a)

$-\overset{\overset{O}{\|}}{C}-OH > -\overset{\overset{O}{\|}}{C}- > -\overset{\overset{O}{\|}}{C}-H > -OH > -SH$ ☐

(b)

$-\overset{\overset{O}{\|}}{C}-OH > -\overset{\overset{O}{\|}}{C}- > -\overset{\overset{O}{\|}}{C}-H > -SH > -OH$ ☐

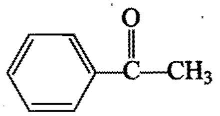
(c)

$-\overset{\overset{O}{\|}}{C}-OH > -\overset{\overset{O}{\|}}{C}-H > -\overset{\overset{O}{\|}}{C}- > -SH > -OH$ ☐

(d)

$-\overset{\overset{O}{\|}}{C}-OH > -\overset{\overset{O}{\|}}{C}-H > -\overset{\overset{O}{\|}}{C}- > -OH > -SH$ ☐

55. What will be the prefix in the following compound?

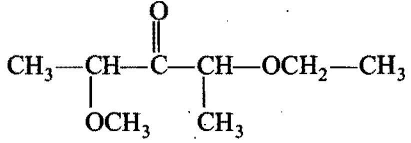

$$\begin{array}{l} \quad\quad HOOC-CH_2 \\ \quad\quad\quad\quad\quad\quad | \\ HOOC-CH_2-CH-CH_2-CH_2-COOH \end{array}$$

(a) methylcarboxy ☐ (b) carboxymethyl ☐
(c) carboxyethyl ☐ (d) ethylcarboxy ☐

56. The IUPAC name of


is:

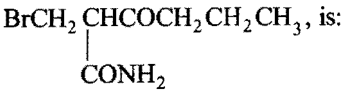
(a) phenylethanone ☐ (b) methylphenylketone ☐
(c) acetophenone ☐ (d) phenylmethylketone ☐

57.

$$CH_3-\underset{\underset{OCH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-OCH_2-CH_3$$

The IUPAC name of this compound is:

(a) 2-ethoxy-4-methoxy-pentan-3-one ☐
(b) 2-methoxy-4-ethoxy-pentan-3-one ☐
(c) 2-ethoxy-3-methoxy-pentan-3-one ☐
(d) none of the above ☐

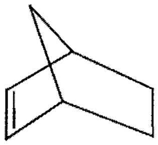
58. The IUPAC name of BrCH$_2$ CHCOCH$_2$CH$_2$CH$_3$, is:

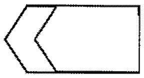


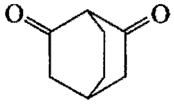
$$\underset{\displaystyle CONH_2}{BrCH_2\,\underset{|}{C}HCOCH_2CH_2CH_3}$$

(a) 2-bromomethyl-3-oxohexanamide ☐
(b) 1-bromo-2-amido-3-oxohexane ☐
(c) 1-bromo-2-amido-n-propylketone ☐
(d) 3-bromo-2-propyl propanamide ☐

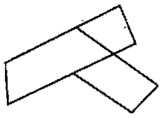
59. Which name is incorrect?

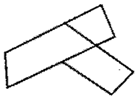
(a)  Bicyclo (2.2.1) hcpt-2-ene

(b)  Bicyclo (3.2.1) octane

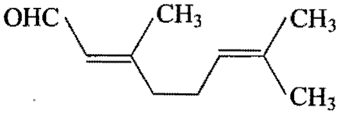
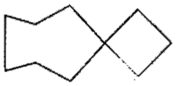
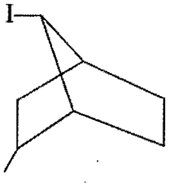
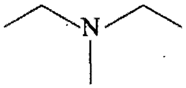
(c) 

Bicyclo (2.2.2) octane-2,6-dione

(d)  Bicyclo (2.2.0) hexane

[**Hint:** The IUPAC name of  is bicyclo (2.2.2) hexane]

60. Select thc correct IUPAC names among the following:

	Compound	**IUPAC name**
1.		3,7-dimethyloct-2,6-dienal
2.		Spiro (3.6) decane
3.		3-Ethyl-7-iodobicyclo (2.2.1) heptane
4.		*N*-ethyl-*N*-methyl ethanamine

(a) 1,2,4 ☐ (b) 1,3,4 ☐
(c) 2,3,4 ☐ (d) 1,2,3 ☐

ANSWERS : BRAIN STORMING PROBLEMS

36. (b)	**37.** (a)	**38.** (b)	**39.** (b)	**40.** (b)	**41.** (b)	**42.** (a)	**43.** (c)	**44.** (a)	**45.** (b)
46. (a)	**47.** (c)	**48.** (d)	**49.** (c)	**50.** (c)	**51.** (b)	**52.** (a)	**53.** (a)	**54.** (d)	**55.** (b)
56. (a)	**57.** (a)	**58.** (a)	**59.** (d)	**60.** (a)					

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

In addition to the standard ring systems (such as cyclohexane), cyclic compounds can also be bicyclic, tricyclic, etc., or they can be spirocyclic, bicyclic or bridge head carbons. The point of attachment of two rings are called bridge head atoms

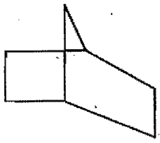
Some bicyclic compounds like camphor are commonly found in plants. Others like norbornane can be synthesized in the laboratory. The formal names of bicyclic and related ring systems are based on:

(1) Total number of atoms in the molecule.

(2) The number of atoms in each bridge connecting the bridge head atoms. These numbers are written in square bracket in decreasing order.

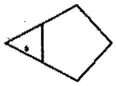
Spirocyclic compounds have two fused rings, but only one bridge head atom. Spirocyclic compounds are named like bicyclic compounds, but have the prefix spirocyclo.

Answer the following questions:

1. 

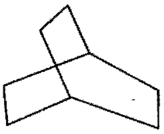
What is the IUPAC name of the above compound?

(a) cyclo [1.2.2] heptane
(b) bicyclo [1.2.2] heptane
(c) bicyclo [2.2.1] heptane
(d) cyclo [2.2.1] heptane

2.  The number of atoms in each bridge are:

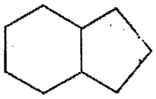
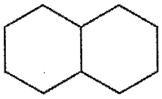
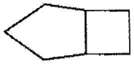
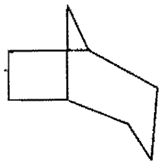
(a) [3.2.1]
(b) [3.1.0]
(c) [1.3.0]
(d) [2.1.0]

3. Select the correct statements about the following compounds:



(a) it is a tricyclic compound
(b) it is bicyclo compound
(c) it is spiro compound
(d) its IUPAC name is bicyclo [2.2.2] octane

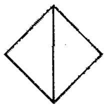
4. Match the List I with List II and select the correct answer from the given codes:

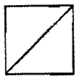
List I (Compounds)	List II (Number of carbons in the bridges)
A. 	(i) [3.2.1]
B. 	(ii) [4.3.0]
C. 	(iii) [4.4.0]
D. 	(iv) [3.2.0]

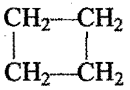
Codes:

(a) (A–ii); (B–iii); (C–iv); (D–i)
(b) (A–i); (B–ii); (C–iii); (D–iv)
(c) (A–iv); (B–iii); (C–ii); (D–i)
(d) (A–ii); (B–iv); (C–iii); (D–i)

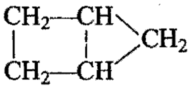
5. Which of the following is the correct structure of bicyclo [1.1.0] butane?

(a) 

(b) 

(c) 

$$\begin{array}{l}CH_2—CH_2\\ |\quad\quad\ \ |\\ CH_2—CH_2\end{array}$$

(d) 

$$\begin{array}{l}CH_2—CH\\ |\quad\quad\ \ |\quad >CH_2\\ CH_2—CH\end{array}$$

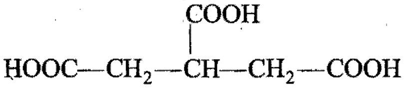
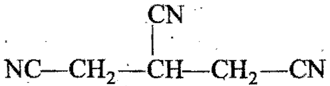
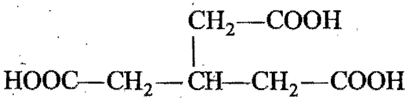
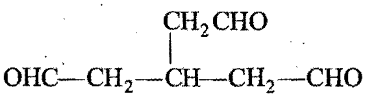
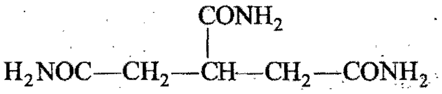
Passage 2

If the organic compound contains more than two similar terminal groups and all of them are directly attached to the principal chain, then none of them forms a part of the principal chain. Special suffixes are used to name these.

Functional group	Suffix
$—CONH_2$	Carboxamide
$—CN$	Carbonitrile
$—CHO$	Carbaldehyde
$—COOH$	Carboxylic acid

Carbon atoms of these terminal groups are not counted in the principal chain. If any one of these terminal groups is not directly attached to the parent chain and forms the part of side chain, then the longest chain is selected containing two such similar groups at its two ends. The groups present in the side chain are treated as substituents and are indicated by suitable prefixes.

Indicate whether the following IUPAC names are **true** (a) or **false** (b).

Compound	IUPAC Name
1.  $HOOC-CH_2-\overset{\overset{COOH}{\vert}}{CH}-CH_2-COOH$ True (a)	Propane-1,2,3-tricarboxylic acid False (b)
2.  $NC-CH_2-\overset{\overset{CN}{\vert}}{CH}-CH_2-CN$ True (a)	3-cyanopentane-1,5-dinitrile False (b)
3.  $HOOC-CH_2-\overset{\overset{CH_2-COOH}{\vert}}{CH}-CH_2-COOH$ True (a)	3-(carboxymethyl) pentane-1,5-dioic acid False (b)
4.  $OHC-CH_2-\overset{\overset{CH_2CHO}{\vert}}{CH}-CH_2-CHO$ True (a)	3-(formylmethyl) pentane-1,5-dial False (b)
5.  $H_2NOC-CH_2-\overset{\overset{CONH_2}{\vert}}{CH}-CH_2-CONH_2$ True (a)	Propane-1,2,3-tricarboxamide False (b)

Passage 3

The priorities for citing principal groups in a carboxylic acid derivative are as follows :

acid > anhydride > ester > acid halide > amide > cyanide

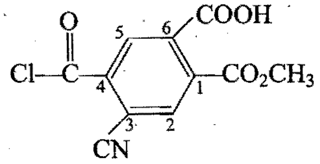
All of these groups have citation priority over aldehydes and ketones as well as the other functional groups.

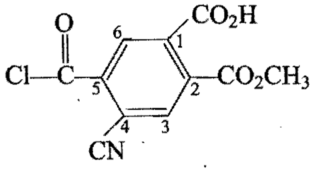
Name of carboxylic acid derivatives when used as substituent groups are :

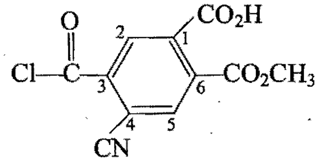
Group	Name
$-COOH$	carboxy
$-\overset{\overset{O}{\Vert}}{C}-OCH_3$	methoxy carbonyl
$-\overset{\overset{O}{\Vert}}{C}-OC_2H_5$	ethoxy carbonyl
$-CH_2-\overset{\overset{O}{\Vert}}{C}-OH$	carboxy methyl
$-O-\overset{\overset{O}{\Vert}}{C}-CH_3$	acetoxy
$-\overset{\overset{O}{\Vert}}{C}-Cl$	chloroformyl
$-\overset{\overset{O}{\Vert}}{C}-NH_2$	carbamoyl

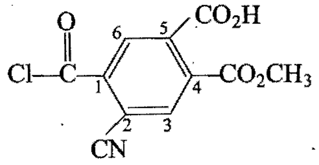
Answer the following questions:

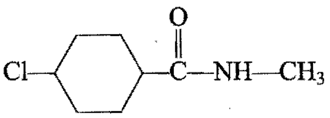
1. Which of the following structures has the correct locants?

(a) 

(b) 

(c) 

(d) 

2. 

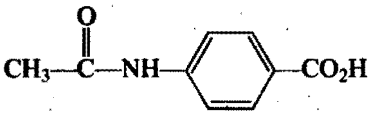
Which of the following is the correct IUPAC name of the above compound?

(a) *p*-acetamido chlorocyclohexane

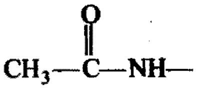
(b) 4-chloro-*N*-methylcyclohexane carboxamide

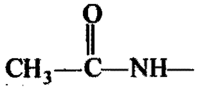
(c) *N*-methyl amido chlorocyclohexane

(d) none of the above

3. 

Which among the given statements is/are correct about the above compound?

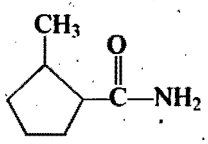
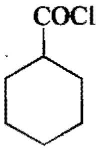
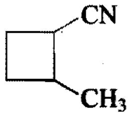
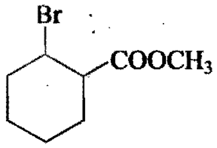
(a)  $CH_3-\overset{O}{\overset{\|}{C}}-NH-$ group is principal group

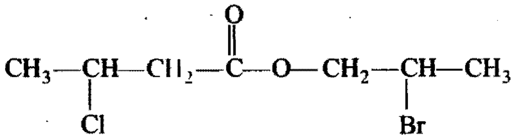
(b)  $CH_3-\overset{O}{\overset{\|}{C}}-NH-$ will be considered as substituent group

(c) Locant number 1 will be assigned to —COOH

(d) *p*-acetamidobenzoic acid is its systematic name

4. For which of the following compounds, the IUPAC name is wrong?

	Compound	IUPAC name
(a)		2-methyl cyclopentane carboxamide
(b)		Cyclohexaneoyl chloride
(c)		2-methylcyclobutane carbonitrile
(d)		Methyl,2-bromocyclohexane carboxylate

5. 

$$CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{Br}{\underset{|}{CH}}-CH_3$$

Select the correct IUPAC name among the following:

(a) 3-chlorobutyl-2-bromopropanoate

(b) 2-chlorobutyl-3-bromopropanoate

(c) 2-bromopropyl-3-chlorobutanoate

(d) β-bromopropyl-β-chlorobutyrate

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	1. (c)	2. (b)	3. (b,d)	4. (a)	5. (a,b)
Passage 2	1. (a)	2. (b)	3. (a)	4. (a)	5. (a)
Passage 3	1. (b)	2. (b)	3. (b,c,d)	4. (b)	5. (c)

4

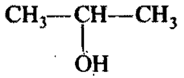
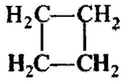
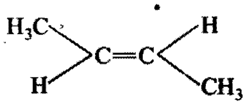
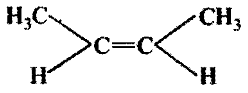
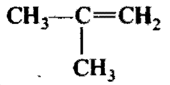
ISOMERISM

4.1 INTRODUCTION

The molecular structure of the organic compounds plays a very important role in the study of organic chemistry. There are numerous examples where it is observed that the same molecular formula can represent more than one compound having different properties. For example, ethyl alcohol and dimethyl ether have the same molecular formula (C_2H_6O) but show different physical and chemical properties.

Ethyl alcohol (C_2H_6O) CH_3CH_2OH	**Dimethyl ether (C_2H_6O) CH_3-O-CH_3**
1. It is a liquid.	It is a gas.
2. Its boiling point is 78°C.	Its boiling point is –24°C.
3. It reacts vigorously with sodium and evolves hydrogen.	It does not react with sodium.
4. It reacts with HI and forms ethyl iodide, C_2H_5I.	It reacts with HI and forms methyl iodide, CH_3I.

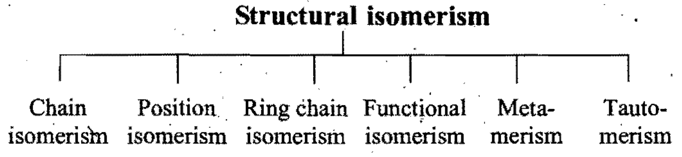
Some other examples are:

Molecular formula	**Some possible compounds**		
C_4H_{10}	$CH_3CH_2CH_2CH_3$ *n*-Butane ;	 $CH_3-\overset{\overset{CH_3}{\mid}}{CH}-CH_3$ Isobutane	
$C_2H_4O_2$	CH_3COOH Acetic acid ;	$HCOOCH_3$ Methyl formate	
$C_3H_6O_2$	CH_3CH_2COOH Propionic acid ;	$HCOOC_2H_5$ Ethyl formate ;	CH_3COOCH_3 Methyl acetate
C_3H_8O	$CH_3CH_2CH_2OH$ *n*-Propylalcohol ;	 $CH_3-\underset{\underset{OH}{\mid}}{CH}-CH_3$ Isopropylalcohol ;	$CH_3-O-C_2H_5$ Ethyl methyl ether
C_4H_8	$CH_3-CH_2-CH=CH_2$ But-1-ene ;	 Cyclobutane ;	$CH_3CH=CHCH_3$ But-2-ene
	 *Trans*-2-butene ;	 *Cis*-2-butene ;	 $CH_3-\underset{\underset{CH_3}{\mid}}{C}=CH_2$ 2-Methylpropene

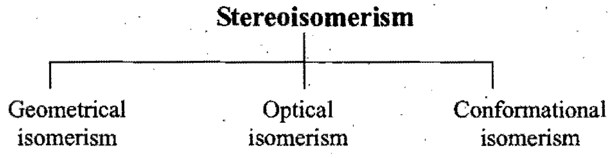
Such organic compounds having same molecular formula but differing from each other at least in some physical properties or chemical properties or both are known as isomers and the phenomenon is known as isomerism. The term isomer was first introduced by **Berzelius** (Greek : *Iso* = equal, *meros* = parts). The difference in properties of isomers is due to the difference in the relative arrangements of various atoms or groups present in their molecules. There are two main types of isomerism:

1. Structural isomerism or constitutional isomerism
2. Space or stereoisomerism

1. Structural isomerism : It is due to the difference in the manner in which the constituent atoms or groups are linked to one another within the molecule, without any reference to space. Structural isomers are compounds having same molecular formula but different structural formulae. Structural isomerism is further classified into different types:



2. Space or stereoisomerism : It is due to the difference in relative arrangement of atoms or groups in space. Stereoisomers are compounds having the same molecular and structural formulae, but different spatial arrangement of atoms or groups. The spatial arrangement of atoms or groups is also referred to as configuration of the molecule. It is further classified into three types :

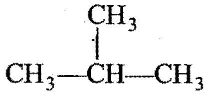


A brief review of various types of structural isomerism is given below:

4.2 CHAIN OR NUCLEAR ISOMERISM

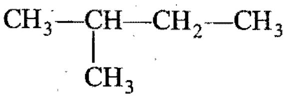
This type of isomerism is due to difference in the arrangement of carbon atoms constituting the chain, *i.e.*, straight or branched chain of carbon atoms. It is also known as **nuclear** or skeletal isomerism. The isomers showing chain isomerism belong to same homologous series. The simplest compound exhibiting this type of isomerism is of molecular formula C_4H_{10} (butane). It exists in two forms,

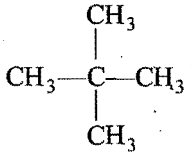
$CH_3CH_2CH_2CH_3$;
n-Butane (Butane)
(Straight carbon chain)


$CH_3-CH(CH_3)-CH_3$
Isobutane (2-Methylpropane)
(Branched carbon chain)

Pentane (C_5H_{12}) exists in three isomers,

$CH_3CH_2CH_2CH_2CH_3$;
n-Pentane (Pentane)

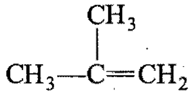

$CH_3-CH(CH_3)-CH_2-CH_3$
Isopentane (2-Methylbutane)


$CH_3-C(CH_3)_2-CH_3$
Neopentane
(2,2-Dimethylpropane)

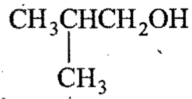
The number of theoretical possible isomers of a given formula increases rapidly with the increase of the number of carbon atoms. Thus, there are 5 hexanes, 9 heptanes, 18 octanes, 35 nonanes and 75 decanes.

Besides hydrocarbons, this type of isomerism is possible in other homologous series.

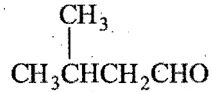
C_4H_8 $CH_3CH_2CH{=}CH_2$; But-1-ene


$CH_3-C(CH_3){=}CH_2$
2-Methylpropene

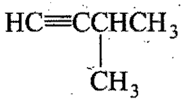
$C_4H_{10}O$ $CH_3CH_2CH_2CH_2OH$; Butan-1-ol


$CH_3CH(CH_3)CH_2OH$
2-Methylpropan-1-ol

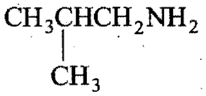
$C_5H_{10}O$ $CH_3CH_2CH_2CH_2CHO$; Pentanal


$CH_3CH(CH_3)CH_2CHO$
3-Methylbutanal

C_5H_8 $HC{\equiv}CCH_2CH_2CH_3$; Pent-1-yne


$HC{\equiv}CCH(CH_3)CH_3$
3-Methylbut-1-yne

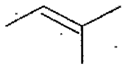
$C_4H_{11}N$ $CH_3CH_2CH_2CH_2NH_2$; Butan-1-amine


$CH_3CH(CH_3)CH_2NH_2$
2-Methylpropan-1-amine

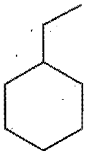
SOME SOLVED PROBLEMS

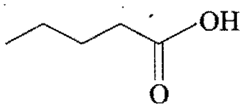
Example 1. *Select the pair of chain isomers among the following:*

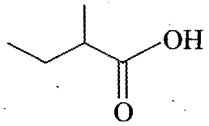
(*i*)

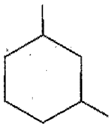

(*ii*)


(*iii*)


(*iv*)


(*v*)


(*vi*)


(*vii*)


(*viii*)


Solution: (ii) and (iii) ; (iv) and (vii); (v) and (vi); (i) and (viii).

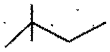
Example 2. *Write down all structural isomers of* C_6H_{14}. *Indicate chain and position isomers among them.*

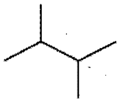
Solution:

(a) 
n-Hexane

(b) 
2-Methylpentane

(c) 
3-Methylpentane

(d) 
2,2-Dimethylbutane

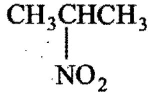
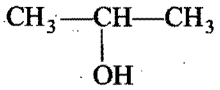
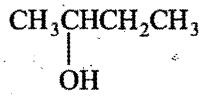
(e) 
2,3-Dimethylbutane

Chain isomers: (a), (b),(c), (d), (e)
Position isomers : (i) (b) and (c); (ii) (d) and (e)

4.3 POSITION ISOMERISM

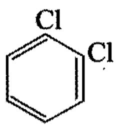
It is due to the difference in the positions occupied by the particular atom or group (substituents) in the same carbon chain or due to different positions of double or triple bonds in alkenes and alkynes.

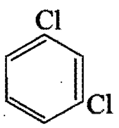
Examples :

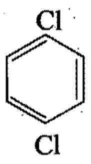
C_4H_8	$CH_3CH_2CH{=}CH_2$; But-1-ene	$CH_3CH{=}CHCH_3$ But-2-ene
C_4H_6	$CH_3CH_2C{\equiv}CH$; But-1-yne	$CH_3C{\equiv}CCH_3$ But-2-yne
C_3H_7Cl	$CH_3CH_2CH_2Cl$; 1-Chloropropane	$CH_3CHClCH_3$ 2-Chloropropane
$C_3H_7NO_2$	$CH_3CH_2CH_2NO_2$; 1-Nitropropane	 $CH_3CH(NO_2)CH_3$ 2-Nitropropane
C_3H_8O	$CH_3CH_2CH_2OH$; Propan-1-ol (*n*-Propyl alcohol)	 $CH_3{-}CH(OH){-}CH_3$ Propan-2-ol (Isopropyl alcohol)
$C_4H_{10}O$	$CH_3CH_2CH_2CH_2OH$; Butan-1-ol	 $CH_3CH(OH)CH_2CH_3$ Butan-2-ol

Note: Aldehydes, carboxylic acids (and their derivatives) and cyanides do not exhibit position isomerism.

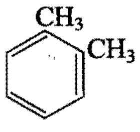
$C_6H_4Cl_2$

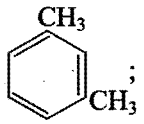

o-Dichloro-benzene ;

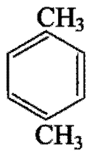

m-Dichloro-benzene ;


p-Dichlorobenzene

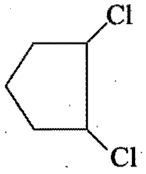
C_8H_{10}

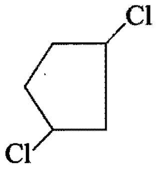

o-Xylene ;


m-Xylene ;


p-Xylene

$C_5H_8Cl_2$

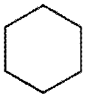
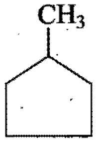
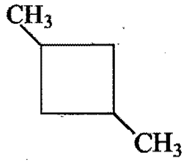

1,2 ;

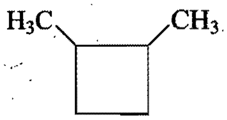
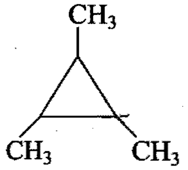

1,3

Dichlorocyclopentane

Example 3. *Give the possible cyclic isomers of formula* C_6H_{12}.

Solution :

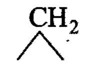

;

;

;

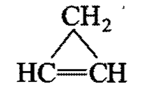

;


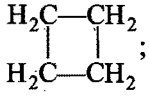
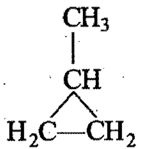
4.4 RING-CHAIN ISOMERISM

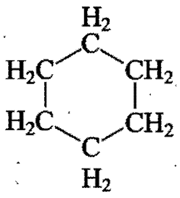
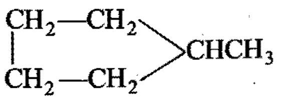
This type of isomerism is due to different modes of linking of carbon atoms, *i.e.*, the isomers possess either open chain or closed chain structures.

Examples :

C_3H_6 $CH_3{-}CH{=}CH_2$; Propene ;

Cyclopropane

C_3H_4 $CH_3{-}C{\equiv}CH$; Propyne ;

Cyclopropene

C_4H_8 $CH_3CH_2CH{=}CH_2$; But-1-ene ;

Cyclobutane ;

Methylcyclo-propane

C_6H_{12}

Cyclohexane ;

Methylcyclopentane

$CH_3CH_2CH_2CH_2CH=CH_2$
Hex-1-ene

It can be included in functional isomerism, if ring chain isomerism is not mentioned.

4.5 FUNCTIONAL ISOMERISM

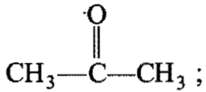
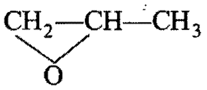
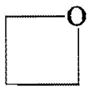
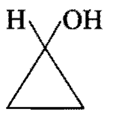
Compounds having same molecular formula but different functional groups in their molecules show functional isomerism and are called functional isomers. As the functional group determines largely the properties of a compound, such isomers differ in their physical and chemical properties.

Examples :

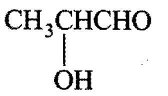
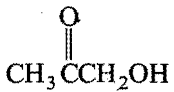
(i) Alcohols and Ethers ($C_nH_{2n+2}O$)

C_2H_6O	CH_3CH_2OH Ethyl alcohol	$H_3C—O—CH_3$ Dimethyl ether
C_3H_8O	$CH_3CH_2CH_2OH$ *n*-Propyl alcohol	$C_2H_5—O—CH_3$ Ethyl methyl ether
$C_4H_{10}O$	$CH_3CH_2CH_2CH_2OH$ *n*-Butyl alcohol	$C_2H_5—O—C_2H_5$ Diethyl ether

(ii) Aldehydes, Ketones and Unsaturated alcohols, Ethers and other Cyclic compounds . . . etc., ($C_nH_{2n}O$)

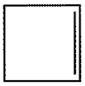
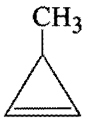
C_3H_6O	CH_3CH_2CHO Propionaldehyde	 $CH_3—\overset{\overset{O}{\Vert}}{C}—CH_3$ Acetone
	 1,2-Epoxy propane (2-Methyl oxirane)	$H_2C=CH—CH_2OH$ Prop-2-en-1-ol (Allyl alcohol)
 1,3-Epoxy propane (Oxetane)	$H_2C=CH—O—CH_3$ Methyl vinyl ether	 Cyclopropanol

(iii) Acids, Esters and Hydroxy carbonyl compounds . . . etc., ($C_nH_{2n}O_2$)

$C_2H_4O_2$	CH_3COOH Acetic acid	$HCOOCH_3$ Methyl formate
$C_3H_6O_2$	CH_3CH_2COOH Propionic acid	CH_3COOCH_3 Methyl acetate
	 $CH_3\underset{\underset{OH}{\vert}}{C}HCHO$ 2-Hydroxypropanal	 $CH_3\overset{\overset{O}{\Vert}}{C}CH_2OH$ 1-Hydroxy-propan-2-one

(iv) Alkynes Alkadienes and cycloalkenes (C_nH_{2n-2})

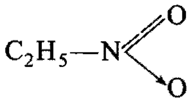
C_4H_6	$CH_3CH_2—C\equiv CH$ But-1-yne	$H_2C=CH—CH=CH_2$ Buta-1,3-diene
	$CH_3—C\equiv C—CH_3$ But-2-yne	$H_2C=C=CH—CH_3$ Buta-1,2-diene

 Cyclobutene	 3-Methyl cyclopropene	 1-Methyl cyclopropene

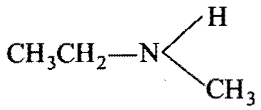
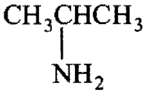
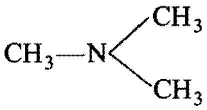
(v) Cyanides and Isocyanides (—CN and —NC)

C_2H_3N	CH_3CN Methyl cyanide	CH_3NC Methyl isocyanide

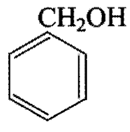
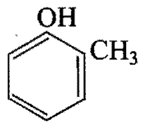
(vi) Nitro alkanes and Alkyl nitrites (—NO_2 and —O—N=O)

$C_2H_5NO_2$	 Nitroethane	$C_2H_5—O—N=O$ Ethyl nitrite

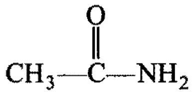
(vii) Amines (Primary, Secondary and Tertiary)

C_3H_9N	$CH_3CH_2CH_2NH_2$ Propan-1-amine	 *N*-Methylethanamine
	 $CH_3\underset{\underset{NH_2}{\vert}}{C}HCH_3$ Propan-2-amine	 *N*, *N*-Dimethyl-methanamine

(viii) Alcohols and Phenols

C_7H_8O	 Benzyl alcohol	 *o*-Cresol

(ix) Oximes and Amides

C_2H_5NO	$CH_3CH=NOH$ Acetaldoxime	 $CH_3—\overset{\overset{O}{\Vert}}{C}—NH_2$ Acetamide

(x) Thio alcohols and Thio ethers

C_2H_6S	C_2H_5SH Ethyl thioalcohol	$CH_3—S—CH_3$ Dimethyl thioether

4.6 METAMERISM

It is the isomerism in the same homologous series. It is due to the presence of different alkyl groups attached to the same polyvalent functional group or atom (*i.e.*, —O—, —S—, —NH— and —CO—). So, the compounds having same molecular formula but different structural formulae due to different (size or nature) alkyl groups on either side of the functional group are called metamers and the phenomenon is known as **metamerism.**

Examples :

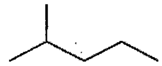
$C_4H_{10}O$	$C_2H_5OC_2H_5$ Diethyl ether	$C_3H_7OCH_3$ Methyl propyl ether

Solution: (ii) and (iii) ; (iv) and (vii); (v) and (vi); (i) and (viii).

Example 2. *Write down all structural isomers of* C_6H_{14}. *Indicate chain and position isomers among them.*

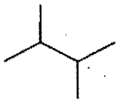
Solution:

(a) 
n-Hexane

(b) 
2-Methylpentane

(c) 
3-Methylpentane

(d) 
2,2-Dimethylbutane

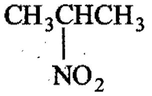
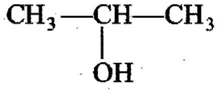
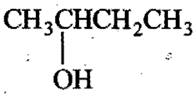
(e) 
2,3-Dimethylbutane

Chain isomers: (a), (b),(c), (d), (e)
Position isomers : (i) (b) and (c); (ii) (d) and (e)

4.3 POSITION ISOMERISM

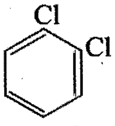
It is due to the difference in the positions occupied by the particular atom or group (substituents) in the same carbon chain or due to different positions of double or triple bonds in alkenes and alkynes.

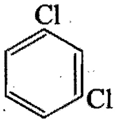
Examples :

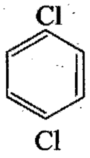
C_4H_8	$CH_3CH_2CH{=}CH_2$; But-1-ene	$CH_3CH{=}CHCH_3$ But-2-ene
C_4H_6	$CH_3CH_2C{\equiv}CH$; But-1-yne	$CH_3C{\equiv}CCH_3$ But-2-yne
C_3H_7Cl	$CH_3CH_2CH_2Cl$; 1-Chloropropane	$CH_3CHClCH_3$ 2-Chloropropane
$C_3H_7NO_2$	$CH_3CH_2CH_2NO_2$; 1-Nitropropane	 $CH_3\underset{\underset{NO_2}{\vert}}{C}HCH_3$ 2-Nitropropane
C_3H_8O	$CH_3CH_2CH_2OH$; Propan-1-ol (*n*-Propyl alcohol)	 $CH_3—\underset{\underset{OH}{\vert}}{CH}—CH_3$ Propan-2-ol (Isopropyl alcohol)
$C_4H_{10}O$	$CH_3CH_2CH_2CH_2OH$; Butan-1-ol	 $CH_3\underset{\underset{OH}{\vert}}{C}HCH_2CH_3$ Butan-2-ol

Note: Aldehydes, carboxylic acids (and their derivatives) and cyanides do not exhibit position isomerism.

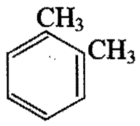
$C_6H_4Cl_2$

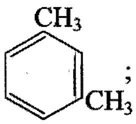
 ;
o-Dichloro-benzene

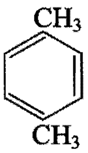
 ;
m-Dichloro-benzene


p-Dichlorobenzene

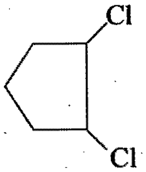
C_8H_{10}

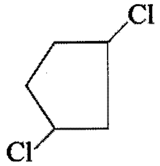
 ;
o-Xylene

 ;
m-Xylene


p-Xylene

$C_5H_8Cl_2$

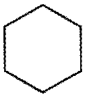
 ;
1,2

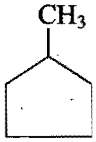

1,3

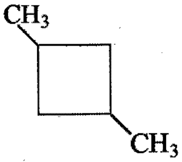
Dichlorocyclopentane

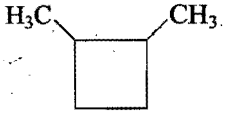
Example 3. *Give the possible cyclic isomers of formula* C_6H_{12}.

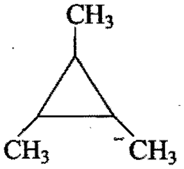
Solution :

 ;

 ;

 ;

 ;

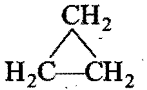


4.4 RING-CHAIN ISOMERISM

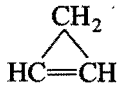
This type of isomerism is due to different modes of linking of carbon atoms, *i.e.*, the isomers possess either open chain or closed chain structures.

Examples :

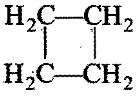
C_3H_6 $CH_3—CH{=}CH_2$; Propene

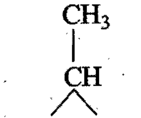

Cyclopropane

C_3H_4 $CH_3—C{\equiv}CH$; Propyne

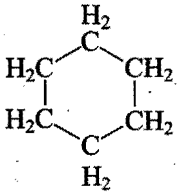

Cyclopropene

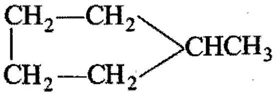
C_4H_8 $CH_3CH_2CH{=}CH_2$; But-1-ene

 ;
Cyclobutane


Methylcyclo-propane

C_6H_{12}

 ;
Cyclohexane


Methylcyclopentane

$CH_3CH_2CH_2CH_2CH{=}CH_2$
Hex-1-ene

It can be included in functional isomerism, if ring chain isomerism is not mentioned.

4.5 FUNCTIONAL ISOMERISM

Compounds having same molecular formula but different functional groups in their molecules show functional isomerism and are called functional isomers. As the functional group determines largely the properties of a compound, such isomers differ in their physical and chemical properties.

Examples :

(i) Alcohols and Ethers ($C_nH_{2n+2}O$)

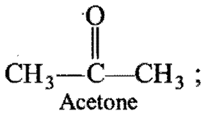
C_2H_6O CH_3CH_2OH ; $H_3C{-}O{-}CH_3$
Ethyl alcohol ; Dimethyl ether

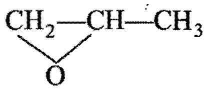
C_3H_8O $CH_3CH_2CH_2OH$; $C_2H_5{-}O{-}CH_3$
n-Propyl alcohol ; Ethyl methyl ether

$C_4H_{10}O$ $CH_3CH_2CH_2CH_2OH$; $C_2H_5{-}O{-}C_2H_5$
n-Butyl alcohol ; Diethyl ether

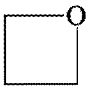
(ii) Aldehydes, Ketones and Unsaturated alcohols, Ethers and other Cyclic compounds . . . etc., ($C_nH_{2n}O$)

C_3H_6O CH_3CH_2CHO ;
Propionaldehyde

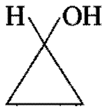

$CH_3{-}\overset{\overset{\Large O}{\|}}{C}{-}CH_3$;
Acetone


1,2-Epoxy propane
(2-Methyl oxirane)

; $H_2C{=}CH{-}CH_2OH$
Prop-2-en-1-ol
(Allyl alcohol)


1,3-Epoxy propane
(Oxetane)

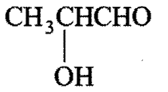
; $H_2C{=}CH{-}O{-}CH_3$;
Methyl vinyl ether

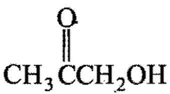

Cyclopropanol

(iii) Acids, Esters and Hydroxy carbonyl compounds . . . etc., ($C_nH_{2n}O_2$)

$C_2H_4O_2$ CH_3COOH ; $HCOOCH_3$
Acetic acid ; Methyl formate

$C_3H_6O_2$ CH_3CH_2COOH ; CH_3COOCH_3
Propionic acid ; Methyl acetate

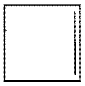

$\underset{\underset{\Large OH}{|}}{CH_3CHCHO}$;
2-Hydroxypropanal

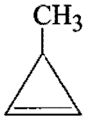

$CH_3\overset{\overset{\Large O}{\|}}{C}CH_2OH$
1-Hydroxy-propan-2-one

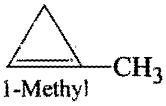
(iv) Alkynes Alkadienes and cycloalkenes (C_nH_{2n-2})

C_4H_6 $CH_3CH_2{-}C{\equiv}CH$; $H_2C{=}CH{-}CH{=}CH_2$
But-1-yne ; Buta-1,3-diene

$CH_3{-}C{\equiv}C{-}CH_3$; $H_2C{=}C{=}CH{-}CH_3$
But-2-yne ; Buta-1,2-diene


Cyclobutene ;


3-Methyl cyclopropene ;

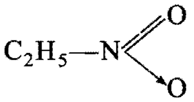

1-Methyl cyclopropene

(v) Cyanides and Isocyanides (—CN and —NC)

C_2H_3N CH_3CN ; CH_3NC
Methyl cyanide ; Methyl isocyanide

(vi) Nitro alkanes and Alkyl nitrites (—NO_2 and —O—N=O)

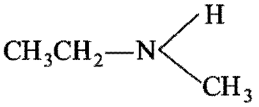
$C_2H_5NO_2$

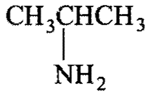

Nitroethane

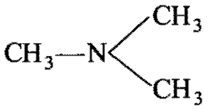
; $C_2H_5{-}O{-}N{=}O$
Ethyl nitrite

(vii) Amines (Primary, Secondary and Tertiary)

C_3H_9N $CH_3CH_2CH_2NH_2$;
Propan-1-amine

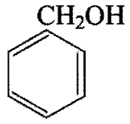

N-Methylethanamine

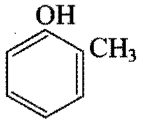

$\underset{\underset{\Large NH_2}{|}}{CH_3CHCH_3}$;
Propan-2-amine


N, *N*-Dimethyl-methanamine

(viii) Alcohols and Phenols

C_7H_8O


Benzyl alcohol ;


o-Cresol

(ix) Oximes and Amides

C_2H_5NO $CH_3CH{=}NOH$;
Acetaldoxime


$CH_3{-}\overset{\overset{\Large O}{\|}}{C}{-}NH_2$
Acetamide

(x) Thio alcohols and Thio ethers

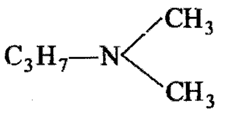
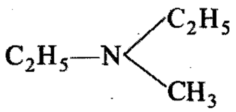
C_2H_6S C_2H_5SH ; $CH_3{-}S{-}CH_3$
Ethyl thioalcohol ; Dimethyl thioether

4.6 METAMERISM

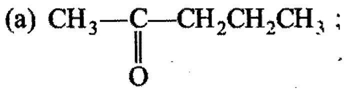
It is the isomerism in the same homologous series. It is due to the presence of different alkyl groups attached to the same polyvalent functional group or atom (*i.e.*, —O—, —S—, —NH— and —CO—). So, the compounds having same molecular formula but different structural formulae due to different (size or nature) alkyl groups on either side of the functional group are called metamers and the phenomenon is known as **metamerism.**

Examples :

$C_4H_{10}O$ $C_2H_5OC_2H_5$; $C_3H_7OCH_3$
Diethyl ether ; Methyl propyl ether

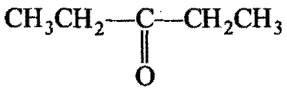
$C_4H_{10}S$	$C_2H_5-S-C_2H_5$; Diethyl thioether	$C_3H_7-S-CH_3$ Methyl propyl thioether
$C_5H_{10}O$	$C_2H_5COC_2H_5$; Diethyl ketone	$C_3H_7COCH_3$ Methyl propyl ketone
$C_4H_{11}N$	$C_2H_5-NH-C_2H_5$; Diethyl amine	$C_3H_7-NH-CH_3$ Methyl propyl amine
$C_5H_{13}N$	 $C_3H_7-N(CH_3)_2$; Dimethyl propyl amine	 $C_2H_5-N(C_2H_5)(CH_3)$ *N*-Ethyl-*N*-methyl ethanamine
$C_6H_{15}N$	$C_3H_7-NH-C_3H_7$; Dipropyl amine	$C_2H_5-NH-C_4H_9$ Butylethyl amine

If same polyvalent functional group is there in two or more organic compounds, then never write chain or position isomerism, it will be metamerism, *e.g.*,

(a) 

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_2CH_3$;

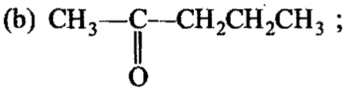
(Pentan-2-one)



$CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

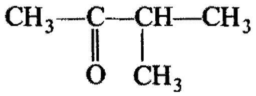
(Pentan-3-one)

are metamers and not position isomers. They can be included in position isomerism, if metamerism is not mentioned.

(b) 

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_2CH_3$;

(Pentan-2-one)



$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(3-Methyl butan-2-one)

are metamers and not chain isomers.

4.7 TAUTOMERISM

This is a special type of functional isomerism where the isomers exist simultaneously in equilibrium with each other. The term **tautomerism** (Greek : *tauto* = same; *meros* = parts) was used by **Laar** in 1885 to describe the phenomenon of a substance reacting chemically according to two possible structures.

The type of isomerism in which a substance exists in two readily interconvertible different structures leading to dynamic equilibrium is known as tautomerism and the different forms are called tautomers (or tautomerides). It is caused by the wandering nature (1,2 or mainly 1,3-migration) of mobile hydrogen atom between two polyvalent atoms within the same molecule. It is also known as **desmotropism**(*desmos* = bond; *tropos* = turn). If the hydrogen atom oscillates between two polyvalent atoms linked together, the system is a **dyad** and if the hydrogen atom travels from first to third in a chain, the system is a **triad.**

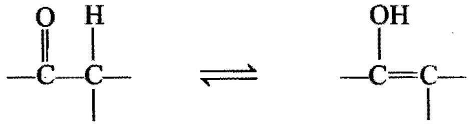
1. Hydrocyanic acid is an example of **dyad** system in which hydrogen atom oscillates between carbon and nitrogen atoms.

$$H-C\equiv N \rightleftharpoons C\overset{\leftarrow}{\equiv}N-H$$

2. Triad system :

(i) Keto-enol system : Polyvalent atoms are oxygen and two carbon atoms.

Examples :



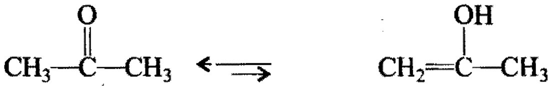
$-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{\underset{|}{C}}- \rightleftharpoons -\overset{\overset{OH}{|}}{C}=\underset{|}{C}-$

(Keto) (Bond energy, 361 kcal) (Enol) (Bond energy. 343 kcal)

The keto form is more stable (by about 18 kcal/mol) than the enolic form.

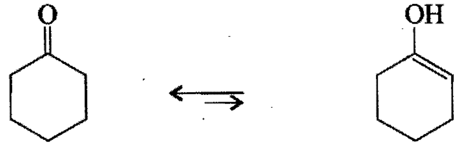
$CH_3-\overset{\overset{O}{\|}}{C}-H \rightleftharpoons CH_2=\overset{\overset{OH}{|}}{C}-H$

Acetaldehyde (Keto form, 100%) Vinyl alcohol (Enolic form, negligible amount)



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_2=\overset{\overset{OH}{|}}{C}-CH_3$

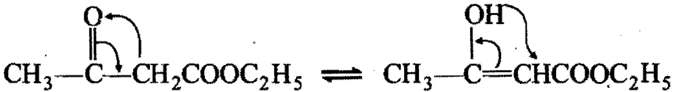
Acetone (Keto form, 100%) Prop-1-en-2-ol (Enolic form, negligible amount)



Cyclohexanone (Keto form, 99%) Cyclohex-1-en-1-ol (Enolic form, 1%) .

The greater stability of keto form than the enol form in all these examples is due to greater strength of C—O, π-bond (87 kcal/mol) as compared to C—C, π-bond (60 kcal/mol).

(a) Acetoacetic ester (Ethyl acetoacetate) :

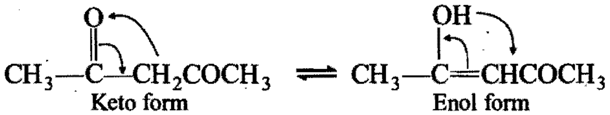


$CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CHCOOC_2H_5$

Keto form Enol form

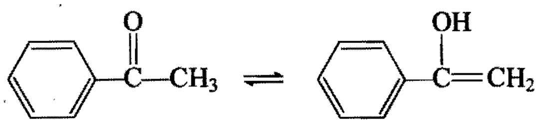
Acetoacetic ester gives certain reactions showing the presence of keto group (reactions with HCN, H_2NOH, $H_2NNHC_6H_5$, etc.) and certain reactions showing the presence of enolic group (reactions with Na, CH_3COCl, NH_3, PCl_5, Br_2 water and colour with neutral $FeCl_3$, etc.).

(b) Acetyl acetone :



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2COCH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CHCOCH_3$

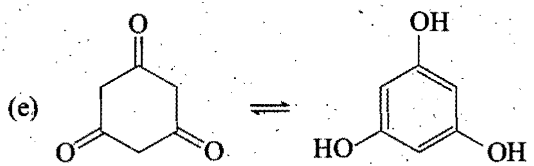
Keto form Enol form

(c) 

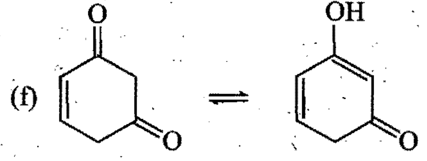
Keto form Enol form

(d) 

Enol form Keto form

(e) 

Keto form Enol form

(f) 

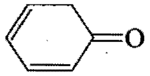
Enolisation: The conversion of keto form into enol form is known as enolisation. The enolisation of a compound has been found to depend upon various factors such as structural factor (Resonance and hydrogen bonding), the temperature and nature of solvent. Experimentally the percentage of enol form has been found to increase in the order:

Simple aldehydes and ketones < β-keto ester < β-diketones having phenyl group < phenols.

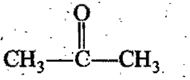
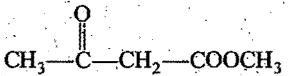
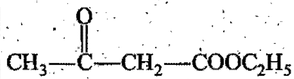
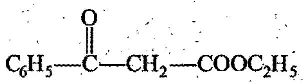
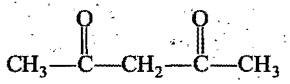
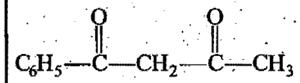
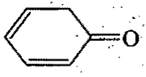
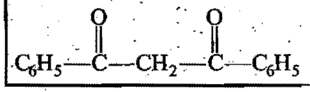
This is because of the fact that there occurs increasingly stabilisation of enol forms of the above type of compounds by resonance and hydrogen bonding than their corresponding keto forms.

Enolisation is in order:

$CH_3COCH_3 < CH_3COCH_2COOC_2H_5 < C_6H_5COCH_2COOC_2H_5 < CH_3COCH_2COCH_3 < CH_3COCH_2COCH_3$

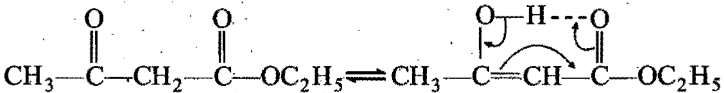
< 

Percentage of enol content in some compounds

Compound	Enol (in %)
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	0.00025
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-COOCH_3$	4.8
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-COOC_2H_5$	7.7
 $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2-COOC_2H_5$	21.0
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$	80.4
 $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$	89.2
	99.99
 $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-C_6H_5$	100.0

Stability of keto and enol forms

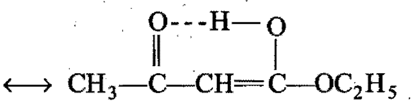
In acetaldehyde and acetone, the amounts of enolic forms are almost negligible. However, if the two keto groups of a compound are separated by methylene group, then enolic form becomes more stable by intramolecular hydrogen bonding (chelation). For example, in acetoacetic ester, the amount of enolic form is about 7%.



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \rightleftharpoons CH_3-C{=}CH-\overset{\overset{O}{\|}}{C}-OC_2H_5$

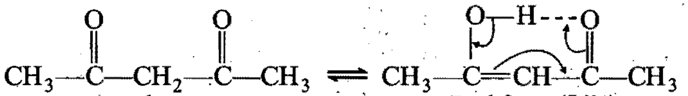
Acetoacetic ester
(1,3-Dicarbonyl compound)
Keto form, (93%)

Enolic form, (7%)



$\longleftrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH{=}C-OC_2H_5$

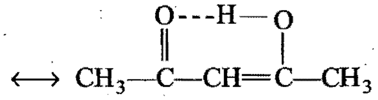
But in acetylacetone (1,3-diketone), the amount of enolic form here is much higher (76%) than even in acetoacetic ester. This is because the keto group is much more electron withdrawing in nature than the ester group.



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-C{=}CH-\overset{\overset{O}{\|}}{C}-CH_3$

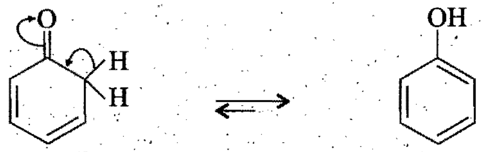
Acetyl acetone
Keto form, (24%)

Enol form, (76%)



$\longleftrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH{=}C-CH_3$

If the enolic form besides H-bonding is also stabilised by conjugation, (*i.e.*, enolic double bond is in conjugation with another double bond or a multiple bond or a benzene ring) the enol content further increases. Thus, the only form which is exhibited in phenol is enolic form.



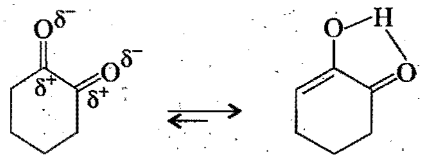
Cyclohexa-2,4-dien-1-one
(Keto form, negligible amount)

Phenol
(Enolic form, totally)

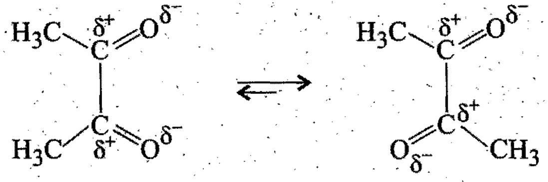
Therefore, higher the stability of the enol form, greater is the enol content.

Enol content of 1,2-cyclohexanedione (99%) is more than the biacetyl (0.0056%). This can be explained as follows:

1,2-cyclohexanedione (cyclic structure) has two keto groups with their dipole pointing in the same direction (syn-conformation). Therefore, the enol form has strong intramolecular H-bonding resulting into increased enol content.



(Keto) (Enol)



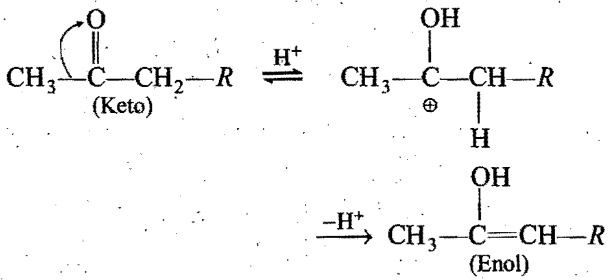
Biacetyl on the other hand can reduce similar repulsion (anti-conformation) by a simple rotation around sigma bond connecting the keto groups.

Effect of solvent on keto-enol contents

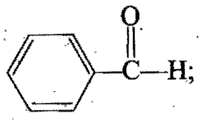
Solvation causes change in entropy effect which is depending on the nature of solvent. In polar (protic) solvents, such as water, alcohol, acetic acid, etc., which form H-bonds with the >C=O group of keto form, decrease the enol content. On the other hand, in non-polar (aprotic) solvents such as benzene or hexane etc. (or even in absence of solvent) there occurs an increase in the enol content in a keto-enol system. For example, enol content of acetoacetic ester is 7% in methanol, 46% in hexane, 0.4% in water and 20% in toluene etc.

Steric factor: For example, the enol content of α-methyl acetyl acetone (44% in gas phase) is much lower than that of acetyl acetone (92% in gas phase). The enol form of α-methyl form has greater internal strain.

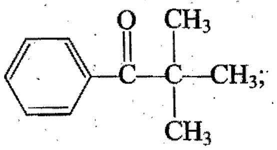
Acid catalysed conversion:



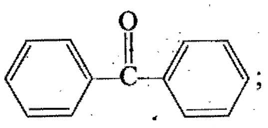
Essential condition for tautomerism : Aldehydes and ketones having atleast one α-hydrogen atom show keto-enol tautomerism. Following compounds do not show tautomerism.



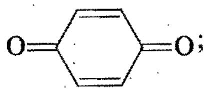
Benzaldehyde



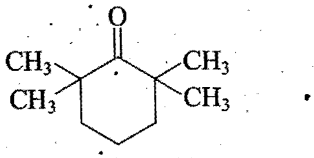
Tert. butyl phenyl ketone



Benzophenone

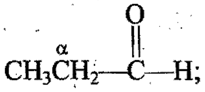


p-Benzoquinone



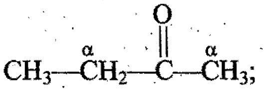
2,2,6,6-Tetramethylcyclohexan-1-one

Thus, propanal, butan-2-one and acetophenone having α-hydrogen atom show keto-enol tautomerism.



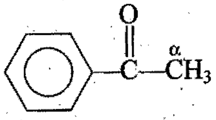
$\overset{\alpha}{CH_3CH_2}-\overset{O}{\overset{\|}{C}}-H$;

Propanal



$CH_3-\overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-\overset{\alpha}{CH_3}$;

Butan-2-one

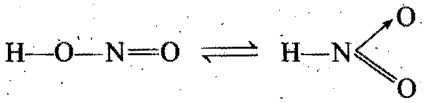


Acetophenone

(ii) Triad system containing nitrogen :

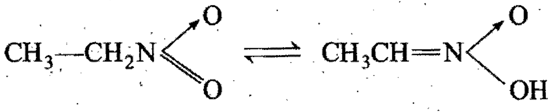
Examples :

(a) Nitrite-nitro system :



Nitrite form Nitro form

(b) Nitro-acinitro system :



Nitro form Aci form

(c) Nitroso-oxime tautomerism

$R_2CH-N=O \rightleftharpoons R_2C=NOH$

Nitroso Oxime (isonitroso)

(d) Imine-enamine tautomerism

$CH_3-CH_2-CH=NH \rightleftharpoons CH_3-CH=CH-NH_2$

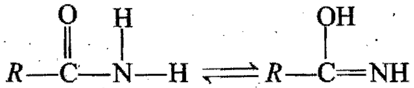
Imine Enamine

(e) Azo-hydrazone tautomerism

$R_2CH-N=N-R \rightleftharpoons R_2C=N-NHR$

Azo form Hydrazone

(f) Amide-imidol tautomerism



$R-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-H \rightleftharpoons R-\overset{OH}{\overset{|}{C}}=NH$

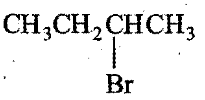
Amide Imidol

Example 4. *Write possible isomers having molecular formulae (a)* C_4H_9Br *(b)* $C_3H_6O_2$. *Give their IUPAC names.*

Solution : (a) (i) $CH_3CH_2CH_2CH_2Br$

1-Bromobutane

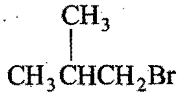
(ii)



$CH_3CH_2\underset{Br}{\underset{|}{C}}HCH_3$

2-Bromobutane

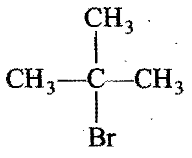
(iii)



$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2Br$

1-Bromo-2-methyl propane

(iv)



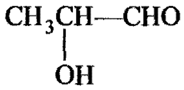
$CH_3-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

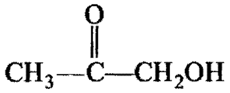
2-Bromo-2-methylpropane

(b) (i) CH_3CH_2COOH (ii) CH_3COOCH_3

Propanoic acid Methyl ethanoate

(iii) $HCOOC_2H_5$
Ethyl methanoate

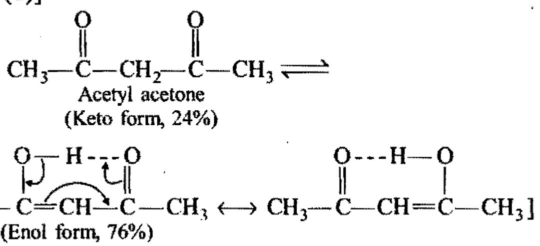
(iv) 
$CH_3CH(OH)—CHO$
2-Hydroxypropanal

(v) 
$CH_3—C(=O)—CH_2OH$
1-Hydroxypropan-2-one

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Which of the following is a dynamic isomerism?
(a) Metamerism (b) Geometrical isomerism
(c) Tautomerism (d) Optical isomerism
[**Ans.** (c)]

2. Enol content is maximum in:
(a) acetone (b) acetophenone
(c) acetic acid (d) acetylacetone
[**Ans.** (d)]

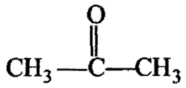
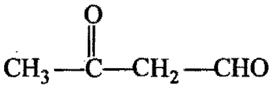
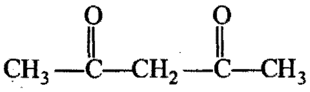
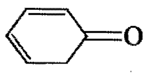
[**Hint:** 

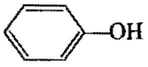
]

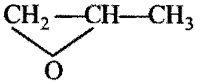
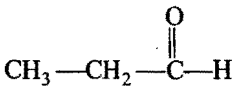
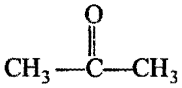
3. Cyclobutane and but-2-ene are the examples of:
(a) position isomerism (b) ring chain isomerism
(c) metamerism (d) geometrical isomerism
[**Ans.** (b)]

4. Which of the following are examples of metamerism?
(a) Ethoxy ethane and 1-methoxy propane
(b) Pentan-2-one and pentan-3-one
(c) N-Methyl propan-1-amine and N-ethyl ethanamine
(d) All of the above
[**Ans.** (d)]

5. *n*-propyl alcohol and isopropyl alcohol are:
(a) position isomers (b) chain isomers
(c) tautomers (d) geometrical isomers
[**Ans.** (a)]

6. Maximum enolisation takes place in:
(a) 
$CH_3—C(=O)—CH_3$
(b) 
$CH_3—C(=O)—CH_2—CHO$
(c) 
$CH_3—C(=O)—CH_2—C(=O)—CH_3$
(d) 
[**Ans.** (d)]

[**Hint:**  will be most stable enol form due to resonance.]

7. Which of the following is(are) an isomer of compound (i)?
(i) 
(ii) 
$CH_3—CH_2—C(=O)—H$
(iii) 
$CH_3—C(=O)—CH_3$
(iv) $CH_3—CH{=}CH—OH$
(a) (ii) (b) (iv)
(c) (ii) and (iii) (d) all of these
[**Ans.** (d)]
[**Hint:** All are structural isomer to each other.]

8. Metamers of ethyl propionate are: **[UPSEE (Engg.) 2007]**
(a) C_4H_9COOH and $HCOOC_4H_9$
(b) C_4H_9COOH and CH_3COOC_3H
(c) CH_3COOCH_3 and $CH_3COOC_3H_7$
(d) $CH_3COOC_3H_7$ and $C_3H_7COOCH_3$
[**Ans.** (d)]

Double bond equivalent or the Index number

With the help of double bond equivalent, the problems on structural isomerism may be easily solved.

$$\text{D.B.E.} = \frac{\Sigma n(v-2)}{2} + 1$$

where n = number of different kinds of atoms present in the molecule,
v = valency of each atom.

e.g., C_4H_6 : $\text{D.B.E.} = \frac{4\times(4-2)+6\times(1-2)}{2}+1$

$$= \frac{8-6}{2}+1 = 2$$

Thus, the compound may contain (i) two double bonds or a triple bond, (ii) one ring and one double bond, (iii) two rings.

Example 5. *Write all the cyclic and acyclic isomers having the molecular formula* C_3H_6O.

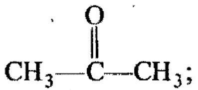
Solution:

$$\text{D.B.E.} = \frac{3\times(4-2)+6\times(1-2)+1\times(2-2)}{2}+1$$

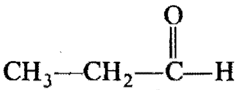
$$= \frac{6-6+0}{2}+1 = 1$$

Thus, molecule may contain a double bond (C=C, or C=O) or a ring. It's possible isomers are:

(a) Acyclic isomers


$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$;

Acetone


$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

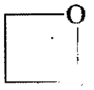
Propanal

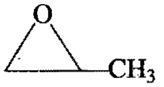
$CH_2{=}CHCH_2OH$; $CH_2{=}CH-O-CH_3$

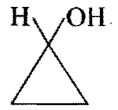
Prop-2-en-1-ol (Allyl alcohol)

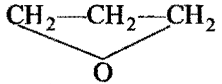
Methoxy ethene (Methyl vinyl ether)

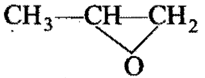
(b) Cyclic isomers


Oxetane or


Propyleneoxide or


Cyclopropanol


1,3-Epoxypropane


1,2-Epoxypropane

Thus, there are total seven isomers.

Note: For writing the structural isomers for any given molecular formula, tautomers are neglected unless otherwise asked for.

4.8 GEOMETRICAL ISOMERISM

A double bond between two carbon atoms consists one sigma (σ) bond and one pi (π) bond. Both the carbon atoms are sp^2-hybridized, giving three hybrid orbitals each. One *p*-orbital of each of the carbon atoms is left as such, *i.e.*, it does not take part in hybridization. The sigma bond between the two carbon atoms is formed by overlap of one hybrid orbital of each of the carbon atom, while π-bond is formed by the overlap of one *p*-orbital of each carbon atom.

Like the *p*-orbitals, a π-bond has two lobes. One half of the π-bond lies above the plane containing the two nuclei and other half lies below the plane (The two carbon atoms and four hybrid orbitals lie in the same plane while the lobes of π-bond lie above and below this plane). **Rotation around π-bond is not possible.** If any attempt is made to rotate one of the carbon atoms, the lobes of *p*-orbitals will no longer remain coplanar, *i.e.*, no parallel overlap will be possible and thus, π-bond will break and it requires the energy of the order of 251 kJ. This is known as **concept of restricted rotation.** In other words, the presence of π-bond makes the position of two carbon atoms rigid, *i.e.*, fixed with respect of each other. The restriction in rotation makes the position of four groups attached to two carbon atoms (two groups linked to each carbon atom utilising hybrid orbitals) fixed in space and is responsible for space isomerism known as geometrical isomerism.

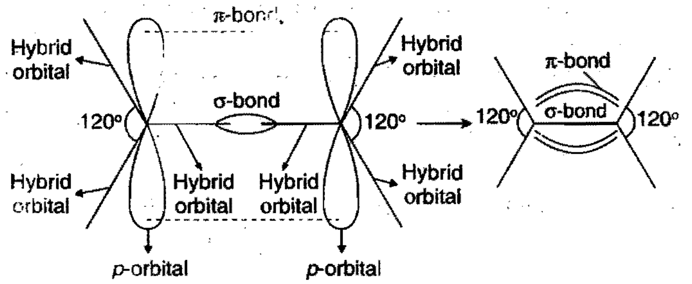
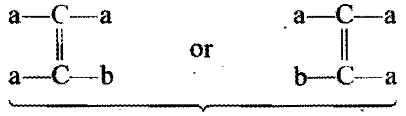


Fig. 4.1 Formation of double bond

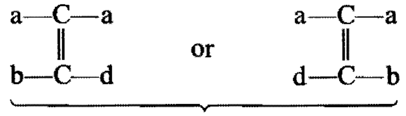
So, in general, the geometrical isomerism is shown by alkenes or their derivatives in which two different atoms or groups are attached to each carbon containing double bond and carbon atoms joined by double bond cannot rotate freely.

Let us consider now the various groups linked to two carbon atoms joined by a double bond.

1st Case: When two groups attached to a carbon atom are same,



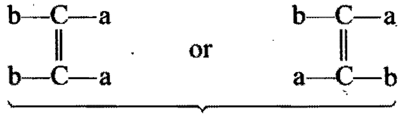
(I)
Both the structures are identical



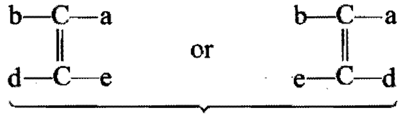
(II)
Both the structures are identical

Geometrical figures in (I) and (II) will be identical, hence, no geometrical isomers are possible.

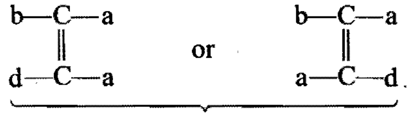
2nd Case: When two groups attached to a carbon atom are different,



(III)
Non-identical



(IV)
Non-identical



(V)
Non-identical

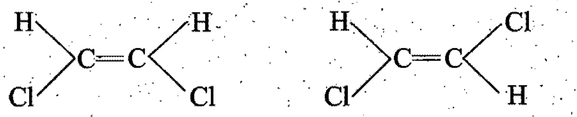
The two geometrical figures [as shown in (III), (IV) and (V)] will be different and hence, geometrical isomers are possible.

Such isomers, which possess the same molecular and structural formula but differ in the arrangement of atoms or groups in space due to hindered rotation around the double bonded atoms, (*i.e.*, $>C{=}C$, $>C{=}N$ and $-N{=}N$) are known as geometrical isomers and the phenomenon is known as geometrical isomerism. The isomer which has similar groups on the same side of the double bonded carbon is called '*cis*' isomer (Latin : *cis* = same side) and the isomer which has similar groups on the opposite side of the double bond is known as '*trans*' isomer (Latin : *trans* = across). However, in cases where all the four groups are different (abC=Cde), it is not possible to decide the *cis* and *trans* isomers.

The compounds like, 1,2-disubstituted alkenes and unsaturated dibasic acids are capable of showing geometrical isomerism.

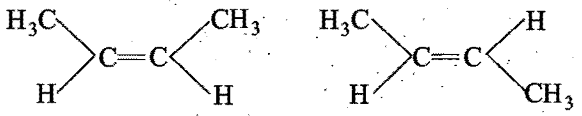
Examples : (a) *Cis* and *Trans* :

(i) 1,2-Dichloroethene



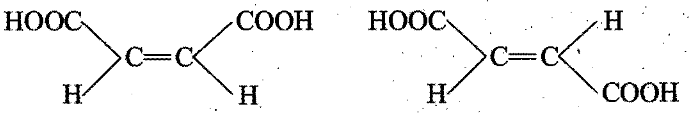
(*Cis*) (*Trans*)

(ii) But-2-ene ($CH_3CH=CHCH_3$)



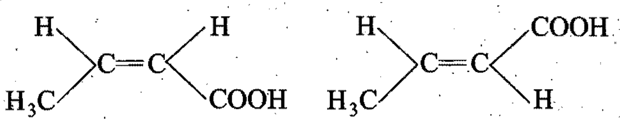
(*Cis*) (*Trans*)

(iii) Maleic and fumaric acids



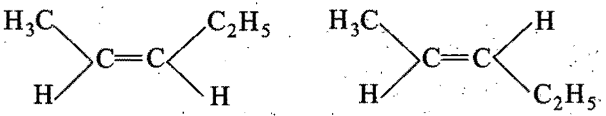
Maleic acid (*Cis*) Fumaric acid (*Trans*)

(iv) Crotonic acid and isocrotonic acid



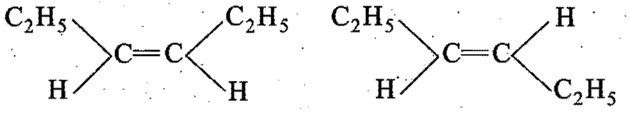
Isocrotonic acid (*Cis*) Crotonic acid (*Trans*)

(v) Pent-2-ene



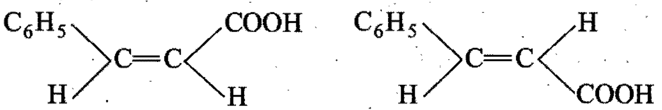
(*Cis*) (*Trans*)

(vi) Hex-3-ene



(*Cis*) (*Trans*)

(vii) Cinnamic acid



(*Cis*) (*Trans*)

(b) Geometrical isomerism in compounds containing C=N and N=N bonds: In addition to alkenes compounds containing C=N (aldoxime and ketoxime) and N=N (azo compounds) bonds also show geometrical isomerism. However, in these cases, 'syn' (for *cis*) and 'anti' (for *trans*) are more commonly used.

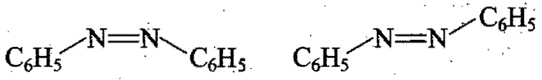
In aldoximes, when —H and —OH groups are on the same side of the double bond, the isomer is known as 'syn' (analogous to *cis*) and when these groups are on opposite sides of the double bond, the isomer is known as 'anti' (analogous to *trans*).

(i)

$$C_6H_5-\underset{\underset{N-OH}{\|}}{C}-H \qquad C_6H_5-\underset{\underset{HO-N}{\|}}{C}-H$$

Syn-benzaldoxime (α), m.pt. = 35°C Anti-benzaldoxime (β), m.pt. = 30°C

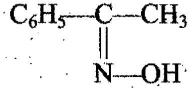
(ii) Similarly, azocompounds are also named



Syn-azobenzene Anti-azobenzene

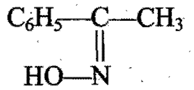
In ketoxime, the prefixes 'syn' and 'anti' indicate the relationship of first group named with respect to —OH group,

(iii)



$$C_6H_5-\underset{\underset{N-OH}{\|}}{C}-CH_3$$

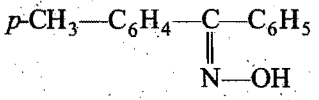
Syn-methyl phenylketoxime
Anti-phenyl methylketoxime



$$C_6H_5-\underset{\underset{HO-N}{\|}}{C}-CH_3$$

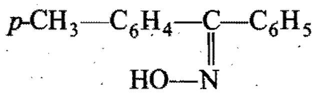
Syn-phenyl methylketoxime
Anti-methyl phenylketoxime

(iv)



$$p\text{-}CH_3-C_6H_4-\underset{\underset{N-OH}{\|}}{C}-C_6H_5$$

Syn-phenyl *p*-tolylketoxime
Anti-*p*-tolyl phenylketoxime



$$p\text{-}CH_3-C_6H_4-\underset{\underset{HO-N}{\|}}{C}-C_6H_5$$

Syn-*p*-tolyl phenylketoxime
Anti-phenyl *p*-tolylketoxime

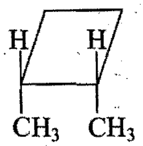
All aromatic ketoximes do not show geometrical isomerism, *e.g.*, $(C_6H_5)_2C=NOH$, benzophenone oxime having two similar aryl groups does not show geometrical isomerism.

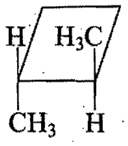
(c) Alicyclic compounds: Geometrical isomerism is also exhibited by disubstituted cyclic compounds which may have hindered rotation due to the reasons other than the presence of double bonds. Thus, alicyclic compounds because of their rigid ring structures also exhibit hindered rotation and geometrical isomerism.

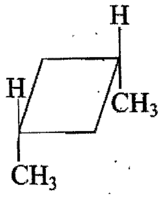
Examples: (i) Cyclopropane 1,2-dicarboxylic acid

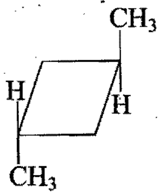
(*Cis*) (*Trans*)

(ii) Cyclobutane 1, 2 and cyclobutane 1, 3-dimethyl derivative

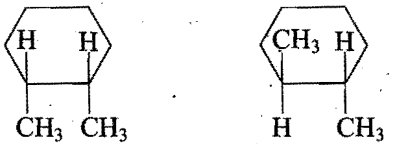

(*Cis*)


(*Trans*)

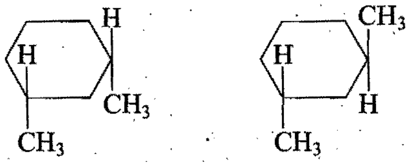

(*Cis*)


(*Trans*)

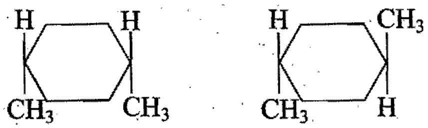
(iii) In contrast cyclohexane shows three position isomers (1,2; 1,3; 1,4-) each has two geometrical forms, *e.g.*,


(*Cis*) (*Trans*)

1,2-Dimethyl cyclohexane

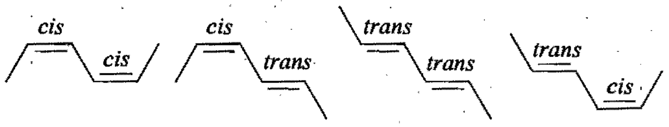

(*Cis*) (*Trans*)

1,3-Dimethyl cyclohexane


(*Cis*) (*Trans*)

1,4-Dimethyl cyclohexane

(d) Alkadienes: For example, hexa-2,4-diene shows different *cis* and *trans* isomers.



Physical properties of *cis-trans* isomers :

(i) melting point : m.p. of *trans*-isomer is more than that of *cis*-isomer.

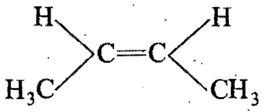
(ii) boiling point : b.p. of *cis*-isomer is more than that of *trans*-isomer.

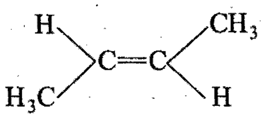
(iii) solubility : The solubility viscosity and refractive index of *cis*-isomer is more than the *trans* isomer in a given solvent.

(iv) dipole moment : In general *cis*-isomer has higher dipole moment than *trans*-isomer as *cis*-isomer of an alkene is found to be more polar than the *trans*-isomer.

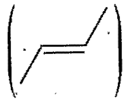
(v) Stability : In general, *trans*-isomer is more stable but less reactive than *cis*-isomers. The stearic repulsion of the groups (same) makes the *cis*-isomer less stable and more reactive than the *trans*-isomer. For example,

But-2-ene :

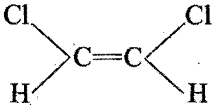

b.pt. = 277 K
(*Cis*)
$\mu = 0.33D$

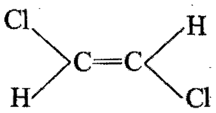

b.pt. = 274 K
(*Trans*)
$\mu = 0.00\,D$


(*Cis*)

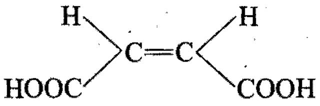

(*Trans*)

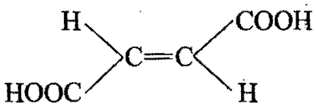
1,2-Dichloroethene:


b.pt. = 333.3 K
(*Cis*)
$\mu = 1.85D$


b.pt. = 320.5 K
(*Trans*)
$\mu = 0.00\,D$

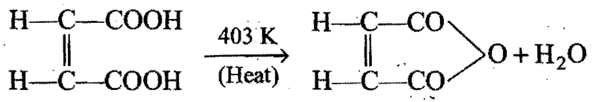
Maleic acid and fumaric acid :


Maleic acid (*cis*-)
m.pt. = 403 K
(Solubility 79 g/100 ml H_2O)


Fumaric acid (*trans*-)
m.pt. = 575 K
(Solubility of 0.7g/100ml H_2O)

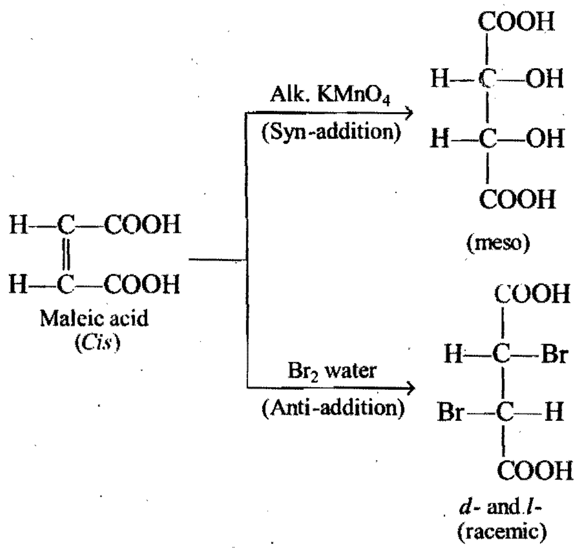
Cis-trans isomers are configuration isomers and called **diastereomers** as they are not mirror images of each other.

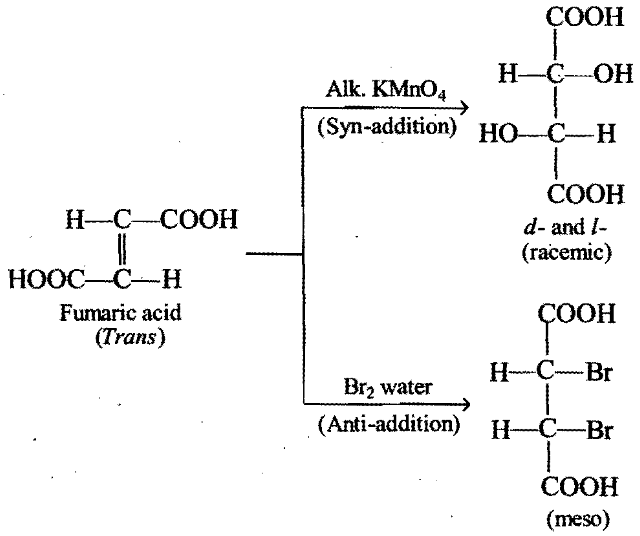
***Cis-trans* isomers have similar but not identical chemical properties.** For example, maleic acid (*cis*-isomer) forms anhydride on heating while fumaric acid (*trans*-isomer) does not give anhydride. This means that in maleic acid, the two —COOH groups are on the same side of double bond and on this basis the configuration of maleic and fumaric acid can be established.

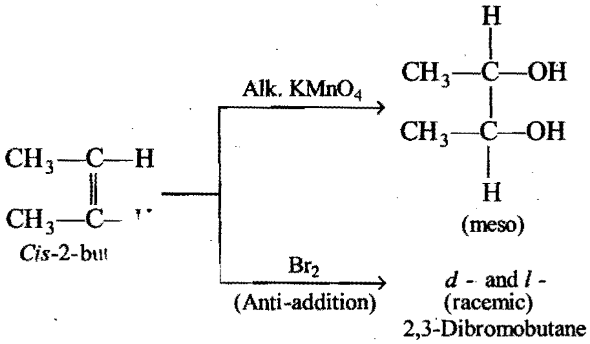


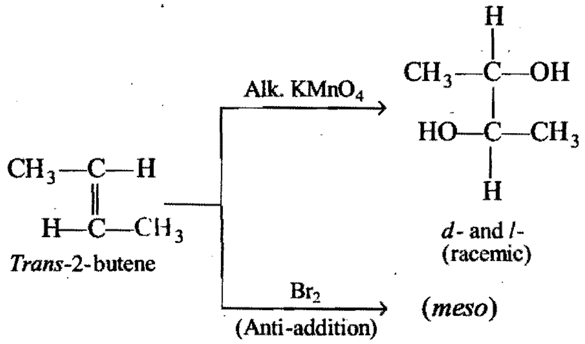
(*Cis*) Maleic acid Maleic anhydride

Further *cis*- and *trans*- isomers behave differently towards alkaline $KMnO_4$ and Br_2 water.



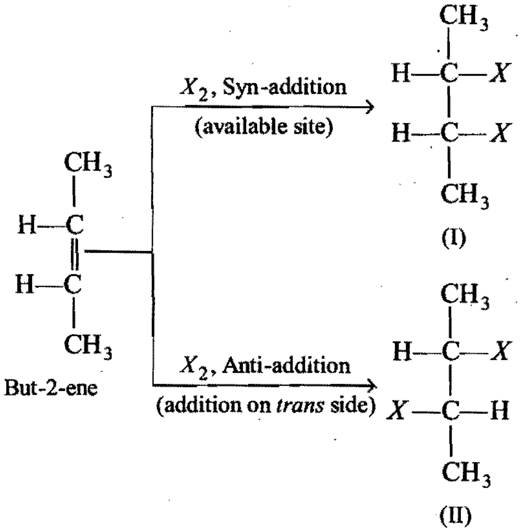


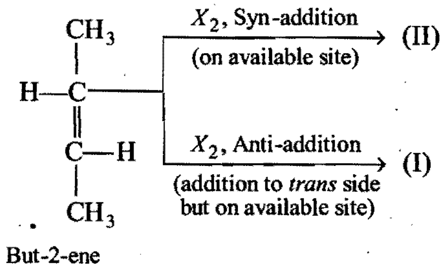




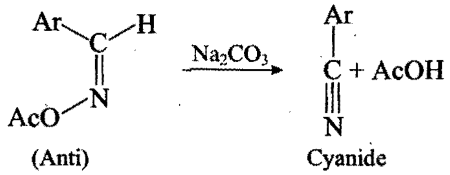
Syn-addition: Addition of electrophile and nucleophile on the available sites (same side of the molecule).

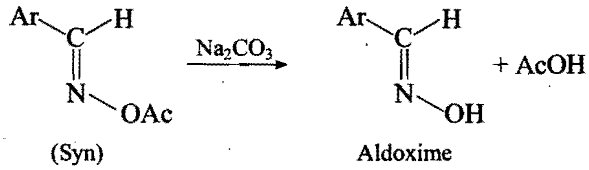
Anti-addition: Addition of these reagents *trans* to available sites (opposite side of the molecule).



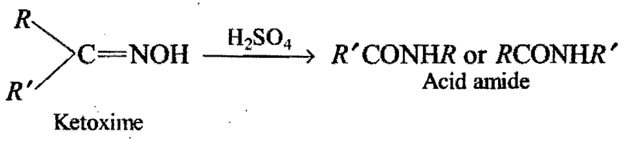


Determination of configuration of aldoxime and ketoximes : The two forms 'syn' and 'anti' of aromatic oximes resemble each other in many ways but differ in the behaviour of their acetyl derivatives towards sodium carbonate solution.



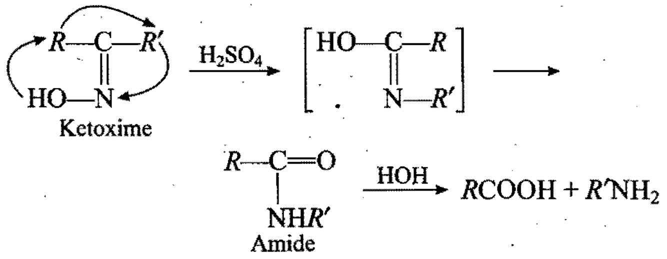


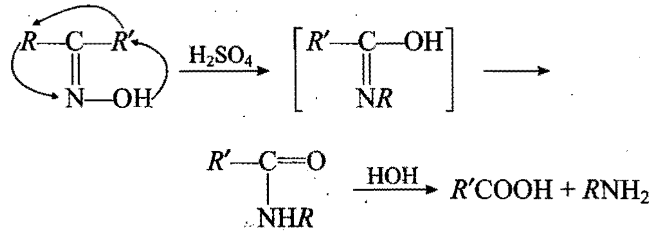
Configuration of ketoximes is determined by **Beckmann rearrangement.**



$$R(R')C{=}NOH \xrightarrow{H_2SO_4} R'CONHR \text{ or } RCONHR'$$

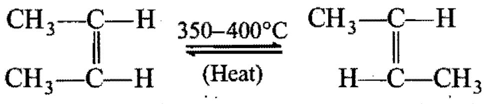
The two different amides can be identified by their hydrolysis to different acids and amines. In this rearrangement the migration of groups is always *trans* (anti) to the leaving group (—OH).



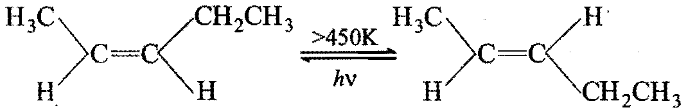


The rearrangement is intramolecular and involves 1,2-shift.

The conversion of *cis*-isomer into *trans*-isomer or *vice-versa* is possible only if either isomer is heated to a high temperature or absorbs energy. The supplied energy (about 62 kcal/mol) breaks the π-bond and the rotation about sigma bond becomes possible. Upon cooling, the reformation of π-bond can take place in two ways forming a mixture of *cis*- and *trans*-isomers.

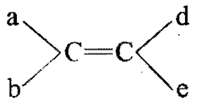


But-2-ene (*cis*) (47%) But-2-ene (*trans*) (53%)



Pent-2-ene (*cis*) Pent-2-ene (*trans*)

***E* and *Z* system of nomenclature :** '*Cis*' and '*trans*' designations cannot be used for highly substituted alkenes if four different atoms or groups are attached to the carbon atoms of a double bond.



In such cases, *E* and *Z* system of nomenclature is used. This system is based on a priority system developed by **Cahn, Ingold** and **Prelog.**

In this system, the two atoms or groups attached to each of the doubly bonded carbon are put in order of precedence (priority) on the basis of sequence rules.

(i) The symbol '***E***' is assigned to an isomer in which the atoms or groups of **higher precedence** are on the **opposite side** (*E* from German word, *Entgegen* = across or opposite).

(ii) The symbol '***Z***' is assigned to an isomer in which the atoms or groups of **higher precedence** are on the **same side** (*Z* from German word, *Zusammen* = together).

E-isomer *Z*-isomer

Note : 1 signifies higher precedence and 2 signifies lower precedence. In most of the cases '*Z*' corresponds to *cis*-form and '*E*' to *trans*-form. However, there are many exceptions.

Sequence rules : The following rules are followed for deciding the precedence order of the atoms or groups.

(1) Higher priority is assigned to the atoms of higher atomic number. For example, the order of precedence in the following atoms,

H, Cl, I, Br is:

I (at. no. 53) > Br (at. no. 35) > Cl (at. no. 17) > H (at. no. 1)

(2) If isotopes of the same element are attached, the isotope with higher mass number is given higher order of precedence. For example, deuterium ($^2_1$D) is assigned higher priority in comparison to hydrogen ($^1_1$H).

(3) In the groups, the order of precedence is also decided on the basis of atomic number of first atom of the group. For example, in the following set,

$$—Cl, —OH, —COOH, —NHCH_3, —SO_3H$$

The order of precedence is:

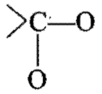
$$\underset{\text{(at. no. 17)}}{\underset{\downarrow}{—Cl}} > \underset{\text{(at. no. 16)}}{\underset{\downarrow}{—SO_3H}} > \underset{\text{(at. no. 8)}}{\underset{\downarrow}{—OH}} > \underset{\text{(at. no. 7)}}{\underset{\downarrow}{—NHCH_3}} > \underset{\text{(at. no. 6)}}{\underset{\downarrow}{—COOH}}$$

When the order of precedence of the groups cannot be settled on the first atom, the second atom or the subsequent atoms in the groups are considered. For example, in the set —CH_2—CH_3, —CH_3, —COOH, the order cannot be decided on the basis of first atom as it is same in all the groups. However, in —CH_2—CH_3, the second atom is carbon, in —CH_3, the second atom is hydrogen while in —COOH, the second atom is oxygen. Hence, the order of precedence is:

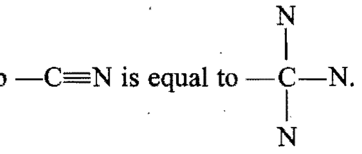
$$\underset{\text{(at. no. = 8)}}{\underset{\downarrow}{—COOH}} > \underset{\text{(at. no. = 6)}}{\underset{\downarrow}{—CH_2—CH_3}} > \underset{\text{(at. no. = 1)}}{\underset{\downarrow}{—CH_3}}$$

(4) A doubly or triply bonded atom is considered equivalent to two or three such atoms. For example,

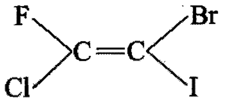
the group >C=O is equal to

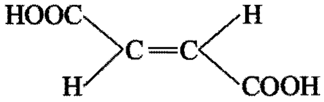


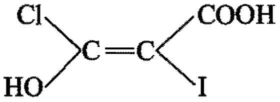
and the group —C≡N is equal to

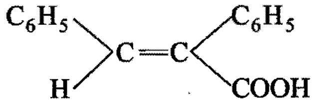


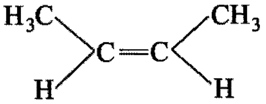
Example 6. *Give the E-Z designation of each of the following:*

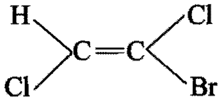
(*i*)


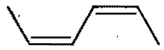
(*ii*)


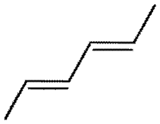
(*iii*)


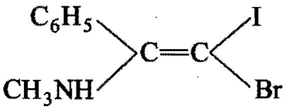
(*iv*)


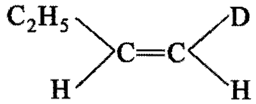
(*v*)


(*vi*)


(*vii*)


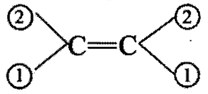
(*viii*)


(*ix*)


(*x*)


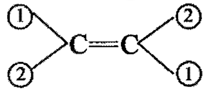
Solution :

(i) Precedence order : —Cl > —F; —I > —Br
① ② ① ②



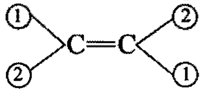
Thus, it is 'Z' isomer.

(ii) Precedence order : —COOH > —H
① ②



The senior groups are on opposite side. Hence, it is the '*E*' isomer.

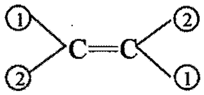
(iii) Precedence order : —Cl > —OH; I > —COOH
① ② ① ②



The senior groups are on the opposite side. Hence, it is the '*E*' isomer.

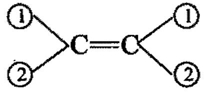
(iv) Precedence order :

C_6H_5— > —H; —COOH > C_6H_5
① ② ① ②



The senior groups are on the opposite side. Hence, it is the '*E*' isomer.

(v) Precedence order : $CH_3 > H$
① ②



The senior groups are on the same side. Hence, it is the '*Z*' isomer.

(vi) Cl > H, Br > Cl, hence, it is '*Z*' isomer.

(vii) It is 2,4-hexadiene. At position 2(CH_3 > H, —CH=CHCH$_3$ > H), it is '*Z*' isomer and also at position 4, it is '*Z*' isomer. Thus, it is (2*Z*, 4*Z*) isomer.

(viii) It is hexa-2,4-diene. At position 2, it is '*E*' isomer and so at position 4. Thus, it is (2*E*, 4*E*) isomer.

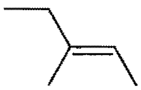
(ix) '*E*' isomer.

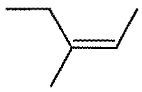
(x) '*Z*' isomer.

Example 7. *Indicate the configurations of the following geometrical isomers*:

(*a*)

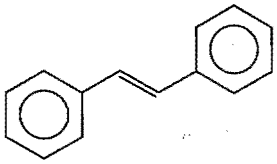

(*b*)

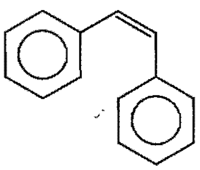

(*c*)


(*d*)


Solution : (a) *Trans*-2-hexene (b) *Cis*-2-hexene (c) *E*-3-methyl-2-pentene (d) *Z*-3-methyl-2-pentene.

Example 8. *Identify 'E' and 'Z' forms of stilbene.*

(*a*)


(*b*)


Solution : (a) '*E*' (b) '*Z*'

Calculation of geometrical isomers in polyenes

(a) When the ends of polyene are different, then the Number of geometrical isomers $= 2^n$
(where n = number of double bonds)
Examples are, $H_3C—CH=CH—CH=CH—Cl$
here $n = 2$, so, the number of geometrical isomers
$= 2^2 = 4$

$C_6H_5—CH=CH—CH=CH—CH=CH—CH=CH—Cl$

here,

$n = 4$, number of geometrical isomers $= 2^4 = 16$

(b) When the ends of polyene are same,

(i) When n is an **even number,** then the number of geometrical isomers $= 2^{(n-1)} + 2^{(n/2-1)}$

For examples,

$X—CH{=}CH—CH{=}CH—CH{=}CH—CH{=}CH—X$

$n = 4$ (even), Number of geometrical isomers

$$= 2^{4-1} + 2^{\frac{4}{2}-1} = 2^3 + 2^1 = 10$$

(ii) When n is an **odd number,** then the number of geometrical isomers $= 2^{(n-1)} + 2^{\left(\frac{n-1}{2}\right)}$

For example,

$CH_3—CH{=}CH—CH{=}CH—CH{=}CH—CH_3$

$n = 3$ (odd), Number of geometrical isomers

$$= 2^{3-1} + 2^{\frac{3-1}{2}} = 2^2 + 2^1 = 6$$

4.9 OPTICAL ACTIVITY

Ordinary light consists of rays of varying wavelengths vibrating in all possible directions perpendicular to the direction of propagation. When ordinary light is passed through a nicol prism (made of calcite, $CaCO_3$), the vibrations are adjusted in a single plane only. **The light whose vibrations occur only in one plane is termed plane polarised or simply polarised.** The device that brings polarisation in light is called a **polariser.**

Some substances have the ability to **rotate the plane polarised light** either to the right (clockwise) or to the left (anticlockwise). These substances are termed as **optically active substance** and the property is called **optical activity.** The apparatus which measures the extent of rotation of the polarised light is called **polarimeter.**

The extent or angle of rotation depends on a number of factors:

(i) Nature of the substance,

(ii) Wavelength of the light used (λ),

(iii) Concentration of the solution (C) in g cm^{-3},

(iv) Nature of the solvent,

(v) Length of the path through which polarised light passes,

(vi) Temperature at which the measurements are made.

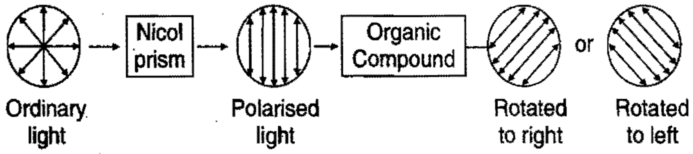


Fig. 4.2

The measurement of optical activity is done in terms of **specific rotation which is defined as the rotation produced by a solution of length of 10 centimetre (one decimetre) and unit concentration (1 g/mL) for the given wavelength of the light at the given temperature.**

$$\text{Specific rotation, } [\alpha]^{t°\text{C}}_{\text{wavelength}} = \frac{\alpha_{\text{obs}}}{l \times C}$$

where, α_{obs} is the rotation observed, l is the length of the solution in decimetre and C is the number of grams in 1 mL of solution. The specific rotation of sucrose at 20°C using sodium light (D-line, $\lambda = 5893$ Å) is $+$ 66.5°C and is denoted as:

$$[\alpha]^{20°\text{C}}_{D} = +66.5°\text{C} \; (C = 0.02 \text{ g/mL water})$$

$+$ sign indicates the rotation in clockwise direction.

Optical isomerism : Compounds having similar physical and chemical properties but differing only in the behaviour towards polarised light are called optical isomers and this phenomenon as optical isomerism.

On the basis of the study of optical activity, the various organic compounds were divided into three types:

(i) The optical isomer which rotates the plane polarised light to the right (clockwise) is known as **dextrorotatory** isomer (Latin : *dexter* = right) or d-form or indicated by +ve sign.

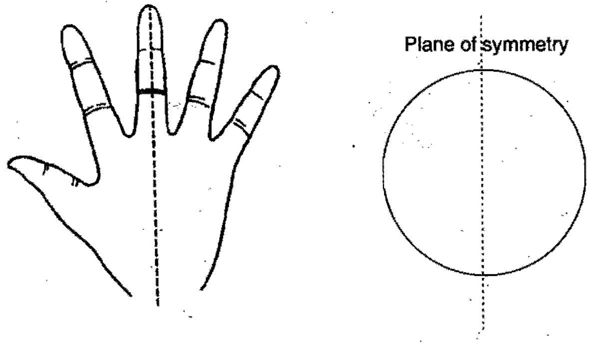
(ii) The optical isomer which rotates the plane polarised light to the left (anticlockwise) is known as **laevorotatory** isomer (Latin : *laevo* = left) or l-form or indicated by –ve sign.

(iii) The optical powers of the above two isomers are equal in magnitude but opposite in sign. An equimolar mixture of the two forms, therefore, will be optically inactive. This mixture is termed **racemic** mixture or dl-form or ($\pm$) mixture.

Lactic acid, tartaric acid, malic acid, amyl alcohol, glucose, sucrose and butan-2-ol are some of the organic compounds which show optical isomerism.

Cause of Optical Activity or Optical Isomerism

A plane which divides an object into two symmetrical halves. Such that one half of the molecule is a mirror image of the other, is said to be **plane of symmetry** or **mirror plane.** An object having no plane of symmetry is called **dissymmetric** or **chiral** (pronounced as ki-ral, Greek word meaning hand). A symmetric object is referred to as **Achiral.** **A dissymmetric** or **chiral object can be defined as the one**



Chiral (two unequal halves)

Achiral (Two equal halves)

Fig. 4.3 Chiral and achiral objects

that is not superimposable on its mirror image. For example, a ball is an achiral object while a hand is a chiral object. Thus, **dissymmetry is the necessary and sufficient condition for the existence of enantiomers.**

Enantiomers

In order to exhibit optical activity, an object must be chiral. Compounds which are mirror images of each other and are not superimposable are termed **enantiomers** (Greek : *enantio* = opposite; *meros* = parts) and the phenomenon is described as enantiomerism. The molecular dissymmetry or chirality is a necessary condition for the existence of enantiomers. A pair of enantiomers have identical physical and chemical properties but differ from each other in their action on plane polarised light. They have identical structures but differ from each other in having different spatial disposition of atoms or groups constituting them.

The concept of chirality and achirality can also be illustrated by alphabet letters. For example, alphabets F, J, K, L, N, P, R, etc., do not have plane of symmetry and hence are **chiral.** On the other hand alphabets such as A, M, O, X, etc., have plane of symmetry and can be superimposed on its mirror image, thus they are **non-chiral.**

Chiral (Non-superimposable) Achiral (Superimposable)

The cause of optical activity was put forward by **van't Hoff** and **Le Bel** in 1867. According to them, the four valencies of carbon atoms are directed towards the four corners of a regular tetrahedron. If there are four different atoms or groups a, b, c, d attached to four corners of a tetrahedron, then two different arrangements are possible which are not superimposable and bear the mirror-image relationship, *i.e.*, act as enantiomers (Fig. 4.4). Hence, **a compound which consists of atleast one asymmetric carbon atom is capable of showing the phenomenon of optical isomerism.**

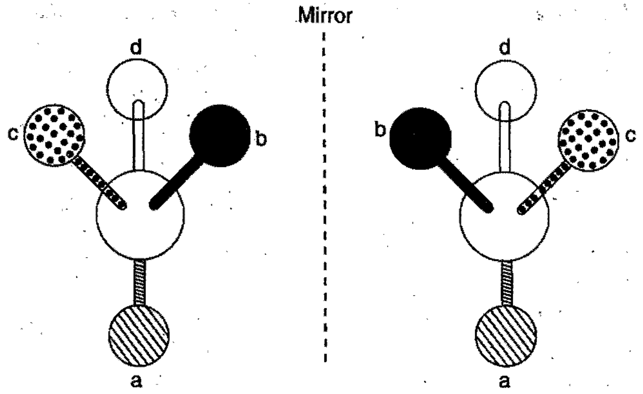


Fig. 4.4

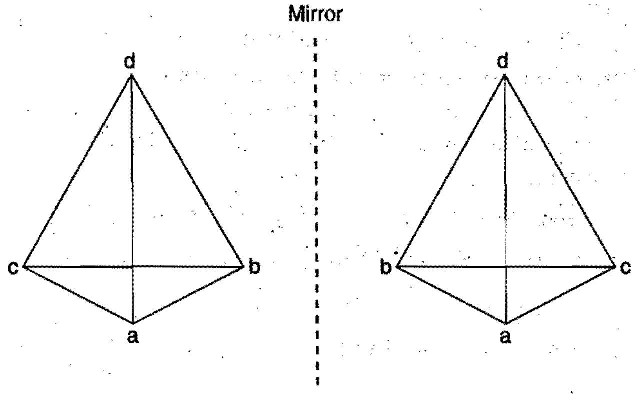
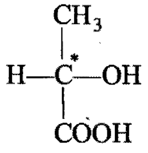


Fig. 4.5

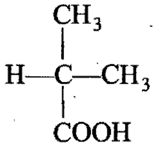
CHIRALITY CENTRE

A carbon atom which is bonded to four different atoms or groups in the molecule is called Chiral carbon or stereo centre or Stereogenic centre or an asymmetric carbon atom (Chirality centre). The molecule having asymmetric carbon atom lacks a plane of symmetry. For asymmetric molecules, the term dissymmetric or chiral molecules is used these days. It is further observed that as soon as any two of the four groups or atoms to an asymmetric carbon atom become identical, the carbon atom becomes symmetric (achiral) and hence, loses its optical activity.



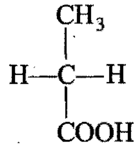
$$\begin{array}{c} CH_3 \\ | \\ H-\overset{*}{C}-OH \\ | \\ COOH \end{array}$$

Lactic acid
(Chiral)
optically active



$$\begin{array}{c} CH_3 \\ | \\ H-C-CH_3 \\ | \\ COOH \end{array}$$

Isobutyric acid
(Achiral)
optically inactive



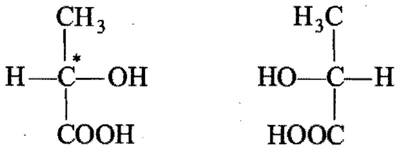
$$\begin{array}{c} CH_3 \\ | \\ H-C-H \\ | \\ COOH \end{array}$$

Propionic acid
(Achiral)
optically inactive

When an interchange of two ligands bonded to an atom results in a new stereoisomer, the atom is termed as **stereogenic centre** (stereocentre).

It is true that most of the compounds which contain chirality centre show optical isomerism. The formulae of a few compounds are given below and each has atleast one chirality centre (stereogenic centre) and hence, optically active. It is marked by asterisk sign (*).

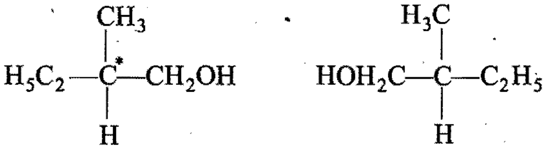
(i)



$$\begin{array}{c} CH_3 \\ | \\ H-\overset{*}{C}-OH \\ | \\ COOH \end{array} \qquad \begin{array}{c} H_3C \\ | \\ HO-C-H \\ | \\ HOOC \end{array}$$

Lactic acid (Two enantiomers)

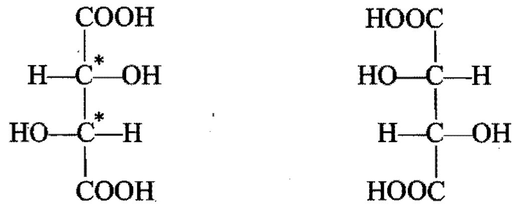
(ii)



$$\begin{array}{c} CH_3 \\ | \\ H_5C_2-\overset{*}{C}-CH_2OH \\ | \\ H \end{array} \qquad \begin{array}{c} H_3C \\ | \\ HOH_2C-C-C_2H_5 \\ | \\ H \end{array}$$

Amyl alcohol (Two enantiomers)

(iii)

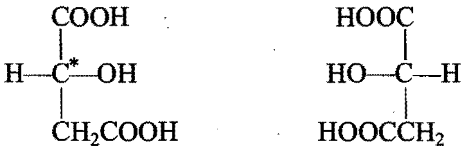


Tartaric acid (Two enantiomers)

(iv)

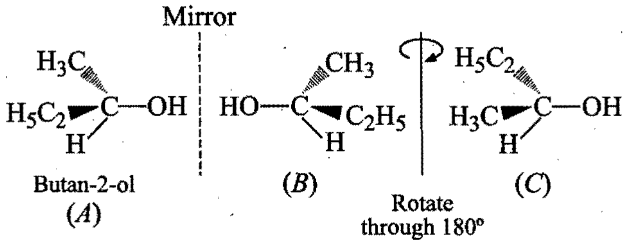
Valeric acid (Two enantiomers)

(v)



Malic acid (Two enantiomers)

(vi)

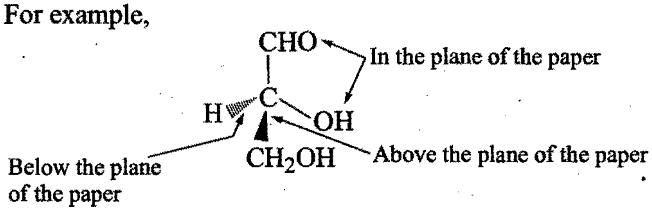


Butan-2-ol is a chiral because (*A*) and its mirror image (*B*) (or *C*) are non-superimposable (Wedge representation).

In all these example, the **mirror image is not superimposable** and so, a single asymmetric carbon atom makes the molecule chiral and hence, optically active. On the other hand, there are certain compounds such as substituted allenes (2,3-pentadiene) and substituted biphenyls which have no asymmetric carbons but are optically active and show optical isomerism.

In **Flying-Wedge representation,** three types of lines are used in a standard way to indicate three dimensional structures in two-dimensional picture. A solid wedge, ▶ (thick line) represents a bond projecting above the plane of the paper toward the observer. Continuous lines,—(solid lines) are bonds in the plane of the paper. A broken wedge, ⫶▸ (dashed lines) is a bond below the plane (*i.e.*, a bond pointing away from the observer).

For example,

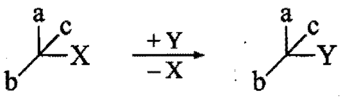


Racemic mixture or racemic modification: It is an equimolecular mixture of two enantiomers (*d*-and *l*-form) and is represented by prefixing *dl* or (±) before the name. The rotation of *d* (or +) form is exactly compensated (cancelled) externally by the same number of molecules of *l* (or –) form and hence, it is **optically inactive** due to external compensation.

The process of conversion of one enantiomer (+ or –) or optically active compound into a racemic mixture (*dl* or ±) is termed as **racemisation.**

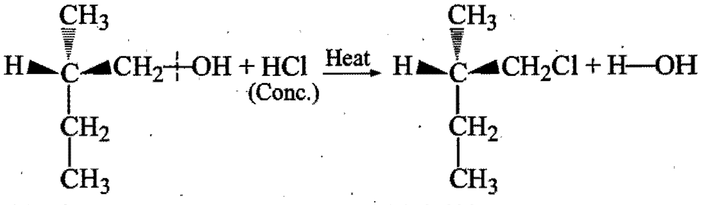
Retention: The relative spatial arrangement of bonds at an asymmetric carbon centre in a chiral molecule remains the same before and after the chemical reaction or transformation, the reaction is said to proceed with retention of configuration.

So, **retention of configuration** means *"the preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction."* For example,



It is also the configurational correlation when a chemical species *Xcabc* is converted into the chemical species *Ycabc* having the same *relative configuration, i.e.*, the retention of configuration occurs in this reaction because the relative configurations of the atoms *b*, *a* and *c* are the same (clockwise from *b* to *c*), both in the reactant and in the product.

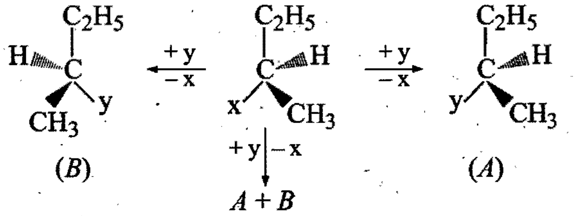
In general, if during a reaction, no bond to the stereocentre is broken, the product will have the same general configuration of atoms or groups around the stereocentre as that of the reactant. Such a reaction provides a method with retention of configuration even though the sign of optical rotation has changed. For example, when (–)-2-methyl butan-1-ol is heated with conc. HCl (or thionyl chloride, $SOCl_2$) it forms (+)-1-chloro-2-methyl butane.



(–)-2-Methyl butan-1-ol

(+)-1-Chloro-2-methylbutane

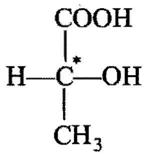
Inversion, retention and racemisation: Whenever in a chemical reaction, a bond is broken at the chiral carbon atom, there are three possibilities. For example, consider the replacement of a group *x* by *y* in the following reaction:



If *A* is the only compound obtained, the process is called as **stereospecific retention** of configuration. If *B* is the only compound obtained, the process is called as **stereospecific inversion** of configuration. If a 50 : 50 (equal) mixture of *A* and *B* is obtained, the process is called as a non-stereospecific reaction or **racemisation** and the product is **optically inactive**, as one isomer will rotate the plane of polarised light in one direction and the other will rotate in opposite direction but to the same extent.

4.10 OPTICAL ISOMERISM OF LACTIC ACID

Lactic acid is an example of a compound which shows optical isomerism. It contains one asymmetric carbon atom.



$$\begin{array}{c} COOH \\ | \\ H-\overset{*}{C}-OH \\ | \\ CH_3 \end{array}$$

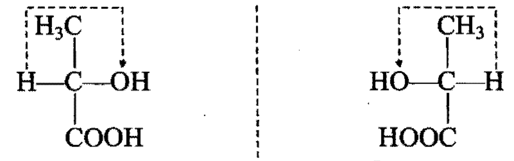
Three forms of lactic acid are known. Two are optically active and third is optically inactive.

(i) Dextrorotatory (*d*-form) or (+) lactic acid : It rotates the plane polarised light to the right. It can be obtained from meat extract. It melts at 26°C and is known as sarcolactic acid.

(ii) Laevorotatory (*l*-form) or (–) lactic acid : It rotates the plane polarised light to the left. It can be obtained during fermentation of sucrose by *Bacillus aceti-lactiti.* It melts at 26°C.

(iii) Racemic (*dl*-form) or (±) lactic acid : This is an equimolecular mixture of *d*- and *l*-forms. It is optically inactive. The inactivity is due to external compensation. It is present in sour milk and can be obtained by synthetic methods. It can be resolved into *d*- and *l*-forms. It melts at 18°C.

Using the projection formula, the two forms (enantiomers) can be represented as:



Dextrorotatory or *d*(+) Lactic acid — Mirror — Laevorotatory or *d*(–) Lactic acid

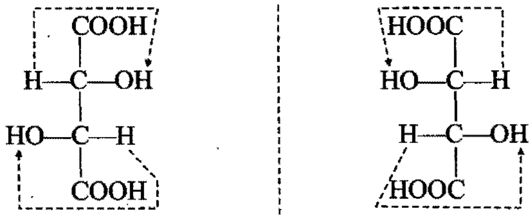
These structures are not identical as they cannot be superimposed on each other. One is the mirror image of the other (*i.e.*, each dextro form has one laevo form).

The direction of rotation is decided by putting an arrow from H— to —OH over (through) a group of lower molecular mass.

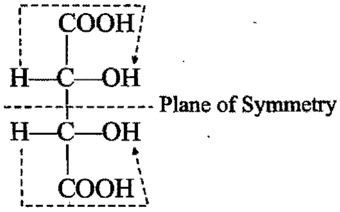
The well known and common examples of compounds having one asymmetric carbon atom are: mandelic acid, malic acid, amino acids, amyl alcohol, valeric acid, glyceraldehyde, 2-butanol, 2-chlorobutane and 3-methylhexane, etc.

4.11 OPTICAL ISOMERISM IN TARTARIC ACID

Tartaric acid has two asymmetric carbon atoms each linked to the same four different groups, *viz.*, —OH, H, —COOH and —CH(OH)COOH. The spatial arrangement of various groups in tartaric acid can be represented in three ways.



Dextro or (+) (I) — Mirror — Laevo or (–) (II)



Meso (III)

Corresponding to these different configurations, tartaric acid exists in four forms:

(i) Dextro-tartaric acid (*d*-form) : This rotates the plane polarised light to the right. Both the asymmetric carbon atoms reinforce each other and cause the rotation of plane polarised light in the same direction, *i.e.*, towards right. It has no plane of symmetry. It occurs in nature and is obtained from natural sources like tamarind and grapes. Its melting point is 170°C.

(ii) Laevo-tartaric acid (*l*-form) : This rotates the plane polarised light to the left. Both the asymmetric carbon atoms rotate the plane of polarised light in the same direction, *i.e.*, towards left. It also has no plane of symmetry. It does not occur in nature and hence, it is prepared by resolving racemic tartaric acid. It melts at 170°C.

Both dextro and laevo forms do not have the plane of symmetry. One is the mirror image of the other. Thus, they are enantiomers.

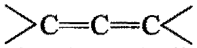
(iii) Meso-tartaric acid : Model (III) represents meso form. It possesses a plane of symmetry and is consequently optically inactive. One of the asymmetric carbon atom turns the plane of polarised light to the right and other to the left and to the same extent so that the rotation due to upper half is compensated by the lower half, *i.e.*, internally compensated. It does not occur in nature and cannot be resolved into *d*- and *l*-forms. It is obtained by synthetic methods. It melts at 143°C.

(iv) Racemic tartaric acid : It is an equimolecular mixture of *d*- and *l*-forms. The rotation of the *d*-form is compensated externally by *l*-form and hence, it is optically inactive due to external compensation. It can be resolved into *d*- and *l*-forms. It can be synthesised in the laboratory or obtained from argol. It melts at 205°C.

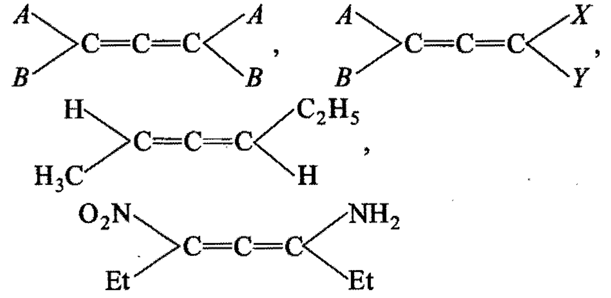
Synthetic acid is always inactive being either racemic or a mixture of racemic and meso variety.

Some special examples of optical isomerism in compounds containing no chiral carbon atom :

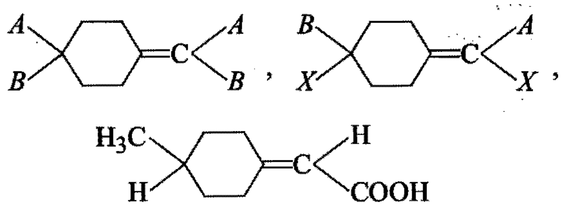
1. **Allenes :** Allenes are the compounds with the general formula,



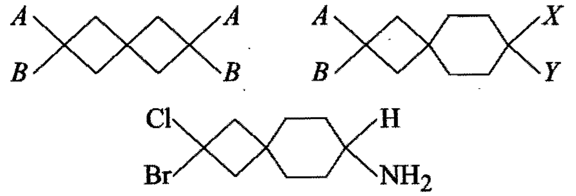
Allenes are found to be optically active when the two groups attached to each terminal carbon atom are different, Examples are :



2. **Alkylidenes :** When one of the C—C double bonds in allenes is replaced by one cyclohexyl ring, the compound is known as alkylidene cycloalkane. Such compounds will be optically active if two groups attached to each terminal carbon atom are different. Examples are :

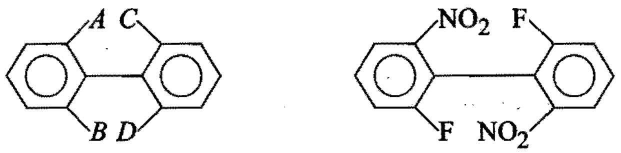


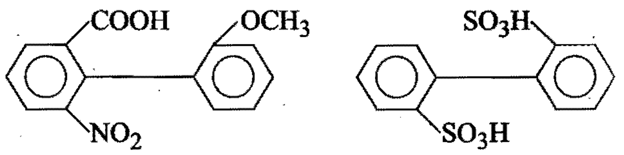
3. **Spiranes :** When both the C—C double bonds (C=C=C) in allenes are replaced by two cycloalkanes (same or different) rings, the system is known as spiranes. Examples are :



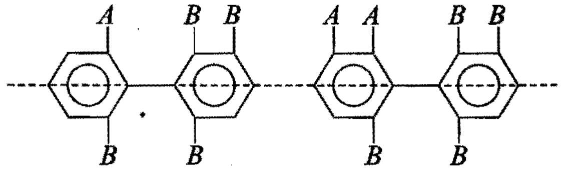
4. **Biphenyls :** They show optical isomerism when the following two conditions are satisfied :

(i) Each ring in biphenyl should have two different ortho substituting groups or the minimum number of substituents should be two *i.e.*, one substituent in each ring. The two substituents must have a large group (bulky) like —NO_2 or —SO_3H groups. Examples are:

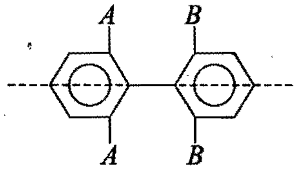




(ii) Each ring should be unsymmetrically substituted, *i.e.*, neither ring should have a plane of symmetry.



(Both rings have no plane of symmetry)



(Both rings have plane of symmetry)

4.12 NUMBER OF POSSIBLE STEREOISOMERS IN COMPOUNDS CONTAINING DIFFERENT NUMBER OF ASYMMETRIC ATOMS

The number of optical isomers of a compound depends on its structure and number of asymmetric carbon atoms present in its molecule. The number of optical isomers is calculated by the application of the following rules:

(i) When the molecule cannot be divided into two equal halves, *i.e.*, **the molecule has no symmetry (unsymmetrical)** and (n) is the number of asymmetric carbon atoms, then

The number of *d*- and *l*-(optically active) forms, $a = 2^n$

and The number of meso-forms, $m = 0$

Total number of optical (stereo) isomers $= a + m = 2^n$

For example, $CH_3—\overset{*}{C}HOH—COOH$ (Lactic acid)

where, $n = 1,\ a = 2^1 = 2,\quad m = 0,\quad r = \frac{2}{2} = 1$

So, total optical isomers = 2 + 0 = 2

(ii) When the molecule can be divided into equal halves, *i.e.*, **the molecule has symmetry** and the number (n) of asymmetric carbon atoms is **even,** then

The number of *d*- and *l*-(optically active) forms, $a = 2^{(n-1)}$

and The number of meso-forms, $m = 2^{(n/2)-1}$

$$\text{Total number of optical isomers} = a + m$$
$$= 2^{(n-1)} + 2^{(n/2)-1}$$

For example, $HOOC—\overset{*}{C}HOH—\overset{*}{C}HOH—COOH$

Where, $n = 2,\ a = 2^{n-1} = 2^{2-1} = 2^1 = 2$

$m = 2^{(n/2-1)} = 2^{(2/2-1)} = 2^0 = 1$

So, total optical isomers = 2 + 1 = 3

(iii) When the molecule can be divided into two equal halves (**symmetrical**) and the number (n) of asymmetric carbon atoms is **odd,** then

The number of d- and l-forms, $a = 2^{(n-1)} - 2^{(n-1)/2}$

and The number of meso-forms, $m = 2^{(n-1)/2}$

Total number of optical isomers $= a + m = 2^{(n-1)}$

For example,

$$CH_2OH—\overset{*}{C}HOH—\overset{*}{C}HOH—\overset{*}{C}HOH—CH_2OH$$

where, $n = 3$, $a = 2^{(n-1)} - 2^{(n-1)/2} = 2^2 - 2^1 = 2$

$m = 2^{(n-1)/2} = 2^{(3-1)/2} = 2^1 = 2$

So, total optical isomers = 2 + 2 = 4

In all the above three cases, the number of racemic forms will be = $a/2$

Example 9. *Mark the asymmetric carbon atoms and give the number of optical isomers in the following compounds:*

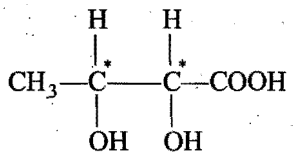
(i) $CH_3—(CHOH)_2—COOH$

(ii) $HOCH_2—(CHOH)_4—CHO$

(iii) $HOCH_2—(CHOH)_4—CH_2OH$

Solution :

(i)



$$CH_3—\overset{H}{\underset{OH}{\overset{*}{C}}}—\overset{H}{\underset{OH}{\overset{*}{C}}}—COOH$$

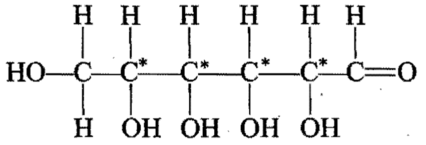
The compound cannot be divided into equal halves and it consists of two asymmetric carbon atoms.

Hence, the number of d- and l- (optically active) isomers, $a = 2^n = 2^2 = 4$

and Number of meso forms, $m = 0$

So, Total optical isomers $= a + m = 4 + 0 = \mathbf{4}$

(ii)



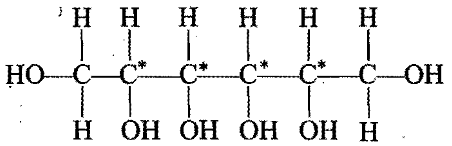
$$HO—\overset{H}{\underset{H}{C}}—\overset{H}{\underset{OH}{C^*}}—\overset{H}{\underset{OH}{C^*}}—\overset{H}{\underset{OH}{C^*}}—\overset{H}{\underset{OH}{C^*}}—\overset{H}{C}=O$$

(Glucose)

where, $n = 4$, $a = 2^4 = 16$, $m = 0$, $r = \frac{16}{2} = 8$

So, Total optical isomers $= 16 + 0 = \mathbf{16}$

(iii)



$$HO—\overset{H}{\underset{H}{C}}—\overset{H}{\underset{OH}{C^*}}—\overset{H}{\underset{OH}{C^*}}—\overset{H}{\underset{OH}{C^*}}—\overset{H}{\underset{OH}{C^*}}—\overset{H}{\underset{H}{C}}—OH$$

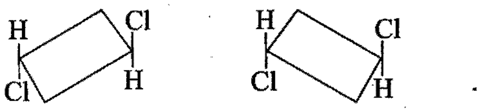
(Sorbitol)

where, $n = 4$, $a = 2^{(4-1)} = 2^3 = 8$, $m = 2^{(4/2-1)} = 2^{(2-1)} = 2$, $r = \frac{8}{2} = 4$

So, Total optical isomers $= 8 + 2 = \mathbf{10}$

Example 10. *Indicate whether the following pairs are identical or enantiomers :*

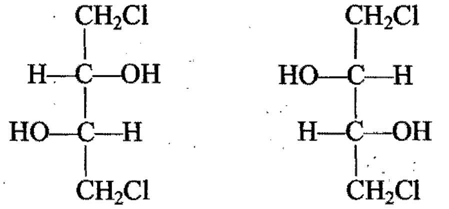
(i)



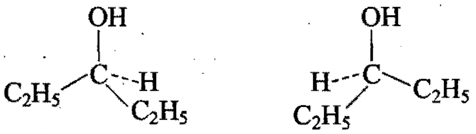
(ii)

(iii)

(iv)



(v)



Solution : Enantiomers (i), (ii), (iii) and (iv); Identical (v).

Example 11. *Calculate the d- and l-isomers formed by the following compound and also give the number of meso forms.*

$HOOC—CH(CH_3)—CHOH—CHBr—CHOH—CH(CH_3)—COOH$

Solution : The compound can be divided into two equal halves and it consists of five asymmetric carbon atoms, *i.e.*, odd number of asymmetric carbon atoms.

Hence, the number of d- and l-isomers

$$= 2^{(n-1)} - 2^{(n-1)/2}$$
$$= 2^{(5-1)} - 2^{(0.5 \times 5 - 0.5)}$$
$$= 2^4 - 2^{(2.5-0.5)} = 2^4 - 2^2$$
$$= 16 - 4 = 12$$

Number of meso isomers $= 2^{(n-1)/2}$

$$= 2^{(2.5-0.5)} = 2^2 = \mathbf{4}$$

So, total number of configurational isomers $= 12 + 4 = \mathbf{16}$

Example 12. *Calculate the number of geometrical isomers in the following polyenes.*

(i) $H_3C—CH=CH—CH=CH—CH=CH—CH=CH—Br$

(ii) $H_3C—CH=CH—CH=CH—CH=CH—CH=CH—CH_3$

(iii) $C_6H_5—CH=CH—CH=CH—CH=CH—C_6H_5$

(iv) $C_6H_5—CH=CH—CH=CH—Cl$

Solution : (i) The molecule has four double bonds and can not be divided into two equal halves (unsymmetrical).

The number of geometrical isomers $= 2^n$

$$= 2^4 = \mathbf{16}$$

(ii) The molecule has four double bonds (even number) and the end of polyene are same (symmetry).

The number of geometrical isomers $= 2^{(n-1)} + 2^{(n/2)-1}$

$$= 2^3 + 2^1 = 8 + 2 = \mathbf{10}$$

(iii) The molecule has three double bonds (odd number).

The number of geometrical isomers $= 2^{(n-1)} + 2^{\frac{(n+1)}{2}-1}$

$$= 2^2 + 2^{2-1} = 4 + 2 = \mathbf{6}$$

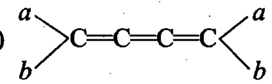
(iv) The molecule has two double bonds and is unsymmetrical.

The number of geometrical isomers $= 2^n$

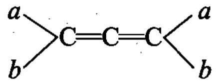
$$= 2^2 = \mathbf{4}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

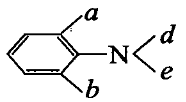
9. Which is optically inactive?

(a) 

$\overset{a}{\underset{b}{>}}C{=}C{=}C{=}C\overset{a}{\underset{b}{<}}$

(b) 

$\overset{a}{\underset{b}{>}}C{=}C{=}C\overset{a}{\underset{b}{<}}$

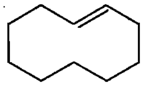
(c) 

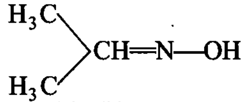
(d) None of these

[**Ans.** (a)]

[**Hint:** Formula trienes show only geometrical isomerism, not optical isomerism because these molecules are planar.]

10. Which will show geometrical isomerism?

(a) $CH_3—CH{=}N—OH$ (b) 

(c) 

$\overset{H_3C}{\underset{H_3C}{>}}CH{=}N—OH$

(d) $HO—N{=}N—OH$

[**Ans.** (a), (b)]

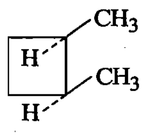
[**Hint:** (c) and (d) are symmetrical molecules, there is no possibility of geometrical isomerism.]

11. Which will show geometrical isomerism?

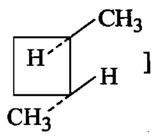
(a) 1,1,2-Trimethyl cyclopropane
(b) 1,2-Dimethyl cyclobutane
(c) Methyl cyclohexane
(d) 3,4-Dimethyl hexane

[**Ans.** (b)]

[**Hint:**



'cis'



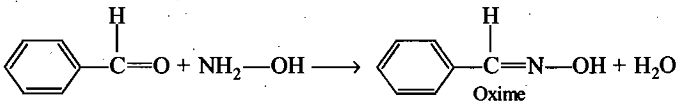
'trans']

12. Which type of isomerism shown by the product of reaction between benzaldehyde and hydroxyl amine is?

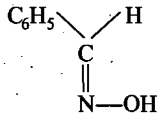
(a) syn and anti (b) *cis* and *trans*
(c) *E* and *Z* (d) None of these

[**Ans.** (a)]

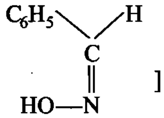
[**Hint:**



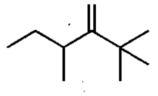
It shows 'syn' and 'anti' isomer.

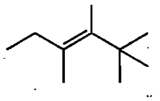


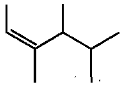
and

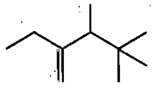
]

13. Which of the following alkenes shown below has the *Z*-configuration of its double bond?

(a) 

(b) 

(c) 

(d) 

[**Ans.** (c)]

4.13 RESOLUTION OF RACEMIC MIXTURES

When an optically active compound is synthesised, the product formed is found to be an optically inactive racemic mixture containing equal proportions of both *d*- and *l*-forms. **The process of separation of a racemic mixture into *d*- and *l*-forms (its enantiomorphs) is called resolution.**

The main difficulty in the process of resolution is that *d*- and *l*-forms have identical physical and chemical properties, so they cannot be separated by ordinary methods. However, the following methods can be used for this purpose:

(i) Mechanical separation : If the *d*- and *l*-forms of a substance exist in well defined crystalline forms, the separation can be done by 'hand picking' with the help of magnifying lens and a pair of tweezers. For example, the *d*- and *l*-forms of sodium ammonium tartarate can be separated by this method. The method has a very limited application and applies to only few crystalline constituents having different shapes.

(ii) Biochemical separation : In this method, the resolution is done by the use of micro-organisms. When certain bacteria or moulds are added to a solution of a racemic mixture, they decompose one of the optically active forms more rapidly than the other. For example, when the mould, *Penicillium glaucum* is allowed to grow in a solution of racemic ammonium tartarate, the mould completely decomposes the *d*- form while *l*-form is left practically unaffected. The main drawback of the method is that half of the material is destroyed during resolution. The process is very slow and only small amounts of the materials can be separated.

(iii) Chemical separation : This is probably the best method of resolution. The racemic mixture is made to combine with another optically active compound and the resulting products (salt-formation) differ in properties, particularly in solubility in various solvents. By fractional crystallisation from a suitable solvent, they can be separated. For example, the racemic mixture of lactic acid is allowed to combine with the optically active base (–) strychnine or (+) brucine. The salts formed are:

(a) (–) Strychnine (+) lactate and

(b) (–) Strychnine (–) lactate.

These two salts formed are no longer mirror image isomers and may be separated by fractional crystallisation and then treatment with dilute mineral acid yields the requisite isomers.

(iv) Chromatographic method (column chromatography)

(v) Selective adsorption method.

Racemisation : It is reverse of resolution, *i.e.*, the conversion of (+) or (–) isomer (optically active compounds) into its racemic mixture (±) is termed **racemisation.** This involves the change of half of the active compound to the isomer of opposite rotation (S_N1 mechanism), resulting the formation of racemic mixture which is always optically inactive, *i.e.*,

$$2\,(+)A \longrightarrow (+)A \quad \text{and} \quad (-)A \text{ or } (\pm) \text{ mixture}$$

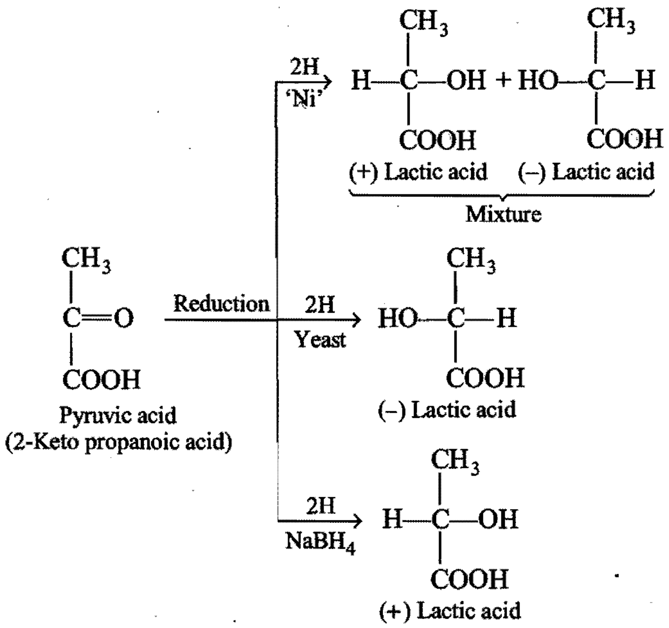
$$\text{or} \quad 2\,(-)A \longrightarrow (+)A \quad \text{and} \quad (-)A \text{ or } (\pm) \text{ mixture}$$

Racemisation can occur either by heat, light or use of chemical reagents (acids, bases), etc.

For example, when a solution of (+) or (–) tartaric acid in water is heated under pressure, it is transformed into a completely inactive mixture of racemic (or also meso) tartaric acid.

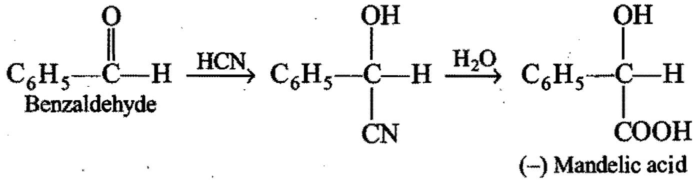
Asymmetric synthesis : The synthesis of an optically active compound (asymmetric) from a symmetrical molecule (having no asymmetric carbon) without resolution to form (+) or (–) isomer directly is termed **asymmetric synthesis.** For example, the reduction of pyruvic acid $(CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-COOH)$ in presence of nickel catalyst gives (±) lactic acid (racemic mixture).

(i) On the other hand, pyruvic acid is reduced to (–) lactic acid only by yeast or to (+) lactic acid with $NaBH_4$

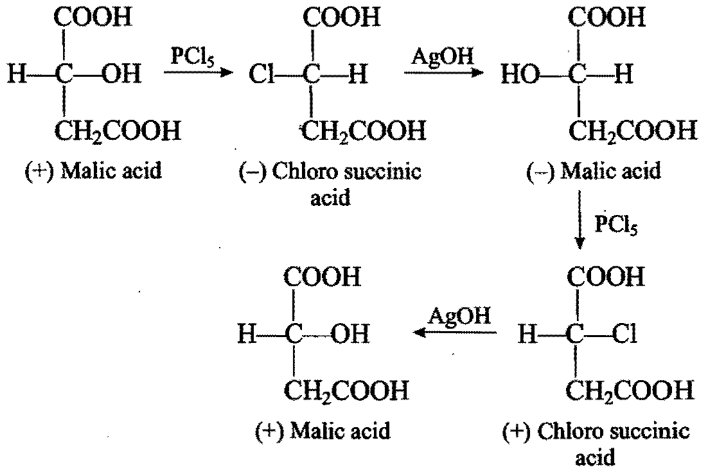


In this reaction, sp^2-hybrid carbon converts into chiral carbon. Out of the two stereoisomers only one is formed. This reaction is known as stereoselective reaction.

(ii) Synthesis of Mandelic acid : (–) Mandelic acid has also been synthesised by treating benzaldehyde with HCN in the presence of optically active enzyme *emulsin* (present in almonds) with subsequent hydrolysis.



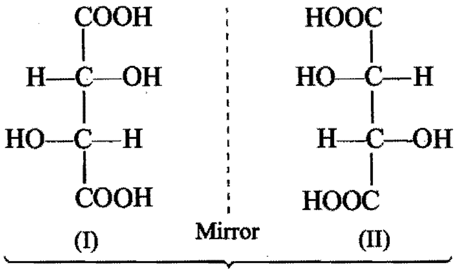
Walden inversion (Optical inversion): The conversion of (+) form of an optically active compound into (–) form of the same or different compound and *vice-versa* is called **Walden Inversion.** When an atom or group directly linked to an asymmetric carbon atom is replaced (inverse), *e.g.*, in S_N2 reaction the configuration of the new compound may be opposite to that of the original, *i.e.*,



Thus, among other factors, the nature of reagent plays an important role in Walden inversion. It has been observed that mild or weak reagent like moist Ag_2O does not affect Walden inversion directly while strong reagents like PCl_5 and KOH (or AgOH) cause this inversion.

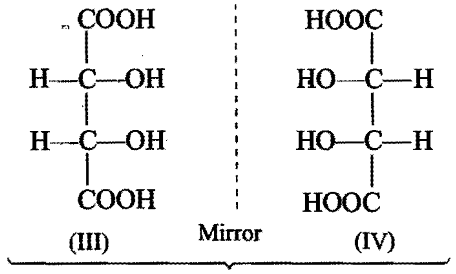
4.14 DIASTEREOMERS

A compound containing one asymmetric carbon atom exists in two stereoisomers which are known as enantiomers and are mirror images of each other. As the number of asymmetric carbon atoms increases, the number of stereoisomers also increases. For example, a compound having two asymmetric carbon atoms can have four stereoisomers as shown below in the case of tartaric acid:



(I) Mirror (II)

One pair of enantiomers

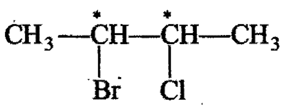


(III) Mirror (IV)

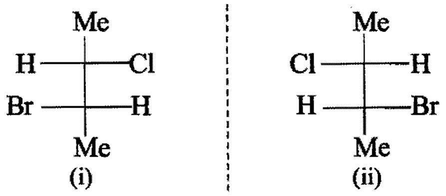
Second pair of enantiomers

(I) is mirror image of (II); similarly (III) and (IV) are mirror images of each other. Thus, the four isomers are two pairs of enantiomers. Now compare (I) with (III); they are neither superimposable nor they are mirror images. They are called diastereomers. (I) and (IV) are also diastereomers, as are (II) and (III) and (II) and (IV).

Another example is 2-bromo-3-chlorobutane. It has two chiral centres (2^n) and can have four stereoisomers or two pairs of enantiomers.

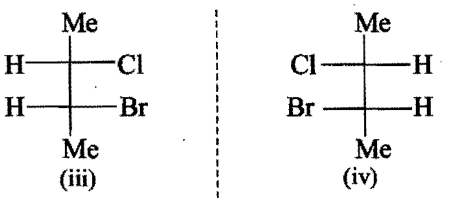


$$CH_3-\underset{Br}{\overset{*}{C}H}-\underset{Cl}{\overset{*}{C}H}-CH_3$$



(i) (ii)

Mirror



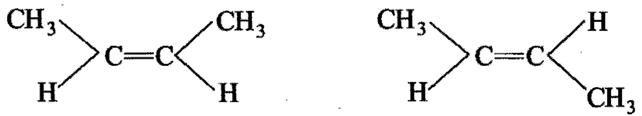
(iii) (iv)

Mirror

(i) is enantiomer of (ii) and diastereomer of (iii) and (iv)
(ii) is enantiomer of (i) and diastereomer of (iii) and (iv)
(iii) is enantiomer of (iv) and diastereomer of (i) and (ii)
(iv) is enantiomer of (iii) and diastereomer of (i) and (ii)

Stereoisomers that are not mirror images (enantiomers) of each other are called diastereomers.

Diastereomers are also encountered in the case of geometrical isomers.



(Cis) *(Trans)*

The important characteristics of diastereomers are:

(i) They show similar but not identical chemical properties. The rates of reactions are different.

(ii) They have different physical properties, such as melting points, boiling points, densities, solubilities, refractive indices, etc.

(iii) They can be easily separated through fractional crystallisation, fractional distillation, chromatography, etc.

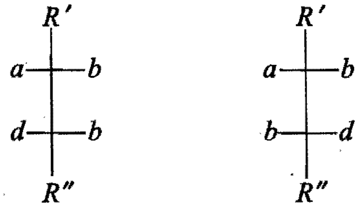
Erythro and threo system

This nomenclature is used only for two adjacent chiral carbon compounds and have the following structure:

$$R'—Cab—Cbd—R''$$

Out of six substituents, the two substituents (*i.e.*, group b) on two chiral centres should be same.

When Fischer projections are drawn for stereoisomers with two adjacent chirality centre the pair of enantiomers with similar groups on the same side of carbon vertical chain is called **erythro form.** The pair of enantiomers with similar groups on the opposite side is called **threo form.**



Erythro form Threo form

The stereoisomers (iii) and (iv) are the **erythro enantiomers** and (i) and (ii) are the **threo enantiomers.**

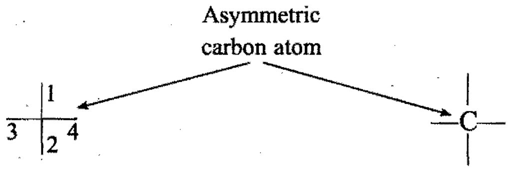
4.15 FISCHER PROJECTION FORMULAE

Emil Fischer (1891) provided an easy method to represent the three dimensional formulae of various organic molecules on paper. Thus, **Fischer projection is a planar representation of the three dimensional structure.**

By convention, the following points are followed in writing the Fischer formula:

(i) The carbon chain of the compound is arranged vertically with the most oxidised carbon at the top.

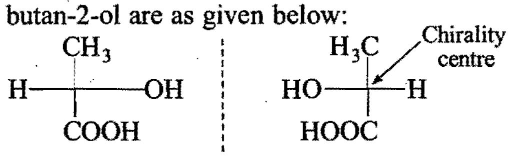
(ii) The asymmetric carbon atom is in the paper plane and is represented at the interaction of crossed lines.



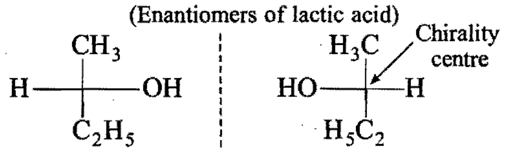
(iii) Vertical lines are used to represent bonds going away from the observer, *i.e.*, groups attached to the vertical lines are understood to be present behind the plane of the paper.

(iv) Horizontal lines represent bonds coming towards the observer, *i.e.*, groups attached to the horizontal lines are understood to be present above the plane of the paper.

The Fischer projection formulae of enantiomers of lactic acid and butan-2-ol are as given below:

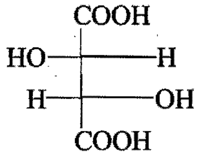


(Enantiomers of lactic acid)

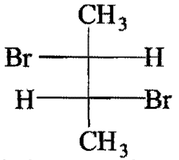


(Enantiomers of butan-2-ol)

Some other Fischer projections are as given below :



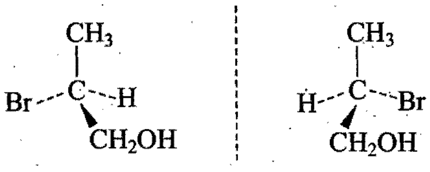
Fischer projection of one of the enantiomers of tartaric acid



Fischer projection of one of the enantiomers of 2,3-dibromobutane

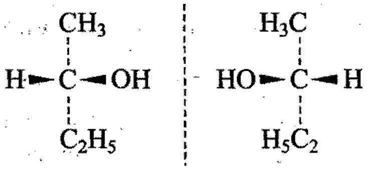
Along with Fischer projection formulae, the enantiomers of a compound can also be represented by the given ways:

(a) Perspective Formulae : For example,



(Enantiomers of 2-bromo-1-propanol)

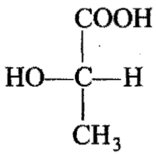
(b) Projection Formulae : For example,



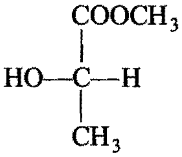
(Enantiomers of butan-2-ol)

4.16 SPECIFICATION OF CONFIGURATION

The arrangement in space of the atoms or groups that characterizes a stereoisomer is called its configuration. A stereoisomer should be recognised by its configuration and not by its property of rotation whether it is dextrorotatory (+) or laevorotatory (–) as the sign of rotation of a stereoisomer is not related to its configuration. A compound and its derivatives having the same configuration may have different sign of rotations. Lactic acid and its ester having same configuration possess opposite sign of rotation.



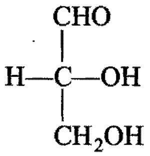
(+) Lactic acid



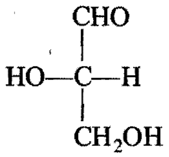
(–) Methyl ester of lactic acid

Two systems have been developed for studying the configuration of stereoisomers.

(i) Relative configuration (*D, L*-nomenclature) : Before 1951, no method was available to determine the **absolute configuration** (actual arrangement of atoms or groups in space) of a stereoisomer. The configuration of various stereoisomers were studied with respect to glyceraldehyde, (*i.e.*, relative configuration) which was taken as an arbitrary standard. Glyceraldehyde having the —OH group on the right and hydrogen atom on the left was arbitrarily given the configurational symbol '*D*' and its mirror image with —OH group on the left and hydrogen atom on the right was given the configurational symbol '*L*'.



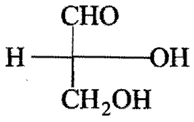
D-form
(—OH group on the right side)



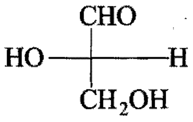
L-form
(—OH group on the left side)

Any stereoisomer which can be obtained from or converted into *D*-glyceraldehyde will belong to *D*-series. Similarly, any stereoisomer which can be obtained from or converted into *L*-glyceraldehyde will belong to *L*-series. The sign (+) or (–) added after *D*- and *L*-letters indicates the direction of the optical rotation. An optical active substance having *D*-configuration can be dextro (+) or laevorotatory (–). Similarly, an optical active substance having *L*-configuration can be dextro (+) or laevorotatory (–).

Now, the comparison can be made with the absolute configurations of glyceraldehyde as given below:

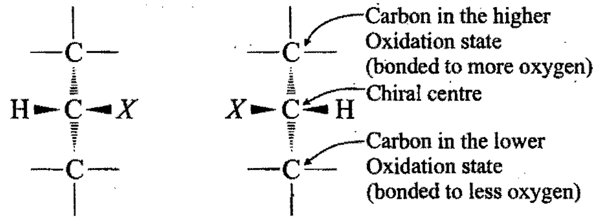


D (+) Glyceraldehyde

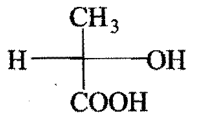


L (–) Glyceraldehyde

For Example, the most oxidised carbon attached to the chiral centre is placed on the top of vertical line and the group with carbon atom forming a part of the chain is kept at the bottom of vertical line. The horizontal line represents the remaining atoms or groups projected towards the observer.

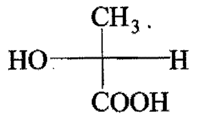


Other examples are lactic acid, glyceric acid, glucose and fructose, etc.



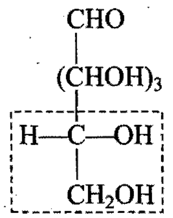
$$\begin{array}{rcl} & \mathrm{CH_3} & \\ \mathrm{H} & + & \mathrm{OH} \\ & \mathrm{COOH} & \end{array}$$

D (+) Lactic acid



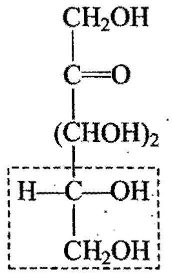
$$\begin{array}{rcl} & \mathrm{CH_3} & \\ \mathrm{HO} & + & \mathrm{H} \\ & \mathrm{COOH} & \end{array}$$

L (–) Lactic acid



$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{(CHOH)_3} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

D(+) Glucose

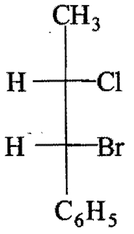


$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{(CHOH)_2} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

D(–) Fructose

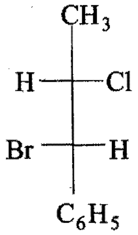
(In sugar series, the letters *D*- and *L*- are related to the configuration of the last but one C-atom in a molecule.)

Example 13. *Which of the following compounds are erythro and threo enantiomers?*



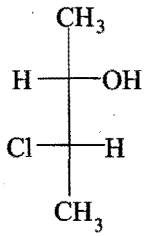
$$\begin{array}{rcl} & \mathrm{CH_3} & \\ \mathrm{H} & + & \mathrm{Cl} \\ \mathrm{H} & + & \mathrm{Br} \\ & \mathrm{C_6H_5} & \end{array}$$

(*i*)



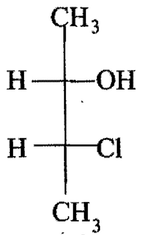
$$\begin{array}{rcl} & \mathrm{CH_3} & \\ \mathrm{H} & + & \mathrm{Cl} \\ \mathrm{Br} & + & \mathrm{H} \\ & \mathrm{C_6H_5} & \end{array}$$

(*ii*)



$$\begin{array}{rcl} & \mathrm{CH_3} & \\ \mathrm{H} & + & \mathrm{OH} \\ \mathrm{Cl} & + & \mathrm{H} \\ & \mathrm{CH_3} & \end{array}$$

(*iii*)



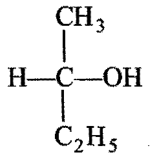
$$\begin{array}{rcl} & \mathrm{CH_3} & \\ \mathrm{H} & + & \mathrm{OH} \\ \mathrm{H} & + & \mathrm{Cl} \\ & \mathrm{CH_3} & \end{array}$$

(*iv*)

Solution : Structures (i) and (iv) are *erythro* enantiomers because the two like H-atoms are on the same side in Fischer projection formula.

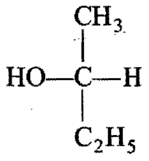
Structures (ii) and (iii) are *threo* enantiomers.

(ii) Absolute configuration (*R* and *S* systems of nomenclature): Butan-2-ol molecule can have the following two different configurations:



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{C_2H_5} \end{array}$$

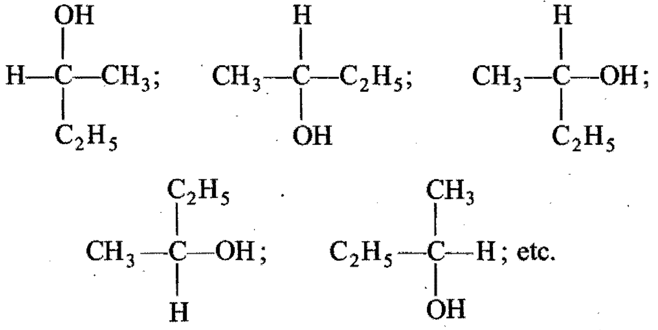
(I)



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{C_2H_5} \end{array}$$

(II)

The formula of butan-2-ol can be represented in a number of ways, *e.g.*,



$$\begin{array}{c} \mathrm{OH} \\ | \\ \mathrm{H{-}C{-}CH_3}; \\ | \\ \mathrm{C_2H_5} \end{array} \quad \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{CH_3{-}C{-}C_2H_5}; \\ | \\ \mathrm{OH} \end{array} \quad \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{CH_3{-}C{-}OH}; \\ | \\ \mathrm{C_2H_5} \end{array}$$

$$\begin{array}{c} \mathrm{C_2H_5} \\ | \\ \mathrm{CH_3{-}C{-}OH}; \\ | \\ \mathrm{H} \end{array} \quad \begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{C_2H_5{-}C{-}H}; \text{ etc.} \\ | \\ \mathrm{OH} \end{array}$$

The above formulae represent either configuration (I) or configuration (II). In order to designate these configurations, a system of nomenclature called **Cahn-Ingold-Prelog** system has been developed. The important features of the system are:

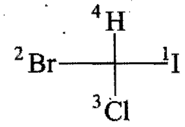
Step 1. Order of Priority: The four different groups attached to the chiral carbon atom are assigned a priority or order of precedence 1, 2, 3 or 4 on the basis of **sequence rules** (see **Sec. 4.8**). 1 is the highest priority group and 4 is the lowest, ($i.e., 1 > 2 > 3 > 4$).

Sequence Rule I. If all the four atoms attached to chirality centre are different, their priority numbers are decided on the basis of their atomic numbers. The atom of higher atomic number gets the higher priority.

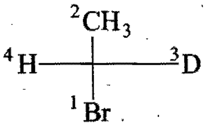
For example, in the compound, bromochloroiodo methane (CHClBrI), the order of decreasing priority is I = (1), Br = (2), Cl = (3) and H = (4).

If two of the atoms attached to chirality centre are isotopes of the same element, then atom of higher mass number gets higher priority.

For example, in the compound, α-deuterio ethylbromide [$CH_3^*CH(D)Br$], the order of decreasing priority is: Br = (1), CH_3 = (2), D = (3) and H = (4).



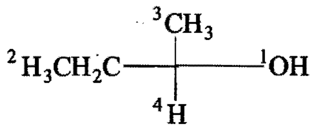
$$\begin{array}{rcl} & {}^{4}\mathrm{H} & \\ {}^{2}\mathrm{Br} & + & {}^{1}\mathrm{I} \\ & {}^{3}\mathrm{Cl} & \end{array}$$



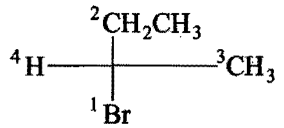
$$\begin{array}{rcl} & {}^{2}\mathrm{CH_3} & \\ {}^{4}\mathrm{H} & + & {}^{3}\mathrm{D} \\ & {}^{1}\mathrm{Br} & \end{array}$$

Rule II. If two of the atoms attached to chirality centre are same and their priority sequence unable to be decided on the basis of **rule I,** in such cases the relative priorities can be decided by comparing the second (or even third) atom of the respective group.

For example, in butan-2-ol, the chiral carbon is attached to OH, H, CH_3, CH_3CH_2 groups. The priorities of CH_3 and CH_3CH_2 groups cannot be decided by rule I. In CH_3 group, the second atoms are H, H, H while in CH_3CH_2 group, the second atoms are C, H, H. Now by comparison, C has higher atomic number than H, therefore CH_3CH_2 group gets priority over CH_3 group. Hence, the sequence of priority for butan-2-ol is; OH = (1), CH_3CH_2 = (2), CH_3 = (3) and H = (4). The other example is 2-bromobutane.

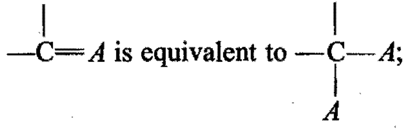


Butan-2-ol

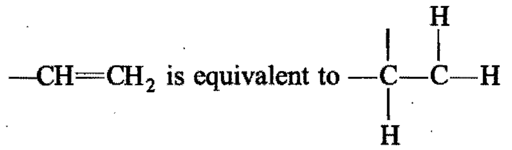


2-Bromobutane

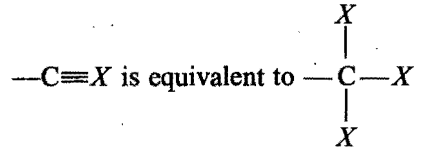
Rule III. This is an extension of rule II. If the second atom is attached by double bond or triple bond, then double bonds are treated as they have two single bonds and triple bonds have three single bonds respectively. In other words, each doubly bonded atom is duplicated and triply bonded atom is triplicated. Thus,



$-C{=}A$ is equivalent to $-\underset{A}{C}-A$;

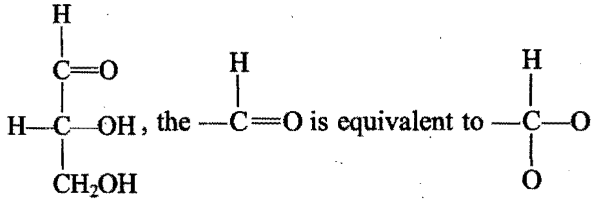


$-CH{=}CH_2$ is equivalent to $-\underset{H}{C}-\overset{H}{C}-H$



$-C{\equiv}X$ is equivalent to $-\overset{X}{\underset{X}{C}}-X$

For example, in glyceraldehyde

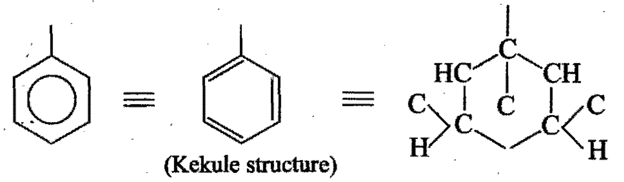


$H-\overset{H-C=O}{\underset{CH_2OH}{C}}-OH$, the $-\overset{H}{C}{=}O$ is equivalent to $-\overset{H}{\underset{O}{C}}-O$

and —OH has the highest priority of all the substituents in glyceraldehyde. Thus, O, O, H of —CHO gets priority over O, H, H of —CH_2OH. Hence, the order of decreasing priority is:

$-OH = (1)$, $-CHO = (2)$, $-CH_2OH = (3)$ and $-H = (4)$

In case of phenyl (C_6H_5) group



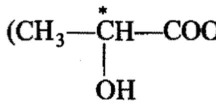
(Kekule structure)

The C, C, C of phenyl group gets priority over C, C, H of isopropyl group. In general, the decreasing order of priority in phenyl, ethynyl (acetylenic), ethenyl (vinyl) and isopropyl groups are as follows:

$C_6H_5- > -C{\equiv}CH > -CH{=}CH_2 > -CH(CH_3)_2$

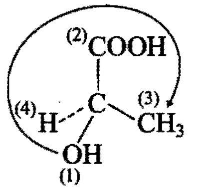
Step 2. After deciding the priority of four atoms or groups attached to the chirality centre, the molecule (formula) is now rotated so that the group of lowest priority (4) is directed away from the eye (viewer). The arrangement of remaining three groups is viewed in decreasing order of their priorities, *i.e.*, from 1 to 2 to 3. In looking so, if the eye travels in a **clockwise** direction, the configuration is specified as ***R*** (from Latin word *rectus* meaning right), while in case eye travels in the **anticlockwise** direction, the configuration is specified as ***S*** (from Latin word *sinister* meaning left).

The given examples illustrate the above procedure.

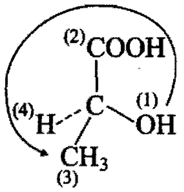


(i) **Lactic acid :** $(CH_3-\underset{OH}{\overset{*}{C}H}-COOH)$. The sequence of priority of various groups attached to chirality centre is:

$-OH = (1)$, $-COOH = (2)$, $-CH_3 = (3)$ and $H = (4)$

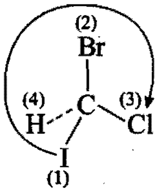


R-(Clockwise)

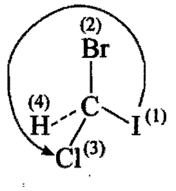


S-(Anticlockwise)

(ii) **Bromo chloro iodomethane:** ($\overset{*}{C}HClBrI$). The sequence of priority is I = (1), Br = (2), Cl = (3) and H = (4).



R-(Clockwise)



S-(Anticlockwise)

The priority order is as follows:

I, Br, Cl, SO_3H, SH, F, O*R*, OH, NO_2 NR_2, NH*R*, NH_2, COO*R*, COOH, $CONH_2$, $COCH_3$, CHO, CH_2OH, CN, CR_3, C_6H_5, $-C{\equiv}CH$, $-CH{=}CH_2$, CHR_2, CH_2R, CH_3, D and H.

(iii) When the molecule contains more than one chiral centre, the same procedure is applied to each.

Note : (i) A racemic mixture is designated as (*R*, *S*).

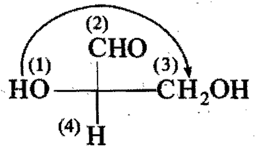
(ii) The direction of rotation of plane-polarized light has nothing to do with *R*-*S* notation. An *R*- or *S*-compound may be either dextrorotatory or laevorotatory.

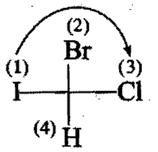
Assigning of *R* and *S* configuration from Fischer projections containing one chirality centre.

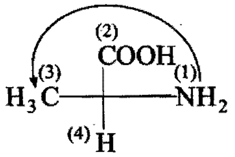
Step 1. Assign priorities to the four atoms or groups attached to chiral centre in the usual way.

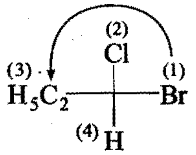
Step 2. As per the priority rules, the atom (H) or group of lowest priority is to be brought vertically (upward or downward) in the Fischer projection and directed away from the viewer. Now, determine the direction of rotation while going from 1 to 2 to 3 of remaining three groups and assign *R* or *S* configuration. This step is carried out differently in the following ways:

(i) When atom or group of lowest priority is at the bottom of vertical line. Move the eye in order of decreasing priority to determine the configuration.

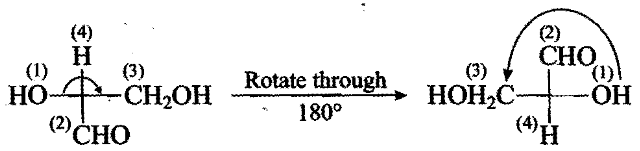

R-Glyceraldehyde (Clockwise)


R-Bromochloroiodomethane (Clockwise)


S-(Anticlockwise)

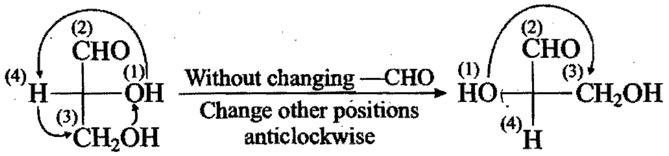

S-(Anticlockwise)

(ii) When atom or group of lowest priority is at the top of vertical line. In such a case rotate the entire molecule through 180°, so that the atoms or groups of lowest priority come at the bottom. Now, move the eye in order of decreasing priority to determine the configuration.



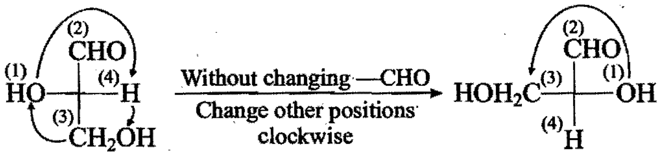
S-Glyceraldehyde (Anticlockwise)

(iii) When atom or group of lowest priority appears at the left hand side on the horizontal line. Then without changing the position at the top of vertical line, change the positions of other atoms or groups in anticlockwise direction till the group of lowest priority comes at the bottom of vertical line. Now, note the movement of eye in order of decreasing priority to determine the configuration.



R-Glyceraldehyde (Clockwise)

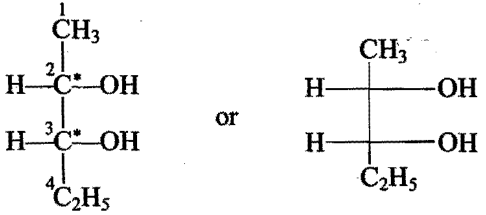
(iv) When atom or group of lowest priority appears at the right hand side on the horizontal line. Then without changing the position at the top of vertical line, change the positions of other atoms or groups till the group of lowest priority comes at the bottom of vertical line. Now, determine the configuration in a usual manner.



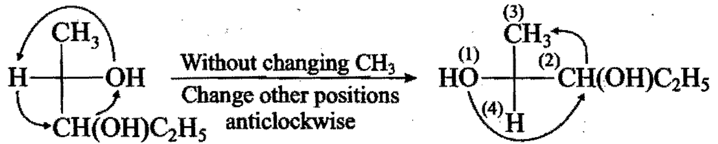
S-Glyceraldehyde (Anticlockwise)

Assigning of *R* and *S* configurations from Fischer projection containing two chirality centre.

If a molecule contains two or more chiral carbon atoms, then configuration (*R* or *S*) of each of the chirality centre is assigned separately following the sequence rules as discussed earlier. For example,

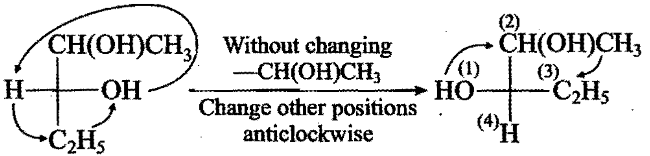


For chiral carbon 2,



S-(Anticlockwise)

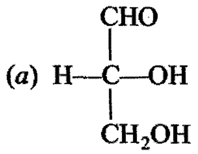
For chiral carbon 3,

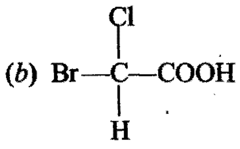


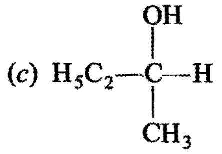
R-(Clockwise)

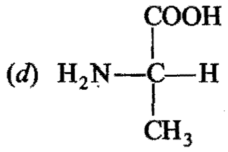
Thus, the compound is $(2S, 3R)$ pentane-2,3-diol.

Example 14. *Assign R or S configuration to each of the following compounds*:

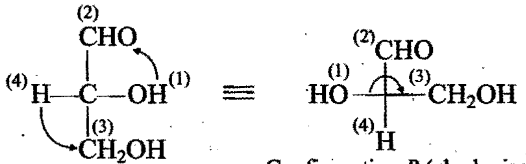

$$(a)\ \begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ CH_2OH \end{array}$$


$$(b)\ \begin{array}{c} Cl \\ | \\ Br-C-COOH \\ | \\ H \end{array}$$


$$(c)\ \begin{array}{c} OH \\ | \\ H_5C_2-C-H \\ | \\ CH_3 \end{array}$$

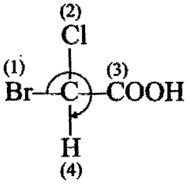

$$(d)\ \begin{array}{c} COOH \\ | \\ H_2N-C-H \\ | \\ CH_3 \end{array}$$

Solution : (a) Order of priority is
$-OH > -CHO > -CH_2OH > -H$.

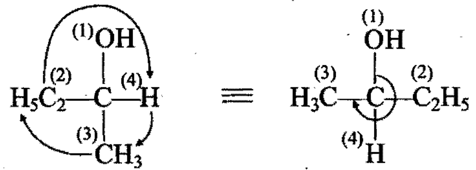

Configuration *R* (clockwise)

Note : The lowest priority group is positioned at the bottom and away from the observer. This is done by interchanging groups bonded to the asymmetric carbon. The interchange operation is always done in pairs to avoid a configuration change.

(b) Order of priority is $-Br > -Cl > -COOH > -H$

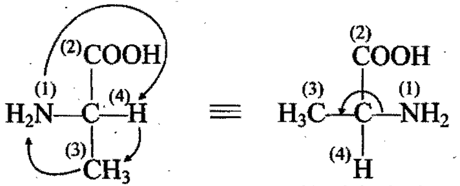

Configuration *R* (Clockwise)

(c) Order of priority is:
$—OH > —C_2H_5 > —CH_3 > —H$



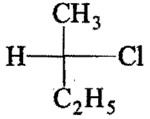
R-(Clockwise)

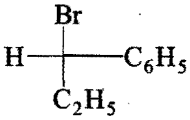
(d) Order of priority is
$—NH_2 > —COOH > —CH_3 > H$

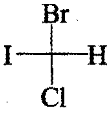


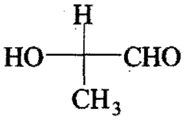
S-(Anticlockwise)

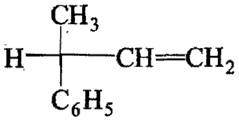
Example 15. *Assign R or S configurations of the following Fischer projections*:

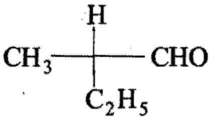
(a)


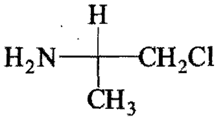
(b)


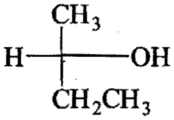
(c)


(d)


(e)


(f)


(g)


(h)


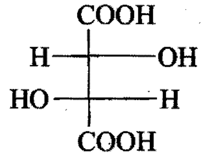
Solution : (a) R, (b) S, (c) S, (d) R, (e) R, (f) R, (g) R, (h) S.

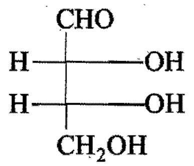
Example 16. *Assign the priority order number to the following atoms or groups*:

(a) $—OH, —CH_2OH, —CHO, —H$
(b) $—CHO, —CH_2OH, —CH_3, —OH$
(c) $C_6H_5—, —CH(CH_3)_2, —H, —NH_2$
(d) $—CH(CH_3)_2, —CH{=}CH_2, —C{\equiv}CH, C_6H_5—$
(e) $—CH_3, —CH_2Br, —CH_2OH, —CH_2Cl$
(f) $—OCH_3, —N(CH_3)_2, —CH_3, —H$
(g) $—CH{=}CH_2, —CH_3, C_6H_5—, —CH_2CH_3$
(h) $(CH_3)_2CH—, —Cl, —CH_2CH_2CH_2Br, —CH_2CH_2Br$
(i) $—Cl, —Br, —I, —NH_2$

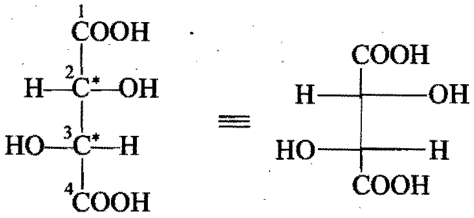
Solution : (a) 1, 3, 2, 4 (b) 2, 3, 4, 1
(c) 2, 3, 4, 1 (d) 4, 3, 2, 1
(e) 4, 1, 3, 2 (f) 1, 2, 3, 4
(g) 2, 4, 1, 3 (h) 2, 1, 4, 3
(i) 3, 2, 1, 4

Example 17. *Assign R or S configuration from Fischer projection of the following structures*:

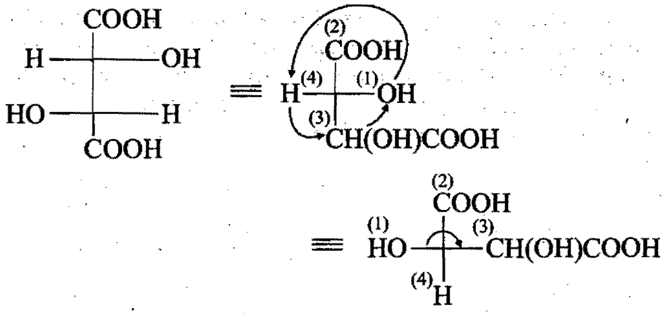
(a)


(b)


Solution : (a) Order of priority for both chiral centres is $—OH > —COOH > —CH(OH)COOH > —H$.

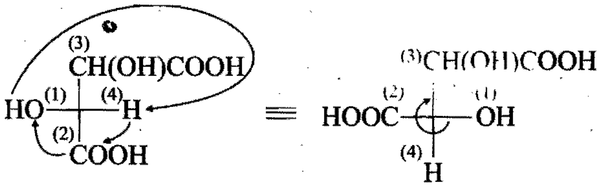


For chiral carbon 2,



Configuration R (at C_2)
(Clockwise)

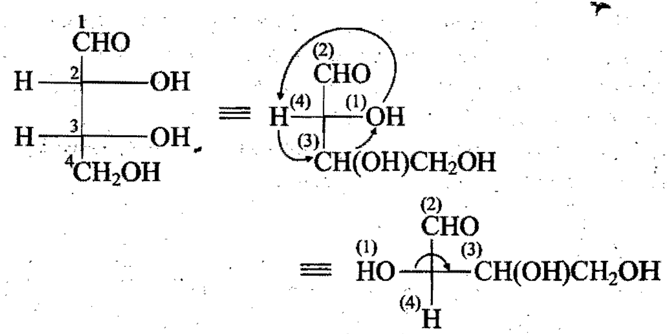
For chiral carbon 3,



Configuration R (at C_3)
(Clockwise)

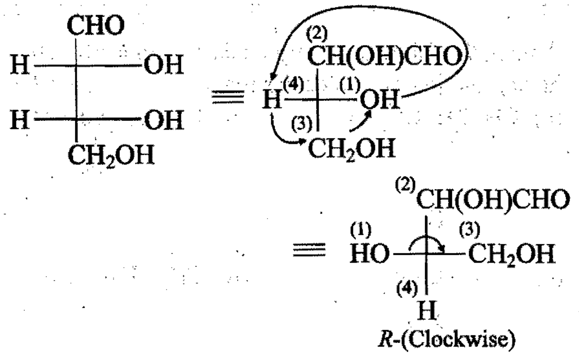
Thus, the compound is (2R, 3R)-2,3-dihydroxy butanedioic acid (Tartaric acid).

(b) Order of priority for chiral carbon 2, is:
$—OH > —CHO > —CH(OH)CH_2OH > —H$



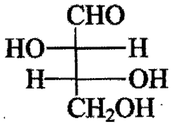
R-(Clockwise)

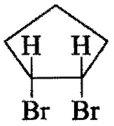
Order of priority for chiral carbon 3, is:
$—OH > —CHOHCHO > —CH_2OH > —H$

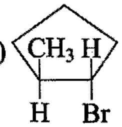


Thus, the compound is (2*R*, 3*R*)-2,3,4-trihydroxy butanal.

Example 18. *Assign the configuration of each chirality centre in the following structures:*

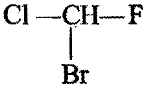
(*a*)


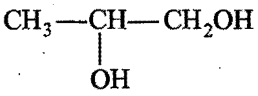
(*b*)


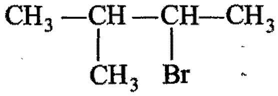
(*c*)


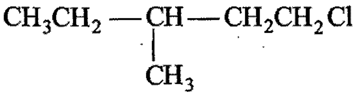
Solution : (a) $2S, 3R$ (b) $1S, 2R$ (c) $1S, 2S$.

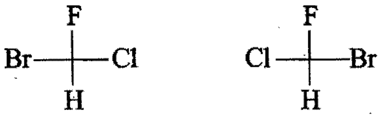
Example 19. *Draw enantiomers of each of the following compounds using Fischer projection formula:*

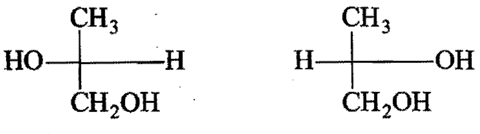
(*i*)

$\mathrm{Cl{-}\underset{\underset{Br}{|}}{CH}{-}F}$

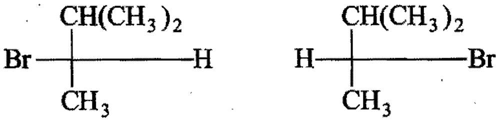
(*ii*)

$\mathrm{CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_2OH}$

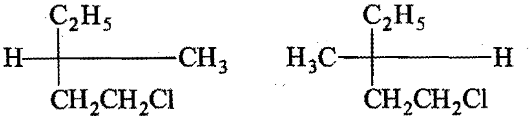
(*iii*)

$\mathrm{CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}\underset{\underset{Br}{|}}{CH}{-}CH_3}$

(*iv*)

$\mathrm{CH_3CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2CH_2Cl}$

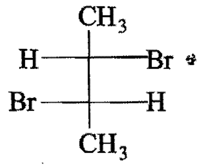
Solution : (i)


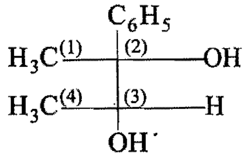
(ii)


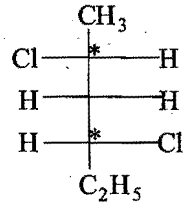
(iii)


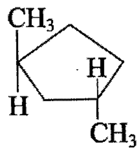
(iv)


Example 20. *Assign R and S configurations to each chiral centre in the following Fischer projection:*

(*i*)


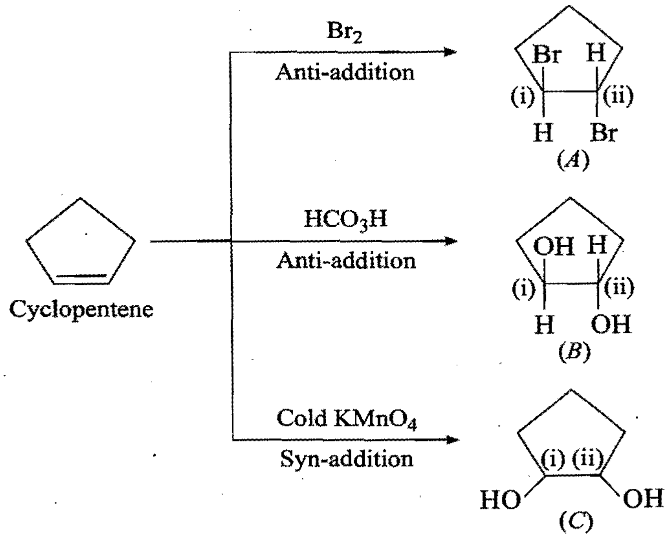
(*ii*)


(*iii*)


(*iv*)


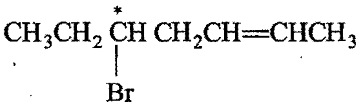
Solution : (i) $2R, 3S$ (ii) $2S, 3R$
(iii) $2R, 4R$ (iv) $1S, 3R$

Example 21. *In the following reactions, assign R and S configuration to the products formed:*



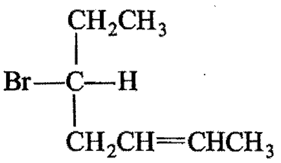
Solution: (*A*) (i) —*R*, (ii) —*R*, (*B*) (i) —*R*, (ii) —*R*, (*C*) (i) —*R*, (ii) —*S*.

Example 22. *The following compound has only one chirality centre, why then does it have four stereoisomers?*

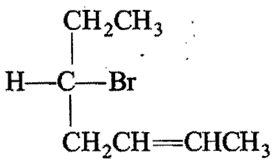

$\mathrm{CH_3CH_2\overset{*}{\underset{\underset{Br}{|}}{CH}}\,CH_2CH{=}CHCH_3}$

Solution: Along with one chirality centre, it also have one unsymmetrical (C=C) bond. Thus, there are:

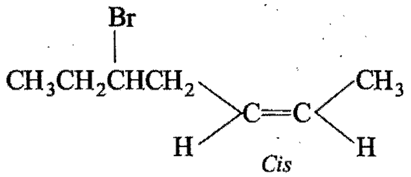
(i) two optical stereoisomers



and

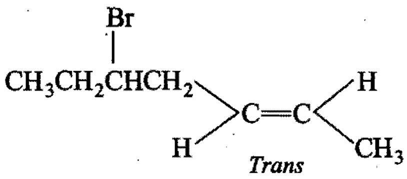


(ii) and two geometrical isomers



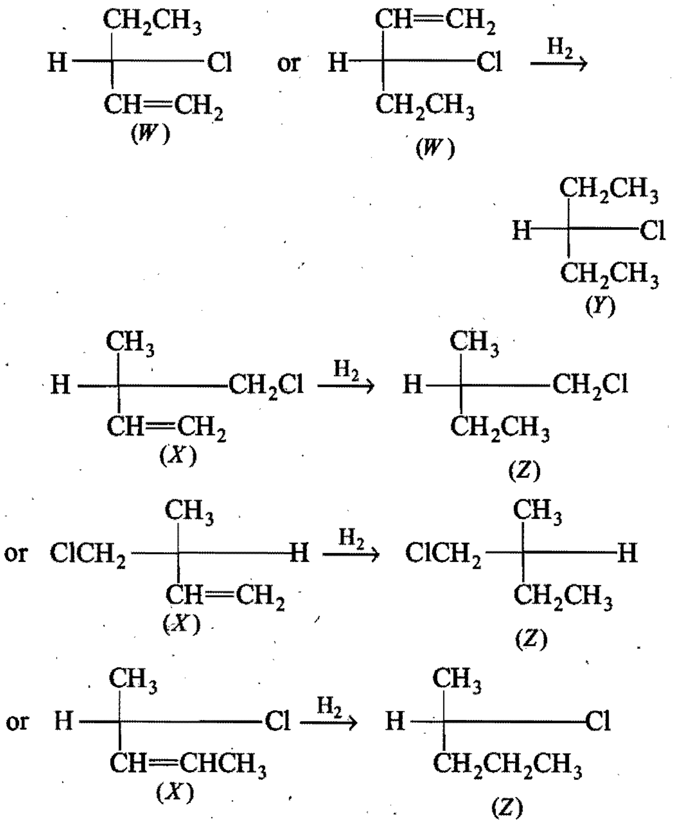
Cis

and

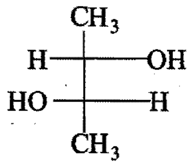


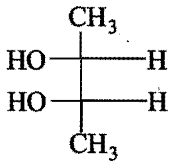
Example 23. *(W) and (X) are optically active isomers of* C_5H_9Cl. *(W) on treatment with one mole of* H_2 *is converted to an optically inactive compound (Y), but (X) gives an optically active compound (Z) under the same conditions. Give the structure of (Y) and configuration of (W), (X) and (Z) in Fischer projections.* **[Roorkee 2000]**

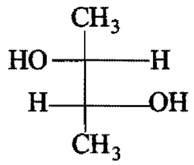
Solution :



Example 24. *Identify the pairs of enantiomers and diastereomers from the following compounds (I), (II) and (III):* **[IIT 2000]**


(I)


(II)


(III)

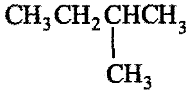
Solution : Structures (I) and (III) are **enantiomers** because these are mirror image of each other.

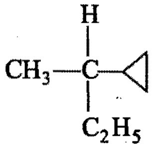
Structures (I) and (II); (II) and (III) are **diastereomers** because these are not mirror image of each other.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

14. Among the following compounds, the optically active alkane having the lowest molecular mass is: **[AIEEE 2004]**

(a) $CH_3CH_2CH_2CH_3$

(b) 
$CH_3CH_2CH(CH_3)CH_3$

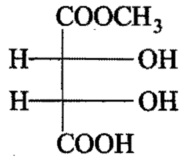
(c) 

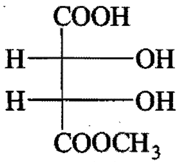
(d) $CH_3CH_2—C\equiv CH$

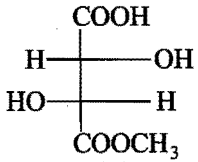
[**Ans.** (c)]

[**Hint:** Optically active due to the presence of chiral carbon atom.]

15. The correct statement about the compounds (*A*), (*B*) and (*C*) is:


(*A*)


(*B*)


(*C*)

[UPSEAT 2004]

(a) (*A*) and (*B*) are identical
(b) (*A*) and (*B*) are diastereomers
(c) (*A*) and (*C*) are enantiomers
(d) (*A*) and (*B*) are enantiomers

[**Ans.** (b)]

[**Hint:** They are neither superimposable nor they are mirror images.]

16. The number of isomeric pentyl alcohols possible are: **[DCE 2009]**

(a) two (b) four
(c) six (d) eight

[**Ans.** (d)]

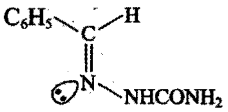
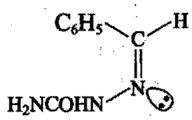
[**Hint:** Sec Art. 9.4, problem 2]

17. Which of the following will form two isomers with semicarbazide?

(a) Benzaldehyde (b) Acetone
(c) Benzoquinone (d) Benzophenone

[**Ans.** (a)]

[**Hint :** $\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + \underset{\text{Semicarbazide}}{H_2NNHCONH_2} \longrightarrow \underset{\text{Semicarbazone}}{C_6H_5CH{=}NNHCONH_2}$

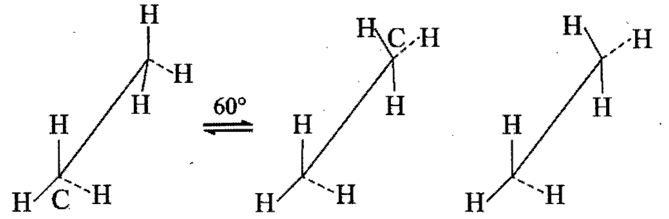

and

]

4.17 CONFORMATIONAL ISOMERISM

The sigma bond joining the two carbon atoms as in ethane is cylindrically symmetrical about the nuclear axis. This symmetry of the bond permits the free rotation of the two carbon atoms with respect to each other along the bond axis without breaking the bond. If one CH_3 group is kept stationary and other methyl group is allowed to rotate through C—C axis, an infinite number of atomic arrangements are possible depending upon the angle through which the CH_3 group is rotated. **The different arrangements of atoms in space that result from the free rotation of groups about C—C bond axis are called conformations or conformational isomers or rotational isomers and the phenomenon as conformational isomerism.** The basic structure of the molecule and various bond lengths and bond angles, however, remain the same in all these arrangements or conformations.

Conformations of Ethane (Sawhorse Projection)

Of the infinite number of possible arrangements of ethane, two conformations represent the extremes. These are called the **eclipsed conformation** (I) and the **staggered conformation** (II). In the case of *eclipsed* conformation, the hydrogens of one carbon atom are directly behind the other, consequently, the repulsion in these atoms is maximum. While in the *staggered* conformation, the hydrogens of the two carbon atoms are staggered with respect to one another. As a result, they are at maximum distance apart and have minimum repulsion between them. Any other arrangement which will be between these two extreme positions as shown in (III) is known as **Gauche** or **Skew form.**

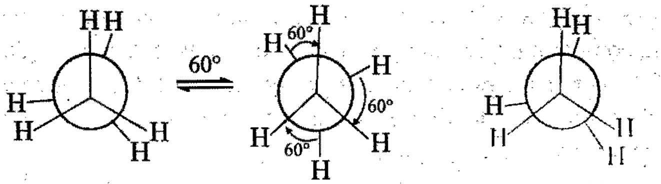


(i) Eclipsed form (ii) Staggered form (iii) Gauche or Skew form

(Sawhorse Projection)

Newman Projection

In Newman projection, the two carbon atoms forming the sigma bond are represented by two circles, one behind the other, so that only the front carbon is seen. The hydrogen atoms attached to the front carbon are represented by C—H bonds from the centre of circle. The C—H bonds of the back carbon are drawn from the circumference of the circle.



(i) Eclipsed form (ii) Staggered form (iii) Gauche or skew form

(Newman Projection)

A rotation of 60° converts a staggered conformation into an eclipsed conformation, or *vice-versa*. Rotation between 0° to 60° generates one of the many other arrangements in between staggered and eclipsed forms. These arrangements are called **Gauche** or **Skew** form.

Relative Stabilities of the Conformations of Ethane

The potential energy of the ethane molecule changes somewhat with rotation around the C—C bond on account of the distance between hydrogen atoms of the two carbon atoms. The potential energy of staggered form is minimum and of eclipsed form is maximum. The difference in the energy content between the two extreme conformations is 3 kcal/mol (or 12.5 kJ mol^{-1}). This small barrier of rotation is also called **Torsional barrier.** This energy is not large enough to prevent rotation. Even at ordinary temperature, the energy barrier is overcome through collisions and thus, the conformations keep on changing from one form to the other. The variation of energy with rotation about C—C bond in ethane has been shown in figure.

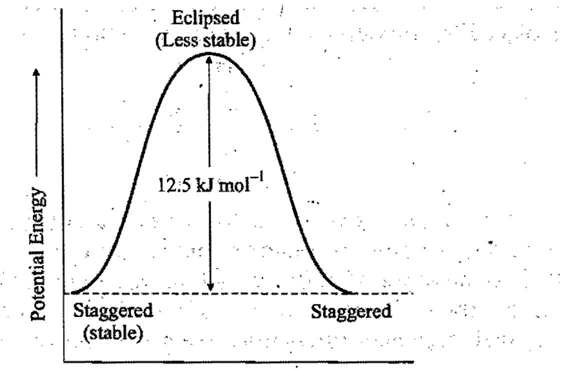


Fig. 4.6

The eclipsed conformation is least stable because the hydrogens and bonding pairs of electrons on adjacent carbon atoms are as near one another as possible. This causes maximum repulsion. Thus, the eclipsed form is less abundant.

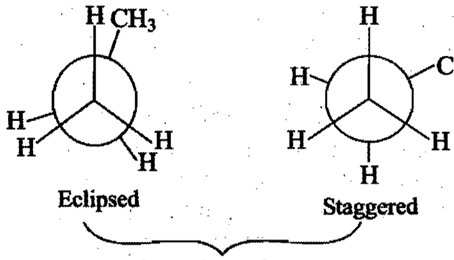
The staggered conformation is most stable because the hydrogens and bonding pairs of electrons are at a maximum distance. This causes minimum repulsion. Thus, this form is most abundant.

The other conformations lie between these two in stability. It is not possible to isolate the different conformations of ethane because they are constantly interconverting. In higher alkanes, one or more hydrogen atoms of ethane are replaced by alkyl groups. Other higher hydrocarbons and substituted ethanes all exist in these conformations. The study of their properties is known as **conformational analysis.**

Conformations of Propane

The conformations of propane are similar to those of ethane except that one of the hydrogen atoms is replaced by a methyl group. The two extreme conformations of propane are shown below **(Newman Projections):**

The difference in the potential energy between these extreme conformations is about 3.4 kcal mol^{-1} (or 14.2 kJ mol^{-1}).

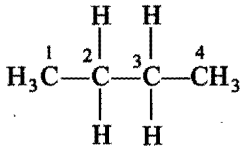


Conformations of propane

Even then, this energy barrier of rotation about C—C bond is so small that it cannot prevent rotation. As a result, the two conformations are readily interconvertible by rotation through an angle of 60° and thus, it is not possible to separate these two conformations.

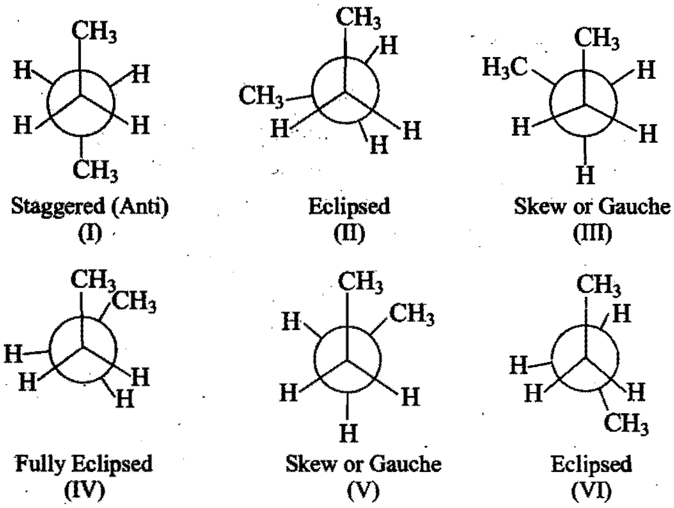
Conformations of Butane

n-Butane molecule can be considered as a dimethyl derivative of ethane in which one H-atom of each carbon is replaced by a methyl group as shown below:



$$H_3\overset{1}{C}-\underset{H}{\overset{H}{\overset{2}{C}}}-\underset{H}{\overset{H}{\overset{3}{C}}}-\overset{4}{C}H_3$$

If now one of these central carbon atoms (C_2 or C_3) is fixed and the other is rotated round the central (C_2-C_3) bond through an angle of 360°, we get many conformations. Out of these only six conformations (60° each time) are important and their Newman Projections are given ahead:



Staggered (Anti) (I)   Eclipsed (II)   Skew or Gauche (III)

Fully Eclipsed (IV)   Skew or Gauche (V)   Eclipsed (VI)

Fig. 4.7 Different conformations of *n*-butane

The maximum staggered conformation (I) is most stable in which methyl groups are far apart as far as possible, due to minimum repulsion between methyl groups and is also called **Anti-conformation.** This on rotation through 60° gives *eclipsed conformation* (II), in which methyl group on one carbon is overlapped by the hydrogen atom on the other carbon.

Other conformations can be obtained by rotating one of the C_2 or C_3 carbon atoms through an angle of 60°. In staggered conformations (III) and (V) (*Skew* or *Gauche*), the methyl groups are so closed that they repel each other (III and V are mirror images). This repulsion causes Gauche conformations to have about 3.8 kJ mol^{-1} more energy than anticonformation. The conformations (II) and (VI) are *partially eclipsed* and unstable because of repulsion. Their potential energy is 14.6 kJ mol^{-1}.

In conformation (IV) (*Fully eclipsed*), the steric strain is maximum, hence, this conformation is most unstable and have potential energy 18.4 kJ mol^{-1}. This is because of repulsion between methyl-methyl group which are very close together.

The **order of stability** of these conformations is:

Anti > Skew or Gauche > Partially Eclipsed > Fully Eclipsed

The energy difference between various conformations is shown below:

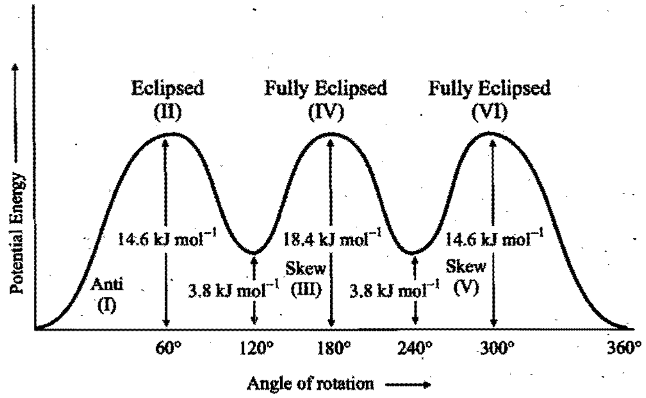


Fig. 4.8

Conformations of Cycloalkane

Conformational isomerism has also been shown in cycloalkane molecules. Cyclopropane and cyclobutane are planar molecules having bond angles of 60° and 90° respectively.

Cyclopropane Cyclobutane Cyclopentane Cyclohexane

The bond angle in these molecules are quite different from the normal tetrahedral bond angle of (109°28′ or 109.5°) which is a normal angle for sp^3-hybridized carbon atoms. This deviation from normal tetrahedral angle introduces considerable angle **strain** in the molecules of these cycloalkanes. Further, greater the deviation from the normal angle, the greater is the strain and greater the instability of the ring compound. For example, cyclopropane with a bond angle of 60° is much strained and hence very reactive. Cyclobutane with a bond angle of 90° is less strained and hence less reactive than cyclopropane.

According to **Baeyer's strain theory,** the amount of the strain is directly proportional to the angle through which a valency bond has deviated from its normal position, *i.e.*, Amount of deviation $(d)=\frac{1}{2}(109°28' - \text{Valency angle})$

e.g., In cyclopropane, $d=\frac{1}{2}(109°28'-60°)=24°44'$

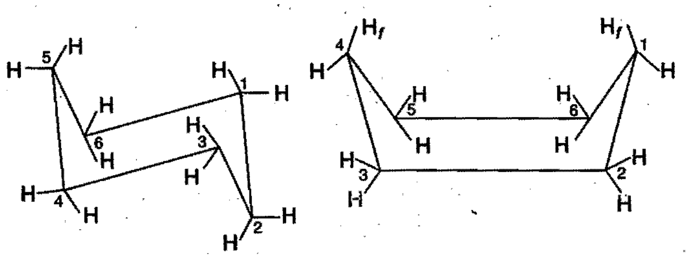
In cyclobutane, $d=\frac{1}{2}(109°28'-90°)=9°44'$

In cyclopentane, $d=\frac{1}{2}(109°28'-108°)=0°44'$

and in cyclohexane, $d=\frac{1}{2}(109°28'-120°)=-5°16'$

Thus, strain is minimum in cyclopentane and hence it is more stable and less reactive than cyclopropane and cyclobutane. As a result, cyclohexane is free from angle of strain and hence is quite stable and unreactive. Therefore, cyclohexane adopts a *non-planar structure.*

According to **Sachse** and **Mohr**, the cyclohexane exists in two *non-planar* or *puckered* (or folded) conformations called the **chair** (*Z* form) and the **boat** (*C* form) conformations as shown in the figure.



Chair conformation
'*Z*' form (staggered form)

Boat conformation
'*C*' form (eclipsed form)

Fig. 4.9 Chair and Boat conformations of cyclohexane

The names of these forms are due to the resemblance of their shapes with chair and boat respectively. Each carbon atom of cyclohexane is bonded to two hydrogens. The bond is one of these hydrogens lies in the plane of the ring. This hydrogen is called **equatorial hydrogen.** The bond to the other hydrogen atom is parallel to the axis; this hydrogen atom is called **axial hydrogen.** Each of six carbon atoms of cyclohexane has one equatorial and one axial hydrogen, in all six axial and six equatorial hydrogen.

Relative Stabilities of Chair and Boat Conformations of Cyclohexane

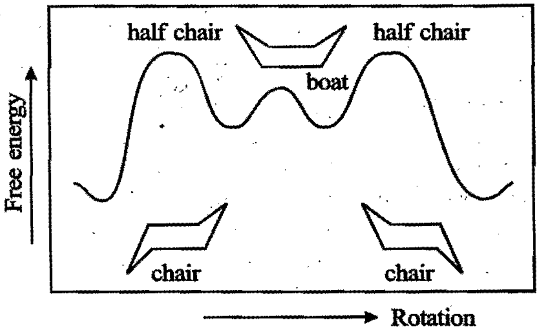
The chair conformation of cyclohexane is more stable than the boat conformation due to the following reasons:

(i) In chair conformation, the adjacent hydrogens on $C_1-C_2, C_2-C_3, C_3-C_4, C_4-C_5, C_5-C_6$ and C_6-C_1 are quite *staggered* (more stable) and the force of repulsion in them is minimum. On the other hand, in boat conformation, the adjacent hydrogen atom on C_2-C_3 and C_5-C_6 are in the less stable *eclipsed* orientations.

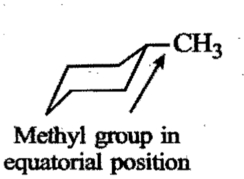
The two forms have not been isolated so far, because the energy difference between the two forms is too small (29.9 kJ mol^{-1}) while 37.7 to 46.0 kJ mol^{-1} is the energy of barrier and one form readily changes into the other.

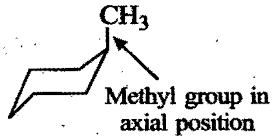
(ii) The two hydrogen atoms (marked as Hf) called the **flag pole hydrogens** and in chair forms, C—H flag poles at C_1 and C_4 are in the *trans* side (distance 2.29Å or 229 pm) having minimum strain and thus more stable. While in boat form the C—H flag poles at C_1 and C_4 are on the same side (distance 1.83 Å or 183 pm) and so steric hindrance is increased and thus stability is decreased.

The following diagram shows the conformations of cyclohexane (and their relative energies) as one chair conformation interconverts to the other chair conformation.



Cyclohexane with methyl group in the equatorial position is more stable than in the axial position.





IMPORTANT POINTS TO REMEMBER (SUMMARY)

- Two or more organic compounds having the same molecular formula but different physical and chemical properties are called isomers and the phenomenon is known as **isomerism.**
- **Structural isomers** are compounds having the same molecular formula but different structures. The isomers differ only in the arrangement of atoms or groups within the molecule, without any reference to space are called structural isomers and the phenomenon is known as **structural isomerism.** It is of the following six types:
- **Chain or nuclear isomerism** is due to the difference in the nature of carbon chain (straight or branched) which forms the nucleus of the molecule.
- **Position isomerism** is due to the difference in the position of the substituent atom or group or an unsaturated linkage in the same carbon chain.
- **Ring chain isomerism** is due to different modes of linking of carbon atoms, *i.e.*, the isomers possess either open-chain or closed-chain structures.
- **Functional isomerism** is due to the difference in the nature of functional group present in the isomers.
- **Metamerism** is due to the difference in the nature of alkyl groups on either side of the same polyvalent atom or functional group (*i.e.*, —O—, —S—, —NH— and —CO—).
- **Tautomerism** is the type of isomerism in which a single compound exists in two readily interconvertible different structures leading to dynamic equilibrium. It is caused by the wandering nature (1,3-migration) of mobile hydrogen atom from one polyvalent atom to the other within the same molecule. Keto-enol system is an important example of tautomerism.
- **Stereoisomerism:** Compounds having the same structural formula but different relative arrangement of atoms or groups in space (configuration) are called stereoisomers and the phenomenon is known as **stereoisomerism.** It is classified into (i) geometrical isomerism (ii) optical isomerism.
- **Geometrical** (or *cis-trans*) **isomerism:** Compounds possess the same structural formula but differ in the spatial arrangement of atoms or groups (or differ in configuration) **around the double bond.** This isomerism is shown by alkenes or their derivatives.
- Geometrical isomerism is possible only when each of the double bonded carbon atoms is attached with two different atoms or groups and carbon atoms joined by double bond cannot rotate freely.
- Similar atoms or groups on the same side of the double bonded carbon are called '*cis*' isomers and similar atoms or groups on the opposite side of the double bonded carbon are called '*trans*' isomers.
- Generally, the *cis*- isomer (*e.g.*, maleic acid) cyclises on heating to form corresponding anhydride while the *trans*- isomer does not form its anhydride at all. The *cis*- isomer of a symmetrical alkene has a definite dipole moment, while the *trans*- isomer has zero dipole moment. In general, *trans*- isomers are more stable than the corresponding *cis*- isomers.
- Geometrical isomerism is also exhibited by compounds containing C═N bond (as in aldoxime), N═N bond (as in azo compounds), cyclic compounds and dienes.
- ***E* and *Z*** system of nomenclature is based on situations when four different atoms or groups are attached to the carbon atoms of a double bond. If two heavier or lighter groups are on same side w.r.t. C═C bond, we call the isomer as **(*Z*-) isomer** (together) and if one heavier and one lighter group is on the opposite side w.r.t. C═C bond, we call it **(*E*-) isomer** (opposite or across).

  E-Z system of nomenclature is based upon the **sequence rules** of Cahn, Ingold and Prelog.
- **Optical isomerism:** Compounds having similar physical and chemical properties and differ only in their behaviour towards plane polarised light are called optical isomers and this phenomenon is known as **optical isomerism.**
- The optical isomer which rotates the plane of polarised light to the **right** (clockwise) is known as **dextrorotatory** or ***d*- form** or **+ve sign** while that which rotates towards **left** (anticlockwise) is known as **laevorotatory or *l*- form or –ve sign.**
- *d*- form (+) and *l*- form (–) are not absolute representations but relative ones. If one isomer is *d*- or (+) then its mirror image is said to be *l* or (–). Thus, *d* and *l* (optical) isomers are also called **enantiomers** and optical isomerism is also called **enantiomerism.** Enantiomers are not superimposable on their mirror image. Such molecules are called **dissymmetric** (having no plane of symmetry) or a **chiral object.** Therefore, dissymmetry is the necessary and sufficient condition for the existence of enantiomers.
- **Chirality centre or stereogenic centre or asymmetric carbon atom:** A carbon atom which is attached to four different atoms or groups in a molecule is called a **chiral** (asymmetric) centre or stereogenic centre and the compounds having chiral centre show optical isomerism. For example, lactic acid, tartaric acid, malic acid and butan-2-ol etc. Carbon atoms with at least two groups identical are said to be **achiral** and the compound is said to have **achirality** and hence, loses its optical activity.
- The number of optical isomers in a compound containing n number of similar asymmetric carbon atoms is always less than 2^n. The classical and most important example of compound containing two similar asymmetric carbon atom is tartaric acid, CH(OH)COOH—CH(OH)COOH which can exist in *d*-form, *l*-form and meso form.

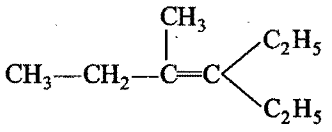
- **Dextro-tartaric acid (*d*-form):** This rotates the plane polarised light to right. The rotation due to the upper half is strengthened by rotation due to lower half. It has no plane of symmetry and occurs in nature.
- **Laevo-tartaric acid (*l*-form):** This rotates the plane polarised light to left. Here again rotation due to upper half is strengthened by rotation due to lower half. It also has no plane of symmetry and does not occur in nature and hence, it is prepared by resolving racemic tartaric acid.

  The *d*- and *l*-tartaric acids are mirror image of each other **(enantiomers).**
- **Racemic (*r*-) tartaric acid:** It is an equimolecular mixture of *d*- and *l*-forms. The rotation of the *d*- form is compensated externally by *l*-form and hence, it is optically inactive due to **external compensation.** It can be resolved into *d*- and *l*-forms.
- **Meso (*m*-) tartaric acid:** It possesses a plane of symmetry and is consequently **optically inactive** and superimposes on its mirror image (*i.e.*, they are identical). The optical inactivity is said to be due to **internal compensation** as the rotation due to upper half of the molecule is balanced by the equal, but opposite rotation due to lower half. It cannot be resolved into active *d*- and *l*-isomers.
- **Resolution of racemic mixture:** The process of separation of racemic mixture (*dl*-) into *d*- and *l*-forms (its enantiomers) is called resolution.
- **Racemization:** It is reverse of resolution, *i.e.*, the process of converting *d*- or *l*-form of an optically active compound into *dl*- (racemic) mixture is termed racemization. Since the rotation of *d*-form is cancelled by equal but opposite rotation of *l*-form, so a racemic mixture (*r*-) is always optically inactive.
- **Asymmetric synthesis:** The synthesis of an optically active compound (chiral centre) from a symmetrical molecule (having no asymmetric carbon) without resolution to form (+) or (–) isomer directly is termed asymmetric synthesis. For example, synthesis of (–) lactic acid from pyruvic acid.
- **Walden Inversion (Optical inversion):** The conversion of *d*- form of an optically active compound into *l*- form of the same or different compound or *vice-versa* is known as Walden inversion. For example, the conversion of *d*-malic acid into *l*-malic acid (or *l*-chloro succinic acid).
- **Diastereomers** are the stereoisomers that are not mirror images (enantiomers) of each other and have different physical and chemical properties.
- **Fischer projection** is a planar representation of the three-dimensional structure as the bonds are projected into the plane of the page, resulting in a cross with asymmetric carbon atom at its centre.
- **Relative configuration (*D*,*L*-nomenclature)**
- ***D*- form:** The enantiomer having hydrogen (H) atom on the left and another group (*X* or —OH) on the right was given *D*-configuration.
- ***L*- form:** The enantiomer with (*X*) or —OH group on the left and hydrogen atom on the right was given the configurational symbol '*L*'.
- **Absolute configuration (*R* and *S* system of nomenclature):** Actual spatial arrangement of atoms or groups (absolute configuration) of each chiral centre in a molecule was devised by Cahn, Ingold and Prelog (CIP).
- The four ligands (atoms or groups) attached to the chiral centre are assigned a sequence of priority according to **sequence rules.**
- *R* (*Rectus* = right) is given to the isomer if sequence is **left to right** (*i.e.*, the eye travels in a clockwise direction).
- *S* (*Sinister* = left) is given to the isomer if sequence is **right to left** (*i.e.*, the eye travels in the anticlockwise direction).
- **Conformational isomerism (conformers):** The different arrangements of atoms in space that result from the free rotation of groups about C—C bond (σ-bond) axis are called conformational (rotational) isomers and the phenomenon is known as **conformational isomerism.**
- Out of the infinite number of possible arrangements of ethane, propane and butane, two conformations represent the extremes. These are called **(i) eclipsed conformation (ii) staggered conformation.**
- Various other structures in between eclipsed and staggered conformations are called **Skew or Gauche conformations.**
- The small increase in electron-electron repulsion (difference in the energy content) upon rotation between the two extreme conformations (*i.e.*, from staggered to an eclipsed) is referred to as **torsional strain** (barrier).
- The eclipsed conformation is least stable while the staggered conformation is most stable. The order of stability of these conformations is :

  Anti > Skew or Gauche > Partially eclipsed > Fully eclipsed.
- **Conformations of cyclohexane:** Sachse and Mohr assumed two non-planar or puckered (or folded) forms of cyclohexane. These are **chair** and **boat** conformations which are free from angle strain. Both forms are interconvertible into each other.
- **Chair conformation or *Z* form** (staggered form) is more stable than **boat conformation or *C* form** (eclipsed form).

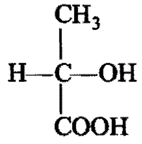
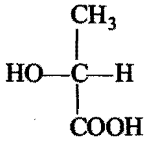
QUESTIONS

❖ Very Short Answer Type

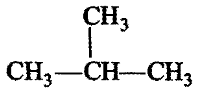
1. Fill in the blanks:
   - (a) The number of possible isomers of C_5H_{12} is ......
   - (b) $CH_3COC_3H_7$ and $C_2H_5COC_2H_5$ show ......
   - (c) An organic compound with the formula $CH_3CH_2CH_2OH$ shows functional isomerism with compound of the structural formula ......
   - (d) Alkenes can exhibit position, chain and ...... isomerism.
   - (e) Tautomerism is also known as ...... isomerism.
   - (f) Hexane has ...... chain isomers.
   - (g) There must be minimum ...... carbon atoms to exhibit chain isomerism.
   - (h) Carboxylic acids and esters are examples of ...... isomerism.
   - (i) Ketones must contain at least ...... carbon atoms in order to exhibit metamerism.
   - (j) *n*-Butane and isobutane are ...... isomers.
   - (k) The structural formula of the compound isomeric with acetone is ......
   - (l) The chain isomers of *n*-pentane are isopentane and ......
   - (m) *n*-Propyl alcohol and isopropyl alcohol are ...... isomers.
   - (n) Metamers belong to ...... class of compounds.
   - (o) But-2-ene and but-1-ene are ...... isomers.
   - (p) But-1-ene and cyclobutane are ...... isomers.
   - (q) The number of isomers of molecular formula C_8H_{10} containing benzene ring are ....
   - (r) The two extreme conformations of ethane are called ...... and ...... conformations.
   - (s) Staggered form of ethane is ...... stable than eclipsed form.
   - (t) Ethyl cyanide and ethyl isocyanide are ...... isomers.
   - (u) The possible number of dichloro derivatives of propane are ......
   - (v) At room temperature, the eclipsed and the staggered forms of ethane interconvert rapidly and ...... be isolated as separate conformers.
   - (w) Which conformer of butane has highest energy ...... and which one has lowest ......
   - (x) Two or more organic compounds having same molecular formula but different properties are known as ...... and the phenomenon as ......
   - (y) Ethyl benzene is ...... isomer to xylenes.
   - (z) The structure of enol form of $CH_3COCH_2COCH_3$ with intramolecular hydrogen bonding is ......
2. Fill in the blanks:
   - (i) Stereoisomers possess ...... molecular and ...... structural formula.
   - (ii) The compound CHCl═CHCl can show ...... isomerism.
   - (iii) Geometrical isomerism is due to ...... rotation of ...... bond.
   - (iv) Isomers which are ...... mirror images are known as ......
   - (v) Optical activity of a compound is measured in terms of ......
   - (vi) *Trans*-forms are ...... stable than *cis*-forms.
   - (vii) Geometrical isomerism is not observed in a molecule if either of the doubly bonded carbon atom has two ...... groups.
   - (viii) Geometrical isomers have ...... physical properties but almost the same ...... properties.
   - (ix) Optical isomers have same physical and chemical properties but differ with respect to rotation of ...... light.
   - (x) A molecule is said to be chiral if it possesses at least ...... carbon atom.
   - (xi) ...... cannot be resolved into *d*- and *l*-forms.
   - (xii) A reaction where diastereomerically different starting materials give diastereomerically different products is called ...... reaction.
   - (xiii) *d*- and *l*- lactic acids are known as ......
   - (xiv) If the replacement of one group at an achiral centre by a new substituent generates a chiral centre, the original molecule is said to be ......
   - (xv) Number of stereoisomers of HOOCCH(OH)COOH is ......
   - (xvi) Enantiomers have asymmetric carbons of different ......
   - (xvii) '*E*' and '*Z*' system of naming geometrical isomers is based on ...... rules.
   - (xviii) Maleic and fumaric acids are a pair of ......
   - (xix) The stereoisomers which are not mirror images to each other are called ......
   - (xx) Fischer projection is a ...... representation of the three dimensional structure.
3. State whether the following statements are **True** or **False:**
   - (a) Members belonging to same class of compounds are called isomers.
   - (b) Isomers have same molecular formula.
   - (c) Can isomer be homologues of each other?
   - (d) *m*-Chlorobromobenzene is an isomer of *m*-bromochlorobenzene.
   - (e) Ethyl alcohol and dimethyl ether are position isomers.
   - (f) All alkenes show *cis-trans* isomerism.
   - (g) 2-Butenedioic acid exhibits *cis-trans* isomerism.
   - (h) The alkene  $CH_3—CH_2—C(CH_3)=C(C_2H_5)_2$ exhibits geometrical isomerism.
   - (i) *Cis-trans* isomers possess different physical properties.
   - (j) *Cis-trans* isomers have different dipole moment.
   - (k) Optically active compounds may exist in four forms.

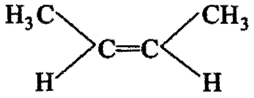
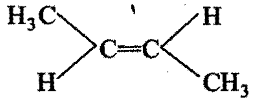
(l) 2,3,4-Trichloropentane has three chiral carbon atoms.
(m) Tartaric acid has two asymmetric carbon atoms.
(n) Every optically active compound has a racemic form.
(o) *d*-form and *l*-form of an optically active compound have same specific rotation with opposite sign.
(p) All forms of compounds containing asymmetric carbon atoms are always optically active.
(q) The compound $CH_3CHOHCOOH$ can have four optical isomers.
(r) In ethane, both eclipsed and staggered forms have same stability.
(s) Propanone does not exhibit the phenomenon of tautomerism.
(t) The specific rotation of a compound is measured by an apparatus called polarimeter.
(u) The first accepted explanation for optical isomerism by certain compounds was given by Le Bel and van't Hoff in 1874.
(v) Only organic molecules can be optically active.
(w) The direction of rotation is denoted by the prefix (+) for dextrorotatory and (–) for laevorotatory enantiomers.
(x) The arrangement in space of the atoms or groups that characterizes a stereoisomer is called its configuration.
(y) Sign of rotation of an enantiomer is related to its configuration.
(z) Diastereomers have different physical properties and similar but not identical chemical properties.

4. Match the following:

[A] (a) A pair of functional isomers
(i)  $H-\overset{CH_3}{\underset{COOH}{C}}-OH$;  $HO-\overset{CH_3}{\underset{COOH}{C}}-H$

(b) A pair of geometrical isomers
(ii) $H_2C{=}CHOH$; CH_3CHO

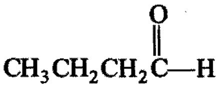
(c) A pair of optical isomers
(iii) $CH_3CH_2CH_2CH_3$;  $CH_3-\overset{CH_3}{CH}-CH_3$

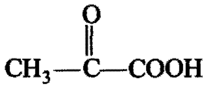
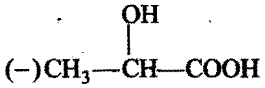
(d) A pair of metamers
(iv)  ; 

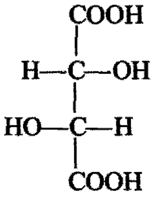
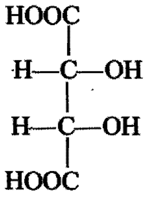
(e) A pair of chain isomers
(v) $CH_3-CH{=}CH-CH_3$; $CH_3-CH_2-CH{=}CH_2$

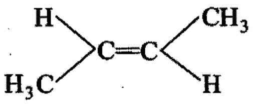
(f) A pair of tautomers
(vi) C_2H_5CHO ; CH_3COCH_3

(g) A pair of position isomers
(vii) $CH_3OC_3H_7$; $C_2H_5OC_2H_5$

(h) Asymmetric synthesis
(viii)  $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-H$; $CH_3CH_2CH{=}CHOH$

(i) A pair of diastereomers
(ix)  $CH_3-\overset{O}{\overset{\|}{C}}-COOH$;  $(-)CH_3-\overset{OH}{CH}-COOH$

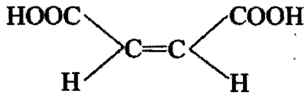
(j) Enolisation
(x)  ; 

[B] (a) *d,l*-mixture
(i) 

(b) *Cis*-isomer
(ii) Eclipsed and staggered forms.

(c) *Trans*-isomer
(iii) Polarimeter

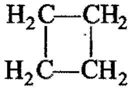
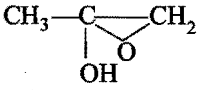
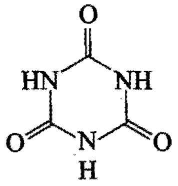
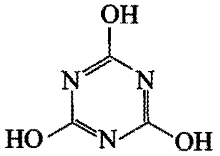
(d) Meso form
(iv) Enantiomers

(e) Conformation
(v) 

(f) Non-superimposable mirror images
(vi) Optically inactive

(g) Specific rotation
(vii) Racemic

5. What isomerism is exhibited by the following pairs of compounds?

(a)	CH_3CH_2CHO	and	CH_3COCH_3
(b)	$C_2H_5OC_2H_5$	and	$CH_3OC_3H_7$
(c)	$CH_3NHC_3H_7$	and	$C_2H_5NHC_2H_5$
(d)	$CH_3CH_2CH{=}CH_2$	and	$CH_3CH{=}CHCH_3$
(e)	$CH_3CH_2CH_2CHO$	and	$CH_3CH_2CH{=}CHOH$
(f)	$(CH_3)_3CH$	and	$CH_3CH_2CH_2CH_3$
(g)	$CH_3CH_2CH_2OH$	and	$CH_3CHOHCH_3$
(h)	$CH_3CH_2CH{=}CH_2$	and	
(i)	CH_3COCH_2OH	and	
(j)		and	

6. Mention the specific type of isomerism exhibited by each of the following pairs:

(a)	1,2-Dibromoethane	and	1,1-dibromoethane
(b)	*n*-Butylalcohol	and	diethylether
(c)	Propionic acid	and	methylacetate
(d)	*o*-Methylphenol	and	benzylalcohol
(e)	Maleic acid	and	fumaric acid
(f)	*n*-Butane	and	isobutane
(g)	*o*-Nitrophenol	and	*m*-nitrophenol
(h)	Acetic acid	and	methyl formate

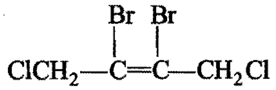
7. Write structural formulae of:
(a) Two enantiomorphs
(b) Two homologues
(c) Two functional isomers
(d) Two geometrical isomers
(e) Two position isomers
(f) Two metamers

8. Write down the name and structure of one isomer of each of the following compounds:
(a) $CH_2{=}CHCH_2CH_3$
(b) CH_3CHCl_2
(c) $(CH_3)_2CHOH$
(d) CH_3COCH_3
(e) CH_3COOH
(f) $CH_3OCH_2CH_2CH_3$
(g) maleic acid
(h) *d*-lactic acid

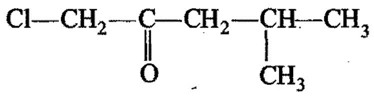
9. Which of the following compounds are optically active compounds?
(i) Butan-1-ol, (ii) Heptan-4-ol, (iii) 2-Chlorobutane, (iv) 3-Chloropentane, (v) Pentan-2-ol, (vi) 2-Bromo-2-methylbutane (vii) Penta-2,3-diene.

[**Hint :** Write down the structures and find out which compound has asymmetric carbon atom. The compound having asymmetric carbon atom shows optical activity.]

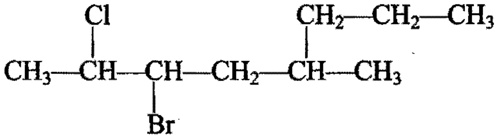
10. State which of these exhibit stereoisomerism and of what type?

(a) 

$ClCH_2-\overset{Br}{\overset{|}{C}}=\overset{Br}{\overset{|}{C}}-CH_2Cl$

(b) 

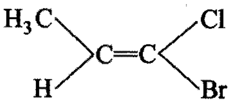
$Cl-CH_2-\underset{O}{\underset{\|}{C}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

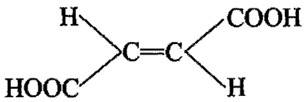
(c) 

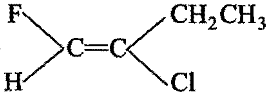
$CH_3-\overset{Cl}{\overset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-CH_2-\overset{CH_2-CH_2-CH_3}{\overset{|}{CH}}-CH_3$

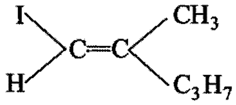
(d) $CH_3-CH_2-CH(OH)COOH$
(e) $CH_3CH{=}CHC_2H_5$
(f) $CH_3CH(Br)COOH$
(g) $H_2C{=}C(CH_3)_2$
(h) $C_2H_5CH{=}CHCl$
(i) 1-Bromo-3-chlorocyclobutane
(j) 1,4-Dimethylcyclohexane

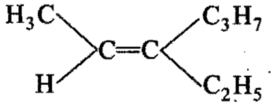
11. [A] Indicate whether each of the following compound is '*E*' or '*Z*':

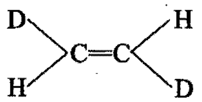
(i) 

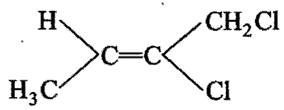
(ii) 

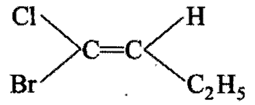
(iii) 

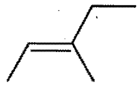
(iv) 

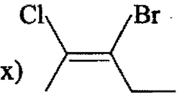
(v) 

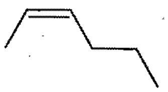
(vi) 

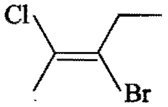
(vii) 

(viii) 

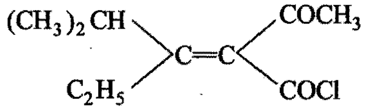
(ix) 

(x) 

(xi) 

(xii) 

(xiii) 

(xiv) 

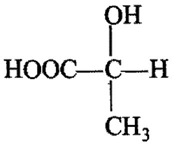
[B] Write the structures of:

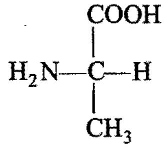
(i) (Z) Penta-1,3-diene
(ii) (E) Penta-1,3-diene
(iii) $(2Z, 4E)$ Hexa-2,4-diene
(iv) $(2E, 4E)$-3-Ethylhexa-2,4-diene
(v) (E)-1-Bromo-1-chloro-2-iodopropene
(vi) (E, Z)-Nona-2,4-diene

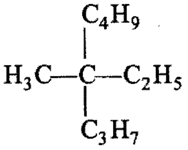
12. Determine the number of optical isomers in the following compounds:

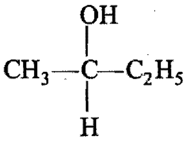
(a) $CH_3CH(OH)COOH$ (b) $HOOC(CHOH)_2COOH$
(c) $HOOC(CHOH)_3COOH$ (d) $CH_3(CHOH)_2COOH$
(e) $CH_3CH(Br)CH(Br)COOH$

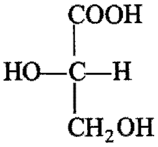
13. (i) Assign ***R*** or ***S*** configuration to each of the following compounds:

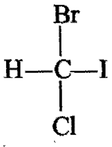
(a)

$\mathrm{HOOC{-}\underset{CH_3}{\overset{OH}{C}}{-}H}$

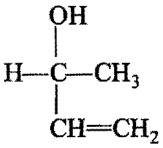
(b)

$\mathrm{H_2N{-}\underset{CH_3}{\overset{COOH}{C}}{-}H}$

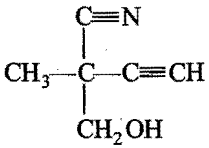
(c)

$\mathrm{H_3C{-}\underset{C_3H_7}{\overset{C_4H_9}{C}}{-}C_2H_5}$

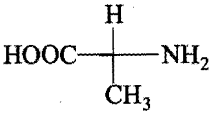
(d)

$\mathrm{CH_3{-}\underset{H}{\overset{OH}{C}}{-}C_2H_5}$

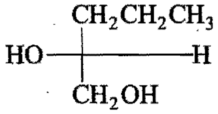
(e)

$\mathrm{HO{-}\underset{CH_2OH}{\overset{COOH}{C}}{-}H}$

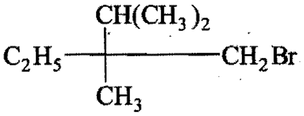
(f)

$\mathrm{H{-}\underset{Cl}{\overset{Br}{C}}{-}I}$

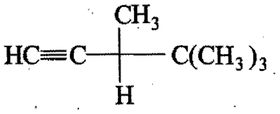
(g)

$\mathrm{H{-}\underset{CH{=}CH_2}{\overset{OH}{C}}{-}CH_3}$

(h)

$\mathrm{CH_3{-}\underset{CH_2OH}{\overset{C{\equiv}N}{C}}{-}C{\equiv}CH}$

(i)

$\mathrm{HOOC{-}\underset{CH_3}{\overset{H}{+}}{-}NH_2}$

(j)

$\mathrm{HO{-}\underset{CH_2OH}{\overset{CH_2CH_2CH_3}{+}}{-}H}$

(k)

$\mathrm{C_2H_5{-}\underset{CH_3}{\overset{CH(CH_3)_2}{+}}{-}CH_2Br}$

(l)

$\mathrm{HC{\equiv}C{-}\underset{H}{\overset{CH_3}{+}}{-}C(CH_3)_3}$

(ii) Write the structures of:

(a) (R)-2-Bromopentane
(b) (S)-3-Bromo-3-chlorohexane

(iii) Draw R and S enantiomers of 3-chloro-1-pentene. **[BCECE 2004]**

(iv) Draw the structures of the possible enantiomers of 3-methyl pent-1-ene.

❖ Short Answer Type

14. Explain with suitable example:

(a) Isomerism (b) Different types of structural isomerism
(c) Chain isomerism (d) Position isomerism
(e) Functional isomerism (f) Metamerism
(g) Tautomerism (h) Ring-chain isomerism
(i) Geometrical isomerism (j) Conformation

15. Explain the following terms:

(a) Stereoisomerism (b) Optical activity
(c) Enantiomers (d) Diastereomers
(e) Racemic mixture (f) Meso form
(g) Asymmetric carbon (h) Configuration
(i) Eclipsed form (j) Staggered form
(k) Walden inversion (l) Chiral molecule
(m) Racemisation (n) Asymmetric synthesis

16. (A) Write the total number of cyclic structural as well as stereoisomers possible for a compound with the molecular formula, C_5H_{10}. **[IIT 2009]**

(B) Write the total number of cyclic isomers possible for a hydrocarbon with the molecular formula, C_4H_6. **[IIT 2010]**

17. (i) Name the hydrocarbon with lowest possible molar mass which has chiral structure.

(ii) Name the lowest possible alkane which has chiral structure.

18. (A) Write the possible isomers of the formula $C_5H_{10}O_2$.

(B) Draw the structures of all isomeric ethers corresponding to the molecular formula, $C_5H_{12}O$.

19. Molecular formula $C_4H_4O_4$ can have four isomers A, B, C and D:

A is dicarboxylic acid giving racemic tartaric acid with alk. $KMnO_4$.

B is dicarboxylic acid giving meso tartaric acid with alk. $KMnO_4$.

C is also dicarboxylic acid giving another monobasic acid on heating.

D is cyclic ester.

Identify A, B, C and D.

20. (A) Write the possible structural isomers of the molecular formula C_7H_{16}.

(B) Write the condensed and bond line structural formulae for all the possible isomers having the molecular formula C_4H_6.

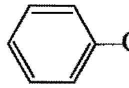
21. Explain that enol form of acetoacetic ester is said to be more volatile than keto form.

22. How many asymmetric carbon atoms are created during the complete reduction of benzil (PhCOCOPh) with $LiAlH_4$? Also write the number of possible stereoisomers in the product.

23. Make structures of 2,3-dibromobutane and assign R and S configuration.

24. Write down the structures of the stereoisomers formed when *cis*-2-butene is reacted with bromine.

25. What are the possible types of compounds that can have a molecular formula C_3H_6O?

26. Write metamers of  —O—CH_2CH_3.

27. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly.

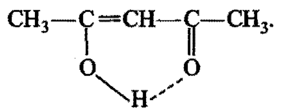
28. C_4H_8 has four isomers. *A*, *B* and *C* decolourise Br_2 water, *D* does not. *A* gives optically inactive meso form, while *B* forms optically inactive mixture of two optically active forms in equal amount. Identify *A*, *B*, *C* and *D*.

29. Explain that α-methyl acetyl acetone undergoes enolisation to a smaller extent than acetyl acetone.

30. Draw the enantiomers of 3-bromo cyclohexene and give *R/S* designation for each.

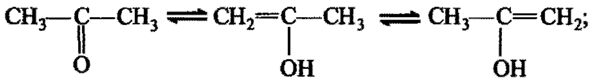
ANSWERS

1. (a) three; (b) metamerism; (c) $CH_3CH_2OCH_3$; (d) geometrical and functional; (e) dynamic; (f) five; (g) four; (h) functional; (i) five; (j) chain; (k) CH_3CH_2CHO; (l) neopentane; (m) position; (n) same; (o) position; (p) ring chain; (q) four; (r) eclipsed, staggered; (s) more; (t) functional; (u) four; (v) cannot; (w) fully eclipsed, anti; (x) isomers, isomerism; (y) chain;

(z) 
$CH_3-\underset{\underset{O}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-CH_3$.

2. (i) same, same; (ii) geometrical; (iii) restricted, double; (iv) non-superimposable, enantiomers; (v) specific rotation; (vi) more; (vii) similar; (viii) different, chemical; (ix) polarized; (x) one asymmetric; (xi) meso form; (xii) stereospecific; (xiii) enantiomers; (xiv) enantiotropic; (xv) zero; (xvi) configuration; (xvii) sequence; (xviii) geometrical or *cis-trans* isomers; (xix) diastereomers; (xx) planar.

3. (a) False—Are called homologues; (b) True; (c) False; (d) False—Same compound; (e) False—Functional isomers; (f) False—Only those in which different atoms or groups are attached with carbon atoms linked by double bond; (g) True; (h) False—Similar groups are attached to one of the carbon atoms linked by double bond. Hence, it does not show geometrical isomerism; (i) True; (j) True; (k) True (dextro, laevo, racemic, meso); (l) False—Two chiral carbon atoms are present; (m) True; (n) True; (o) True; (p) False—Meso form can exist which is non-optical active if there is a plane of symmetry in the molecule; (q) False—Three isomers; (r) False—Different stability; (s) False—Propanone shows tautomerism. The tautomeric forms are


$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_2=\underset{\underset{OH}{|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{OH}{|}}{C}=CH_2$;

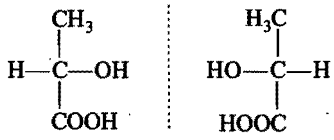
(t) True; (u) True; (v) False—Inorganic molecules can also show optical activity; (w) True; (x) True; (y) False—Not related with configuration; (z) True.

4. [A] (a—vi); (b—iv); (c—i); (d—vii); (e—iii); (f—ii); (g—v); (h—ix); (i—x); (j—viii).

[B] (a—vii); (b—v); (c—i); (d—vi); (e—ii); (f—iv); (g—iii).

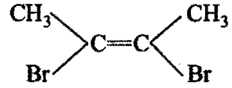
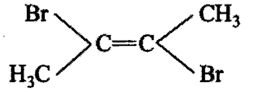
5. (a) Functional, (b) Metamerism, (c) Metamerism, (d) Position, (e) Tautomerism, (f) Chain, (g) Position, (h) Ring-chain, (i) Ring-chain tautomerism, (j) Tautomerism.

6. (a) Position, (b) Functional, (c) Functional, (d) Functional, (e) Geometrical, (f) Chain, (g) Position, (h) Functional.

7. (a) 
$H-\overset{\overset{CH_3}{|}}{\underset{\underset{COOH}{|}}{C}}-OH$; $HO-\overset{\overset{H_3C}{|}}{\underset{\underset{HOOC}{|}}{C}}-H$

(b) CH_3OH; C_2H_5OH

(c) C_2H_5OH; CH_3OCH_3

(d)  ; 

(e) $CH_3CH_2CH_2OH$; $CH_3CHOHCH_3$

(f) $CH_3COC_3H_7$; $C_2H_5COC_2H_5$

8. (a) $CH_3CH=CH-CH_3$ (But-2-ene)

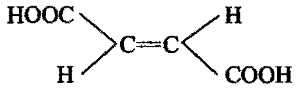
(b) CH_2ClCH_2Cl (1,2-Dichloroethane)

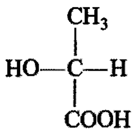
(c) $CH_3CH_2CH_2OH$ (1-Propanol)

(d) CH_3CH_2CHO (Propanal)

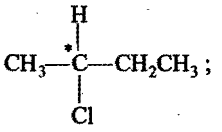
(e) $HCOOCH_3$ (Methylformate)

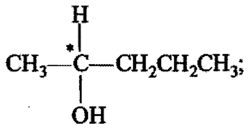
(f) $C_2H_5OC_2H_5$ (Ethoxyethane)

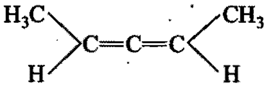
(g) 
(Fumaric acid)

(h) 
$HO-\overset{\overset{CH_3}{|}}{\underset{\underset{COOH}{|}}{C}}-H$
(*l*-Lactic acid)

9. The following compounds possess asymmetric carbon atom and show optical activity.

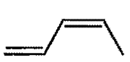
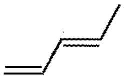
(iii) 
$CH_3-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C^*}}-CH_2CH_3$;
2-Chlorobutane

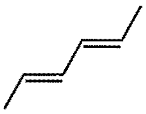
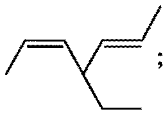
(v) 
$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C^*}}-CH_2CH_2CH_3$;
Pentan-2-ol

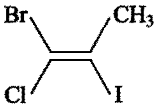
(vii) 
Penta-2,3-diene

10. (a) geometrical isomerism, (c) optical isomerism, (d) optical isomerism, (e) geometrical isomerism, (f) optical isomerism, (h) geometrical isomerism, (i) geometrical isomerism, (j) geometrical isomerism

11. [A] (i) *E*, (ii) *E*, (iii) *E*, (iv) *E*, (v) *Z*, (vi) *E*, (vii) *Z*, (viii) *Z*, (ix) *E*, (x) *Z*, (xi) *Z*, (xii) *E*, (xiii) *Z*, (xiv) *E*.

[B] (i)  ; (ii)  ;

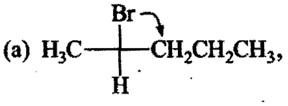
(iii)  ; (iv)  ;

(v)  ; (vi) 

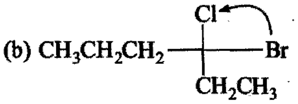
12. (a) 2, (b) 3, (c) 4, (d) 4, (e) 4.

13. (i) (a) *R*-configuration, (b) *S*-configuration, (c) *R*-configuration, (d) *R*-configuration, (e) *S*-configuration, (f) *R*-configuration, (g) *R*-configuration, (h) *S*-configuration, (i) *S*-configuration, (j) *R*-configuration, (k) *S*-configuration, (l) *R*-configuration.

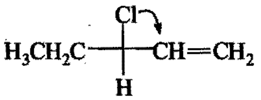
(ii) (a)

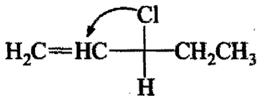


(b)



(iii)

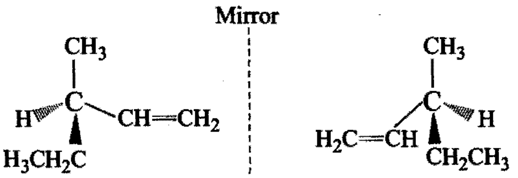




(Clockwise rotation) *R*-configuration

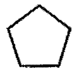
(Anticlockwise rotation) *S*-configuration

(iv) Stereoisomers which are non-superimposable mirror images of each other are called enantiomers. The enantiomers of 3-methyl pent-1-ene are :



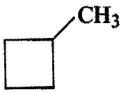
16. (A) For a compound with molecular formula C_5H_{10}, the isomers are as follows:

(i)



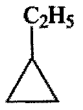
Cyclopentane

(ii)



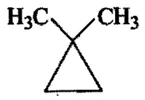
Methylcyclo butane

(iii)



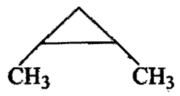
Ethylcyclo propane

(iv)



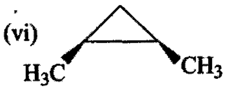
1,1-Dimethyl cyclopropane

(v)

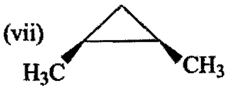


1,2-Dimethyl cyclopropane *cis* (meso)

(vi)



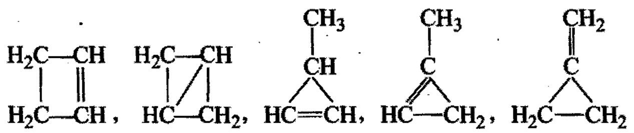
(vii)



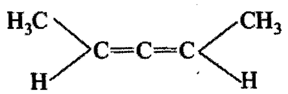
Structure (vi) and (vii) are *trans*-isomers and are same. It can exist in *d*, *l* form.

So, total number of cyclic as well as stereoisomers possible are **seven.**

(B) The possible cyclic isomers of the compound with molecular formula, C_4H_6 are five.

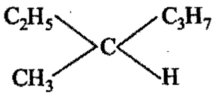


17. (i) Penta-2,3-diene:



(C_5H_8)

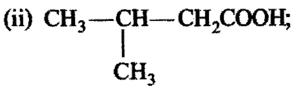
(ii) 3-Methylhexane :



18. (A) (a) Carboxylic acids:

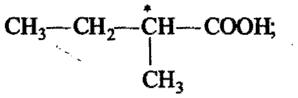
(i) $CH_3CH_2CH_2CH_2COOH$;

(ii)



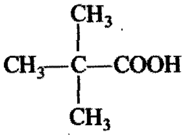
$CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2COOH$;

(iii)



$CH_3-CH_2-\underset{\substack{|\\CH_3}}{\overset{*}{C}H}-COOH$;

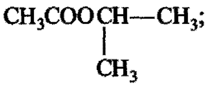
(iv)



$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-COOH$

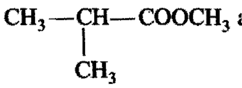
(b) Esters: (i) $CH_3CH_2CH_2COOCH_3$; (ii) $CH_3CH_2COOCH_2CH_3$

(iii) $CH_3COOCH_2CH_2CH_3$; (iv)



$CH_3COO\underset{\substack{|\\CH_3}}{CH}-CH_3$;

(v)



$CH_3-\underset{\substack{|\\CH_3}}{CH}-COOCH_3$ and so on

(c) Hydroxy aldehydes and

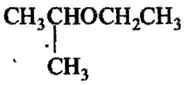
(d) Hydroxy ketones, etc

(B) D.B.E. = $1/2\,[5(4-2)+12(1-2)+1(2-2)]+1=0$.

Since, D.B.E. = 0, therefore, $C_5H_{12}O$ represents only saturated ethers. Its possible isomers are:

(i) $CH_3CH_2CH_2OCH_2CH_3$
1-Ethoxypropane

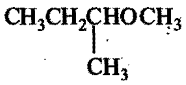
(ii)



$CH_3\underset{\substack{|\\CH_3}}{C}HOCH_2CH_3$
2-Ethoxypropane

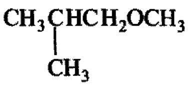
(iii) $CH_3CH_2CH_2CH_2OCH_3$
1-Methoxybutane

(iv)



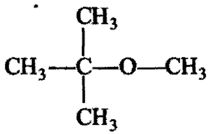
$CH_3CH_2\underset{\substack{|\\CH_3}}{C}HOCH_3$
2-Methoxybutane

(v)



$CH_3\underset{\substack{|\\CH_3}}{C}HCH_2OCH_3$
1-Methoxy-2-methylpropane

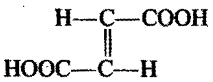
(vi)



$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-O-CH_3$
2-Methoxy-2-methyl propane

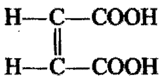
Thus, there are total six isomers.

19. (*A*) Fumaric acid (*trans*)



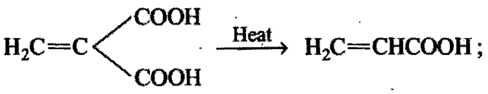
$\begin{matrix}H-C-COOH\\ \|\\ HOOC-C-H\end{matrix}$;

(*B*) Maleic acid (*cis*)

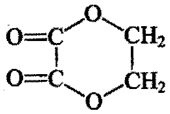


$\begin{matrix}H-C-COOH\\ \|\\ H-C-COOH\end{matrix}$;

(*C*) Ethene dicarboxylic acid



(*D*) Cyclic ester of oxalic acid and glycol.

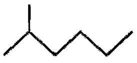


20. (A) C_7H_{16} has nine isomers.

(i)

n-Heptane

(ii)



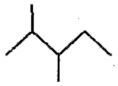
2-Methyl hexane

(iii)

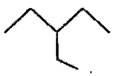
3-Methyl hexane

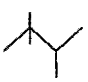
(iv) 
2,2-Dimethyl pentane

(v) 
3,3-Dimethyl pentane

(vi) 
2,3-Dimethyl pentane

(vii) 
2,4-Dimethyl pentane

(viii) 
3-Ethyl pentane

(ix) 
2,2,3-Trimethyl butane

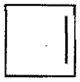
(B) D.B.E. = $1/2\,[4(4-2)+6(1-2)]+1=2$.
Since, D.B.E. = 2, therefore, C_4H_6 has either two double bonds or one triple bond or one double bond and a ring or two rings. The possible isomers are:

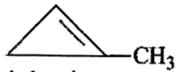
(i) $H_2C{=}CH{-}CH{=}CH_2$ or 
Buta-1,3-diene

(ii) $H_2C{=}C{=}CH{-}CH_3$ or 
Buta-1,2-diene

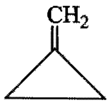
(iii) $CH_3CH_2C{\equiv}CH$ or 
But-1-yne

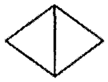
(iv) $H_3C{-}C{\equiv}C{-}CH_3$ or 
But-2-yne

(v) 
Cyclobut-1-ene

(vi) 
1-Methyl cyclopropene

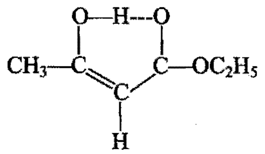
(vii) 
3-Methyl cycloprop-1-ene

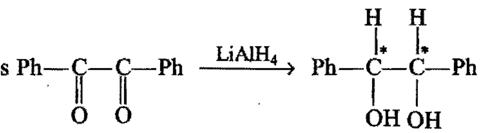
(viii) 
Methylene cyclopropane

(ix) 
Bicyclo (1.1.0) butane

Thus, there are total nine isomers.

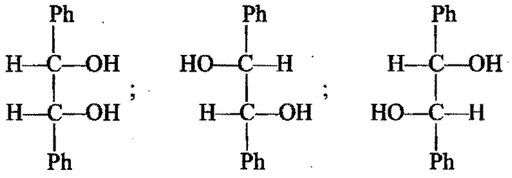
21. It is due to intramolecular H-bonding in enolic form which reduces intermolecular association and lowers the boiling point.

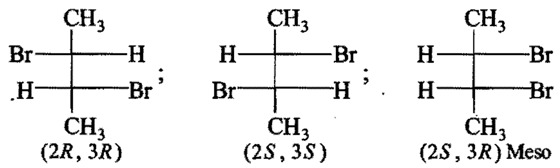


22. The reaction is 

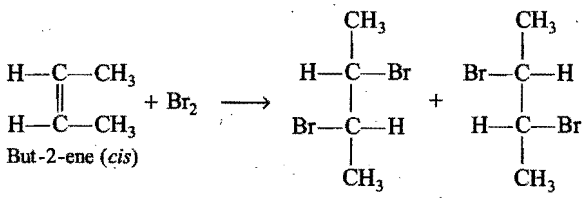
$$Ph{-}\underset{O}{\overset{\|}{C}}{-}\underset{O}{\overset{\|}{C}}{-}Ph \xrightarrow{LiAlH_4} Ph{-}\overset{H}{\underset{OH}{C^*}}{-}\overset{H}{\underset{OH}{C^*}}{-}Ph$$

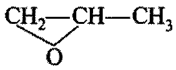
Thus, two asymmetric carbon atoms are created in the reduction product. There are three stereoisomers of the reduction product.

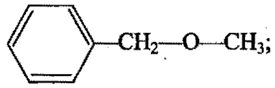
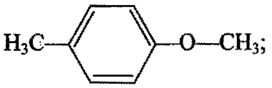


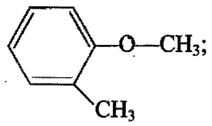
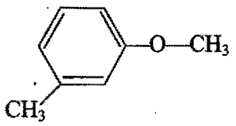
23. 

24. The addition of bromine to the but-2-ene involves anti-addition and thus racemic 2,3-dibromobutane is formed.

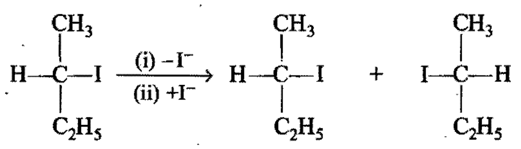


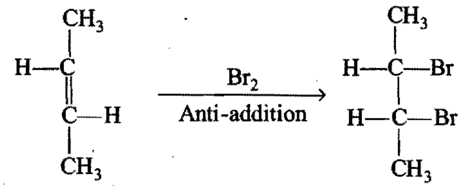
25. An aldehyde, C_2H_5CHO; a ketone, CH_3COCH_3; an unsaturated alcohol, $CH_2{=}CH{-}CH_2OH$; an ether, $CH_2{=}CH{-}O{-}CH_3$ and  , . . ., etc.

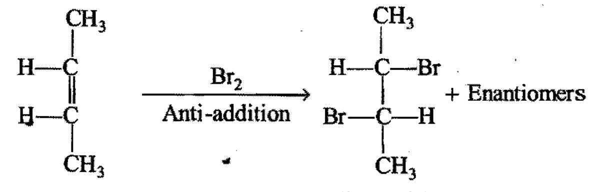
26. (i)  (ii) 

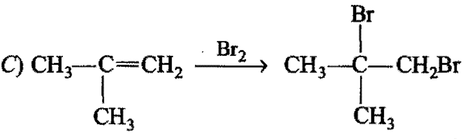
(iii)  (iv) 

27. There occurs breaking and reforming of C—I bond. This results into two enantiomers which form racemic mixture which does not show optical activity due to external compensation.


(Racemic mixture)

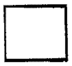
28. (A) 

(B) 

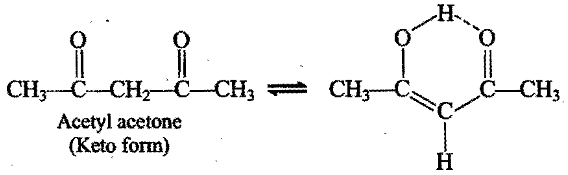
(C) 

$$CH_3{-}\underset{CH_3}{C}{=}CH_2 \xrightarrow{Br_2} CH_3{-}\overset{Br}{\underset{CH_3}{C}}{-}CH_2Br$$

2-Methylpropene (Achiral)

(*D*)  $\xrightarrow{Br_2}$ No reaction

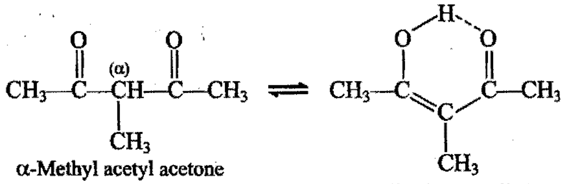
Cyclobutane

29. 

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons$

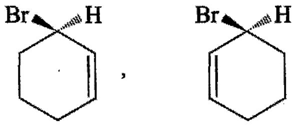
Acetyl acetone
(Keto form)

Enolisation (greater)
due to less strained



α-Methyl acetyl acetone
(Keto form)

Enolisation (smaller)
due to highly strained

30. 

(*R*) , (*S*)

OBJECTIVE QUESTIONS

Set I : This set contains questions with single correct answer.

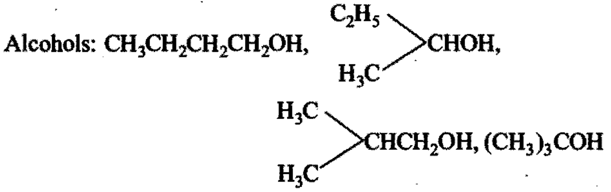
1. Compounds having same number and kind of atoms but different arrangement of atoms in their molecules are called:
(a) allotropes ☐ (b) isotopes ☐
(c) isomers ☐ (d) polymers ☐

2. Isomers have essentially identical:
(a) structural formula ☐ (b) chemical properties ☐
(c) molecular formula ☐ (d) physical properties ☐

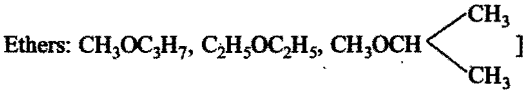
3. Which of the following has asymmetric carbon atom? **[BHU (Med.) 2007]**
(a) $CH_2Cl—CH_2Br$ ☐
(b) CH_3CHDCl ☐
(c) CH_3CHCl_2 ☐
(d) $CH_2Br—CHOH—CH_3$ ☐

4. Total number of isomeric alcohols with formula $C_4H_{10}O$ is:
(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) 4 ☐

5. Number of acyclic isomers represented by molecular formula $C_4H_{10}O$ is: **[PMT (MP) 2006; AFMC 2010]**
(a) 7 ☐ (b) 6 ☐
(c) 4 ☐ (d) 5 ☐
[**Hint :** 4 alcohols and 3 ethers,



Alcohols: $CH_3CH_2CH_2CH_2OH$, $(C_2H_5)(H_3C)CHOH$, $(H_3C)_2CHCH_2OH$, $(CH_3)_3COH$



Ethers: $CH_3OC_3H_7$, $C_2H_5OC_2H_5$, $CH_3OCH(CH_3)_2$]

6. The compound $C_4H_{10}O$ can show: **[JIPMER 2005]**
(a) metamerism ☐ (b) position isomerism ☐
(c) functional isomerism ☐ (d) all of the three ☐

7. The molecular formula of a saturated compound is $C_2H_4Cl_2$. This formula permits the existence of two:
(a) functional isomers ☐ (b) position isomers ☐
(c) optical isomers ☐ (d) *cis-trans* isomers ☐

8. The compound which is not isomeric with diethyl ether is:
(a) methyl *n*-propyl ether ☐ (b) 1-butanol ☐
(c) 2-methyl propan-2-ol ☐ (d) butanone ☐

9. Which type of isomerism is shown by diethyl ether and methyl propyl ether?
(a) Chain ☐ (b) Functional ☐
(c) Metamerism ☐ (d) Position ☐

10. Aldehydes and ketones are:
(a) homologues ☐ (b) isomers ☐
(c) allotropes ☐ (d) polymers ☐

11. Maximum number of isomers for an alkene with molecular formula, C_4H_8 is:
(a) 5 ☐ (b) 4 ☐
(c) 3 ☐ (d) 2 ☐

12. Keto-enol tautomerism is not observed in : **[JEE (WB) 2010]**
(a) $C_6H_5COC_6H_5$ ☐ (b) $C_6H_5COCH{=}CH_2$ ☐
(c) $C_6H_5COCH_2COCH_3$ ☐ (d) $CH_3COCH_2COCH_3$ ☐

13. Isomerism in alkynes is:
(a) functional ☐ (b) optical ☐
(c) geometrical ☐ (d) conformational ☐

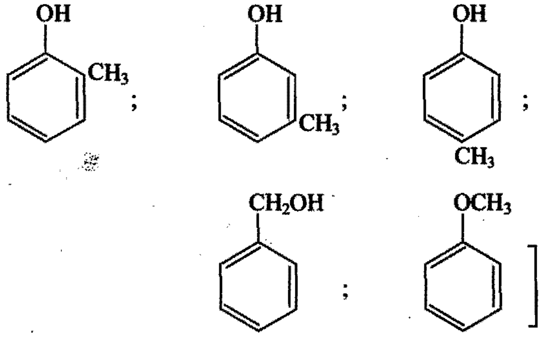
14. The type of isomerism observed in urea molecule is:
(a) chain ☐ (b) position ☐
(c) tautomerism ☐ (d) none of these ☐

15. Which of the following is not an isomer of but-1-yne?
(a) But-2-yne ☐ (b) But-1, 3-diene ☐
(c) But-2-ene ☐ (d) Methyl cyclopropene ☐

16. Number of isomers of molecular formula $C_2H_2Br_2$ is:
(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) 4 ☐

17. C_7H_8O shows how many isomers?
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 5 ☐

[**Hint :**



]

18. CH_3CH_2OH and $CH_3—O—CH_3$ are the examples of: **[CET (Karnataka) 2008; UPSEE (Engg.) 2008]**
(a) functional isomerism ☐ (b) chain isomerism ☐
(c) metamerism ☐ (d) position isomerism ☐

19. The compound which forms only one monochloro product when treated with chlorine is:
(a) *n*-pentane ☐ (b) isopentane ☐
(c) neo-pentane ☐ (d) none of these ☐

20. Stereoisomers have different: **[JIPMER 2008]**
(a) molecular formula ☐ (b) structural formula ☐
(c) configuration ☐ (d) conformation ☐

21. Select the pair of compounds which exhibit *cis-trans* (geometrical) isomerism:
(a) fumaric acid and maleic acid ☐
(b) malonic acid and succinic acid ☐
(c) lactic acid and tartaric acid ☐
(d) acetic acid and crotonic acid ☐

22. The isomerism that arises due to restricted bond rotation is : **[PET (Kerala) 2010]**
(a) optical isomerism ☐ (b) metamerism ☐
(c) position isomerism ☐ (d) functional isomerism ☐
(e) geometrical isomerism ☐

23. Which of the following will have least hindered rotation about carbon-carbon bond?
(a) Ethane ☐ (b) Ethylene ☐
(c) Acetylene ☐ (d) Hexachloroethane ☐

24. A compound contains two dissimilar asymmetric carbon atoms. The number of stereoisomers is: **[DPMT 2006]**
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 1 ☐

25. Isomers which can be interconverted through rotation around a single bond are:
(a) position isomers ☐ (b) enantiomers ☐
(c) metamers ☐ (d) conformers ☐

26. Meso tartaric acid and *d*-tartaric acid are:
(a) position isomers ☐ (b) racemic mixture ☐
(c) enantiomers ☐ (d) diastereomers ☐

27. The number of conformations of ethane is:
(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) infinite ☐

28. Out of the following, the alkene that exhibits optical isomerism is : **[AIEEE 2010]**
(a) 2-methyl-2-pentene ☐ (b) 3-methyl-2-pentene ☐
(c) 4-methyl-1-pentene ☐ (d) 3-methyl-1-pentene ☐

29. Chiral molecules are those which are:
(a) superimposable on their mirror image ☐
(b) not superimposable on their mirror image ☐
(c) unstable molecules ☐
(d) capable of showing geometrical isomerism ☐

30. The method of separation of *d*- and *l*-isomers from the racemic mixture is called:
(a) resolution ☐ (b) dehydration ☐
(c) asymmetric synthesis ☐ (d) Walden inversion ☐

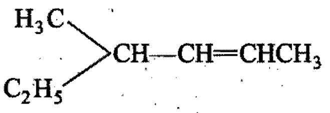
31. Mesotartaric acid is optically inactive due to presence of:
(a) molecular symmetry ☐
(b) molecular asymmetry ☐
(c) external compensation ☐
(d) two asymmetric carbon atoms ☐

32. Two geometrical isomers are given by which of the following compounds?
(a) Ethylidene dibromide ☐
(b) Acetylene tetrachloride ☐
(c) Acetylene tetrabromide ☐
(d) Acetylene dibromide ☐

33. Which one is the correct statement?
(a) (+) tartaric acid and mesotartaric acid are tautomers ☐
(b) (+) tartaric acid and mesotartaric acid are diastereoisomers ☐
(c) (+) tartaric acid and (–) tartaric acid are diastereoisomers ☐
(d) (+) tartaric acid and mesotartaric acid are enantiomers ☐

34. The number of possible alkynes with molecular formula C_5H_8 is:
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 5 ☐

35. Glucose has how many optical isomers?
(a) 8 ☐ (b) 12 ☐
(c) 16 ☐ (d) Cannot be predicted ☐

36. Which of the following compounds can exhibit both geometrical isomerism and enantiomerism?
(a) $CH_3CHOHC_2H_5$ ☐
(b) $CH_3CHOHCOOH$ ☐
(c)  ☐
(d) All of the above ☐

37. During debromination of meso dibromobutane, the major compound formed is:
(a) *n*-butane ☐ (b) 1-butene ☐
(c) *trans*-2-butene ☐ (d) *cis*-2-butene ☐

38. The most stable conformation of ethane is:
(a) boat form ☐ (b) chair form ☐
(c) eclipsed form ☐ (d) staggered form ☐

39. At room temperature the eclipsed and the staggered forms of ethane cannot be isolated because:
(a) both the conformers are equally stable ☐
(b) they interconvert rapidly ☐
(c) there is a large energy barrier of rotation about the σ-bond ☐
(d) the energy difference between the conformers is large ☐

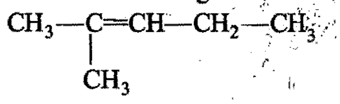
40. The number of geometrical isomers in the following compound $CH_3{-}CH{=}CH{-}CH{=}CH{-}C_2H_5$ is:
(a) 4 ☐ (b) 3 ☐
(c) 2 ☐ (d) 5 ☐

41. Tartaric acid molecule contains two asymmetric carbon atoms. The number of optical isomers of tartaric acid is:
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 5 ☐

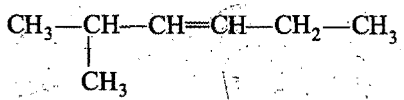
42. Lactic acid shows optical activity in:
(a) solution ☐ (b) liquid state ☐
(c) crystalline state ☐ (d) all of these ☐

43. Enantiomers can be better separated by:
(a) salt formation method ☐
(b) mechanical separation ☐
(c) fractional crystallisation ☐
(d) fractional distillation ☐

44. Which of the following will exhibit chirality?
(a) Neopentane ☐ (b) Isopentane ☐
(c) 3-Methylhexane ☐ (d) 2-Methylhexane ☐

45. Which of the following will not show *cis-trans* isomerism?
(a)  ☐

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH-CH_2-CH_3$

(b) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH=CH-CH_2-CH_3$ ☐

(c) $CH_3-CH=CH-CH_3$ ☐

(d) $CH_3-CH_2-CH=CH-CH_2-CH_3$ ☐

46. How many primary amines are possible for the formula $C_4H_{11}N$?

(a) 1 ☐ (b) 2 ☐

(c) 3 ☐ (d) 4 ☐

47. How many optically active stereoisomers are possible for butane-2,3-diol?

(a) 1 ☐ (b) 2 ☐

(c) 3 ☐ (d) 4 ☐

48. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl butane is:

(a) 2 ☐ (b) 3 ☐

(c) 4 ☐ (d) 1 ☐

49. Tautomerism will be explained by:

(a) $(CH_3)_2NH$ ☐ (b) $(CH_3)_3CNO$ ☐

(c) R_3CNO_2 ☐ (d) RCH_2NO_2 ☐

50. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be: **[IIT 2003]**

(a) optically active mixture ☐

(b) pure enantiomer ☐

(c) meso compound ☐

(d) racemic mixture ☐

51. 2-Methylpenta-2,3-diene is achiral because it has:

(a) a plane of symmetry ☐

(b) a centre of symmetry ☐

(c) a C_2 axis of symmetry ☐

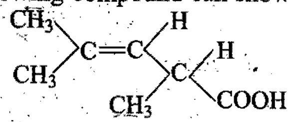
(d) both a plane and a centre of symmetry ☐

52. The racemization of optically active compounds is driven by:

(a) enthalpy ☐ (b) entropy ☐

(c) enthalpy and entropy ☐ (d) element of symmetry ☐

53. The following compound can show:



(a) optical isomerism ☐

(b) geometrical isomerism ☐

(c) optical and geometrical isomerism ☐

(d) tautomerism ☐

54. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive:

(a) optical rotation and is derived from D-glucose ☐

(b) pH in organic solvent ☐

(c) optical rotation and is derived from D-(+)-glyceraldehyde ☐

(d) optical rotation only when substituted by deuterium ☐

55. How many cyclic isomers of C_5H_{10} are possible? **[DPMT 2000]**

(a) 4 ☐ (b) 3 ☐

(c) 2 ☐ (d) 5 ☐

56. Consider the following organic compound ;

$$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_2}-\underset{7}{CH_3}$$

To make it a chiral compound, the attack should be on carbon : **[DCE 2001]**

(a) 1 ☐ (b) 3 ☐

(c) 4 ☐ (d) 7 ☐

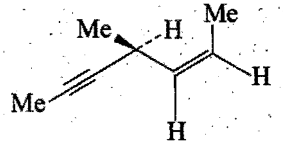
57. A compound with molecular formula C_7H_{16} shows optical isomerism, the compound will be : **[CBSE (Med.) 2001]**

(a) 2, 3-dimethyl pentane ☐

(b) 2, 2-dimethyl pentane ☐

(c) 2-methyl hexane ☐

(d) none of the above ☐

58. 

Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives : **[IIT (S) 2001]**

(a) optically active compound ☐

(b) an optically inactive compound ☐

(c) a racemic mixture ☐

(d) a diastereomeric mixture ☐

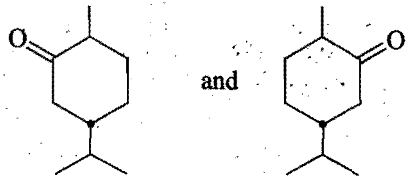
59. The number of isomers for the compound with molecular formula $C_2BrClFI$ is: **[PET (Kerala) 2007]**

(a) 3 ☐ (b) 4 ☐

(c) 5 ☐ (d) 6 ☐

(e) 7 ☐

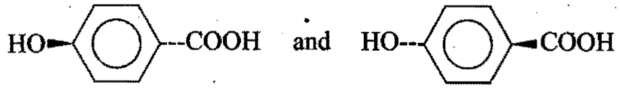
60. The two compounds shown in figure below are :



(a) diastereomers ☐ (b) enantiomers ☐

(c) epimers ☐ (d) regiomers ☐

61. The compounds given below are :



(a) enantiomers ☐ (b) identical ☐

(c) regiomers ☐ (d) diastereomers ☐

62. Which of the following compounds will exhibit geometrical isomerism? **[IIT (S) 2000]**

(a) 1-Phenyl-2-butene ☐

(b) 3-Phenyl-1-butene ☐

(c) 2-Phenyl-1-butene ☐

(d) 1,1-Diphenyl-1-propene ☐

63. Which of the following does not show geometrical isomerism? **[AIEEE 2002]**

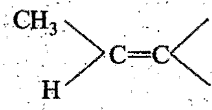
(a) 1,2-Dichloro-1-pentene ☐

(b) 1,3-Dichloro-2-pentene ☐

(c) 1-Dichloro-1-pentene ☐
(d) 1,4-Dichloro-2-pentene ☐

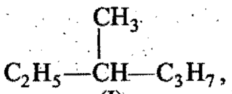
64. A similarity between optical and geometrical isomerism is that: **[AIEEE 2002]**
(a) each forms equal number of isomers for a given compound ☐
(b) if in a compound one is present then so is the other ☐
(c) both are included in stereoisomerism ☐
(d) they have no similarity ☐

65. Which of the following hydrocarbons has lowest dipole moment? **[IIT (S) 2002]**

(a)  ☐

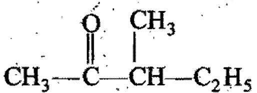
(b) $CH_3—C≡C—CH_3$ ☐
(c) $CH_3—CH_2—C≡C—H$ ☐
(d) $CH_2=CH—C≡CH$ ☐

66. Among the following four structures I to IV:



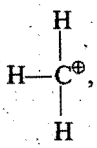
$C_2H_5—\overset{CH_3}{\overset{|}{C}H}—C_3H_7$,

(I)



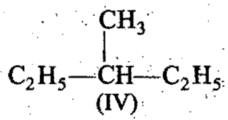
$CH_3—\overset{O}{\overset{||}{C}}—\overset{CH_3}{\overset{|}{C}H}—C_2H_5$

(II)



$H—\overset{H}{\underset{H}{C}}{}^{\oplus}$,

(III)



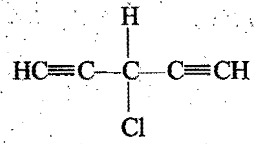
$C_2H_5—\overset{CH_3}{\overset{|}{C}H}—C_2H_5$

(IV)

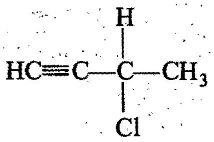
[AIEEE 2003]

(a) all four are chiral compounds ☐
(b) only (I) and (II) are chiral compounds ☐
(c) only (III) is a chiral compound ☐
(d) only (II) and (IV) are chiral compounds ☐

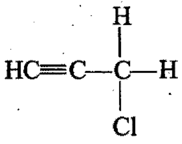
67. Which of the following is most likely to show optical isomerism? **[UPSEAT 2004]**

(a)  ☐

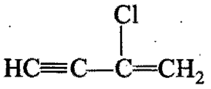
$HC≡C—\overset{H}{\underset{Cl}{C}}—C≡CH$

(b)  ☐

$HC≡C—\overset{H}{\underset{Cl}{C}}—CH_3$

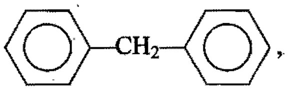
(c)  ☐

$HC≡C—\overset{H}{\underset{Cl}{C}}—H$

(d)  ☐

$HC≡C—\overset{Cl}{C}=CH_2$

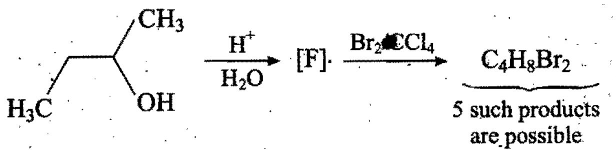
68. The molecular formula of diphenylmethane,



, is $C_{13}H_{12}$;

How many structural isomers are possible when one of the hydrogen is replaced by a chlorine atom? **[CBSE (Med.) 2004]**
(a) 6 ☐ (b) 4 ☐
(c) 8 ☐ (d) 7 ☐

69. Which one of the following will have a meso-isomer also? **[AIEEE 2004; JCECE (Med.) 2008]**
(a) 2-Chlorobutane ☐
(b) 2,3-Dichlorobutane ☐
(c) 2,3-Dichloropentane ☐
(d) 2-Hydroxypropanoic acid ☐

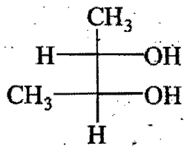
70. 

How many structures of [F] is possible? **[IIT (S) 2003]**
(a) 2 ☐ (b) 5 ☐
(c) 6 ☐ (d) 3 ☐

71. On monochlorination of 2-methylbutane, the total number of chiral compounds is: **[IIT(S) 2004]**
(a) 2 ☐ (b) 4 ☐
(c) 6 ☐ (d) 8 ☐

72. Which type of isomerism is shown by 2,3-dichlorobutane? **[AIEEE 2005]**
(a) Diastereo ☐ (b) Geometrical ☐
(c) Optical ☐ (d) Structural ☐

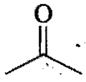
73. Correct configuration of the following is: **[AIIMS 2005]**

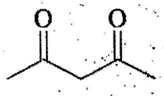


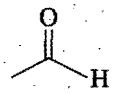
(a) 1*S*, 2*S* ☐ (b) 1*S*, 2*R* ☐
(c) 1*R*, 2*S* ☐ (d) 1*R*, 2*R* ☐

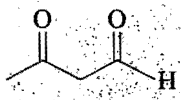
74. Which of the following is optically active? **[BHU 2005]**
(a) Butane ☐ (b) 4-Methyl heptane ☐
(c) 3-Methyl heptane ☐ (d) 2-Methyl heptane ☐

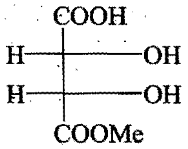
75. Maximum enol content is in: **[DCE 2005; AIIMS 2008]**

(a)  ☐

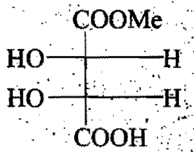
(b)  ☐

(c)  ☐

(d)  ☐

76. 

(I)



(II)

Structures (I) and (II) are: **[DPMT 2005]**
(a) enantiomers ☐ (b) diastereomers ☐
(c) meso compounds ☐ (d) identical ☐

77. The two structures of *D*-glucopyranose forms are: **[IIT(S) 2005]**
(a) anomers ☐ (b) enantiomers ☐
(c) epimers ☐ (d) diastereoisomers ☐

Which of the following will show geometrical isomerism? **[BCECE (Med.) 2005]**
(a) C_2H_5Br ☐ (b) $CH_2(COOH)_2$ ☐
(c) $(CH)_2(COOH)_2$ ☐ (d) C_2H_6 ☐

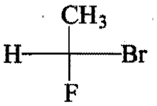
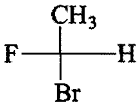
79. Which of the following compounds is expected to be optically active? **[CET (Karnataka) 2006; AFMC 2008]**
(a) $(CH_3)_2CHCHO$ ☐ (b) $CH_3CH_2CH_2CHO$ ☐
(c) $CH_3CH_2CH(Br)CHO$ ☐ (d) $CH_3CH_2CBr_2CHO$ ☐

80. The number of optical isomers of $CH_3CH(OH)CH(OH)CHO$ is: **[PET (Kerala) 2006]**
(a) 0 ☐ (b) 2 ☐
(c) 3 ☐ (d) 4 ☐
(e) 6 ☐

81. Among the following which one can have meso form? **[AIIMS 2006]**
(a) $CH_3CH(OH)CH(Cl)C_2H_5$ ☐
(b) $CH_3CH(OH)CH(OH)CH_3$ ☐
(c) $C_2H_5CH(OH)CH(OH)CH_3$ ☐
(d) $HOCH_2CH(Cl)CH_3$ ☐

82. Which of the following is not chiral? **[CBSE (Med.) 2006]**
(a) 3-Bromopentane ☐
(b) 2-Hydroxy propanoic acid ☐
(c) 2-Butanol ☐
(d) 2,3-Dibromopentane ☐

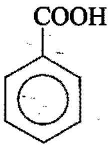
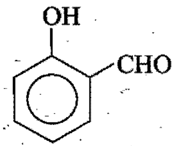
83. Consider the following representation,

they are: **[PMT (Kerala) 2006]**
(a) enantiomers ☐
(b) diastereomers ☐
(c) conformational isomers ☐
(d) identical ☐
(e) *cis-trans* isomers ☐

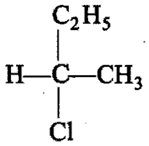
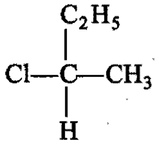
84. The term anomers of glucose refers to: **[AIEEE 2006]**
(a) isomers of glucose that differ in configurations at carbons one and four (C-1 and C-4) ☐
(b) a mixture of (*D*)-glucose and (*L*)-glucose ☐
(c) enantiomers of glucose ☐
(d) isomers of glucose that differ in configuration at carbon one (C-1) ☐

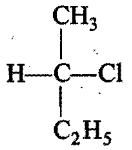
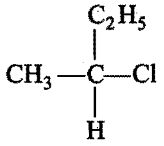
85. Number of primary amines of the formula $C_4H_{11}N$ is: **[BHU 2006]**
(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) 4 ☐

86.

and

are: **[AMU (Med.) 2006]**
(a) position isomers ☐ (b) chain isomers ☐
(c) functional isomers ☐ (d) stereoisomers ☐

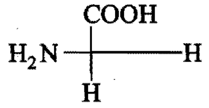
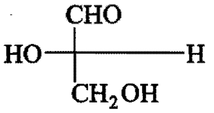
87. Number of structural isomers for C_6H_{14} is: **[IIT 2007]**
(a) 3 ☐ (b) 4 ☐
(c) 5 ☐ (d) 6 ☐

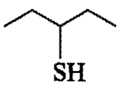
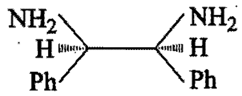
88. $CH_3—CHCl—CH_2—CH_3$ has achiral centre. Which one of the following represents its *R*-configuration? **[CBSE (Med.) 2007]**

(a)  ☐ (b)  ☐

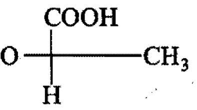
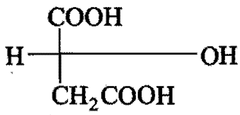
(c)  ☐ (d)  ☐

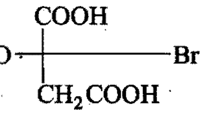
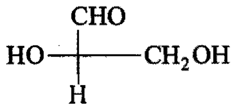
89. Which of the following molecules is expected to rotate the plane of polarised light? **[AIEEE 2007]**

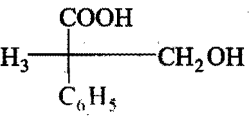
(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

90. Which one of the following molecules has *S*-configuration? **[PMT (Kerala) 2007]**

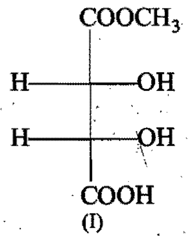
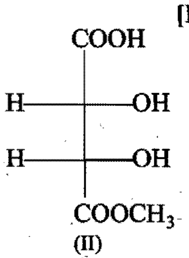
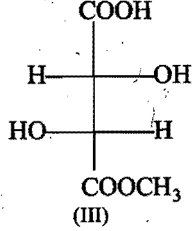
(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

(e)  ☐

91. The major product formed when a 3,3-dimethylbutan-2-ol is heated with concentrated sulphuric acid is: **[PMT (Kerala) 2007]**
(a) 2,3-dimethyl-2-butene ☐
(b) 2,3-dimethyl-1-butene ☐
(c) 3,3-dimethyl-1-butene ☐
(d) *cis* and *trans* isomers of 2,3-dimethyl-1-butene ☐
(e) *cis* and *trans* isomers of 3,3-dimethyl-2-butene ☐

92. The correct statement about the compounds I, II and III is: **[PMT (Kerala) 2007]**

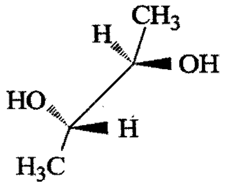

(I)

(II)

(III)

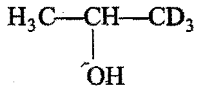
(a) I and II are identical ☐
(b) I and II are diastereomers ☐
(c) I and III are enantiomers ☐
(d) I and II are enantiomers ☐
(e) II and III are enantiomers ☐

93. Geometrical isomerism is possible in: **[JEE (WB) 2007]**
(a) isobutene ☐ (b) acetone-oxime ☐
(c) benzophenone-oxime ☐ (d) acetophenone-oxime ☐

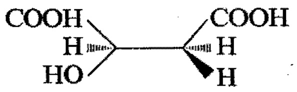
94. Which of the following will have a meso-isomer also? **[UPSEE (Engg.) 2007; AFMC (Med.) 2007]**
(a) 2,3-Dichlorobutane ☐
(b) 2-Chlorobutane ☐
(c) 2,3-Dichloropentane ☐
(d) 2-Hydroxy propanoic acid ☐

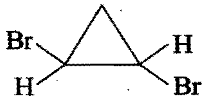
95. Which of the following molecules will not show optical activity? **[PMT (Kerala) 2007]**

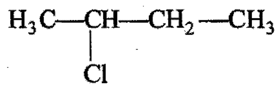
(a)  ☐

(b)  ☐

$H_3C{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CD_3$

(c)  ☐

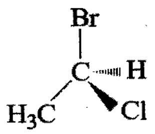
(d)  ☐

(e)  ☐

$H_3C{-}\underset{\displaystyle Cl}{\underset{|}{C}H}{-}CH_2{-}CH_3$

96. Pick out the correct statements: **[PMT (Kerala) 2007]**
(i) if a compound has no asymmetric carbon atom, it is always achiral.
(ii) if a compound has just one asymmetric carbon atom, it is chiral.
(iii) if a compound has more than one asymmetric carbon atoms, it may or may not be chiral.
(a) (i), (ii) and (iii) are correct ☐
(b) (i) and (ii) only are correct ☐
(c) (ii) and (iii) only are correct ☐
(d) only (ii) is correct ☐
(e) only (i) is correct ☐

97. The chirality of the compound



is: **[JIPMER (Med.) 2007]**
(a) *R* ☐ (b) *S* ☐
(c) *Z* ☐ (d) *E* ☐

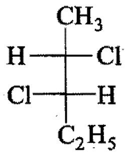
98. Different structures generated due to reaction about C—C axis of an organic molecule, are examples for: **[CET (J & K) 2007]**
(a) geometrical isomerism ☐
(b) optical isomerism ☐
(c) conformational isomerism ☐
(d) structural isomerism ☐

99. The number of geometrical isomers in $CH_3CH{=}CHCH_2CH{=}CH_2$ is: **[DPMT 2007]**
(a) two ☐ (b) three ☐
(c) four ☐ (d) five ☐

100. The total number of isomers in $C_6H_3Cl_3$ is: **[DPMT 2007]**
(a) two ☐ (b) three ☐
(c) four ☐ (d) five ☐

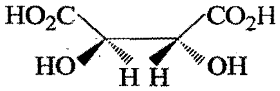
101. How many stereoisomers does this molecule have?
$H_3C{-}CH{=}CHCH_2CHBrCH_3$ **[CBSE (Med.) 2008]**
(a) 2 ☐ (b) 4 ☐
(c) 6 ☐ (d) 8 ☐

102. The absolute configuration of the following:



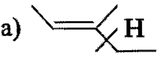
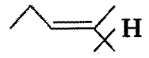
, is: **[DCE(Engg.) 2008]**
(a) 2*S*, 3*R* ☐ (b) 2*S*, 3*S* ☐
(c) 2*R*, 3*S* ☐ (d) 2*R*, 3*R* ☐

103. The absolute configuration of



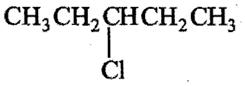
, is: **[AIEEE 2008]**
(a) *S*, *R* ☐ (b) *S*, *S* ☐
(c) *R*, *R* ☐ (d) *R*, *S* ☐

104. C_8H_{16} that can form *cis-trans* geometrical isomers and also has a chiral centre, is: **[AIIMS 2008]**

(a)  ☐ (b)  ☐

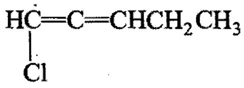
(c) both of these ☐ (d) none of these ☐

105. Which of the following is chiral? **[DPMT 2008]**
(a) $ClCH_2CH_2CH_2CH_2CH_3$ ☐

(b)  ☐

$CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}H}CH_2CH_3$

(c) $ClCH{=}CHCH_2CH_2CH_3$ ☐

(d)  ☐

$H\underset{\displaystyle Cl}{\underset{|}{C}}{=}C{=}CHCH_2CH_3$

106. Of the isomeric hexanes, the isomers that give the minimum and maximum number of monochloro derivatives are respectively: **[PET (Kerala) 2008]**
(a) 2,3-dimethylbutane and *n*-hexane ☐
(b) 3-methylpentane and 2,3-dimethylbutane ☐
(c) 2,2-dimethylbutane and 2-methylpentane ☐
(d) 2,3-dimethylbutane and 2-methylpentane ☐
(e) 2-methylpentane and 2,2-dimethylbutane ☐

107. How many chiral carbon atoms are present in 2,3,4-trichloropentane? **[MGIMS (Wardha) 2008]**
(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) 4 ☐

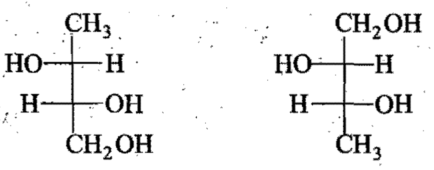
108. The total number of acyclic isomers including the stereoisomers (geometrical and optical), with the molecular formula, C_4H_7Cl is: **[GGSIP (Engg.) 2008]**
(a) 12 ☐ (b) 11 ☐
(c) 10 ☐ (d) 9 ☐

109. Which of the following will exhibit *cis-trans* isomerism? **[JEE (WB) 2008]**
(a) $CH_2Br{-}CH_2Br$ ☐ (b) $CBr_3{-}CH_3$ ☐
(c) $CHBr{=}CHBr$ ☐ (d) $CBr_2{=}CH_2$ ☐

110. Which one of the following compounds is capable of existing in a meso form? **[PET (Kerala) 2008]**
(a) 3,3-Dibromopentane ☐ (b) 4-Bromo-2-pentanol ☐
(c) 3-Bromo-2-pentanol ☐ (d) 2,3-Dibromopentane ☐
(e) 2,4-Dibromopentane ☐

111. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism? **[CBSE (Med.) 2009]**
(a) Butanol ☐ (b) 2-Butyne ☐
(c) 2-Butenol ☐ (d) 2-Butene ☐

112. The two structures written below represent:



[JEE (WB) 2009]
(a) pair of diastereomers ☐
(b) pair of enantiomers ☐
(c) same molecule ☐
(d) both are optically inactive ☐

113. Which of the following compounds will show geometrical isomerism? **[DPMT 2009]**
(a) Cyclohexene ☐
(b) 2-Hexene ☐
(c) 3-Hexyne ☐
(d) 1,1-Diphenyl ethylene ☐

114. A compound is formed by substitution of two chlorine for two hydrogens in propane. The number of possible isomeric compounds is: **[JEE (WB) 2009]**
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 5 ☐

115. The number of stereoisomers possible for a compound of the molecular formula
$CH_3-CH=CH-CH(OH)-Me$ is : **[AIEEE 2009]**
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 6 ☐

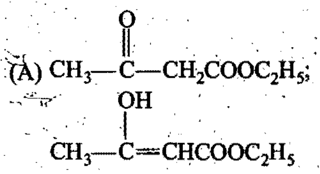
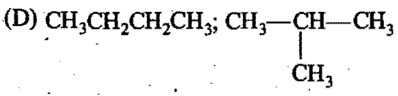
116. Which isomer of hexane has only two different sets of structurally equivalent hydrogen atoms? **[DPMT 2009]**
(a) 2,2-Dimethyl butane ☐ (b) 2-Methyl pentane ☐
(c) 3-Methyl pentane ☐ (d) 2,3-Dimethyl butane ☐

117. The total number of acyclic structural and optical isomers possible for a hydrocarbon of the molecular formula C_7H_{16} is: **[CET (J&K) 2009]**
(a) 6 ☐ (b) 8 ☐
(c) 10 ☐ (d) 12 ☐

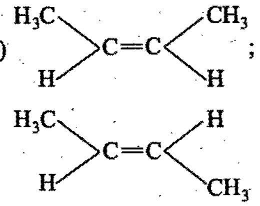
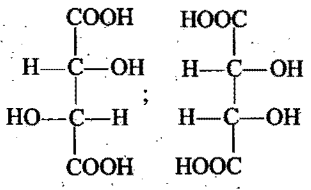
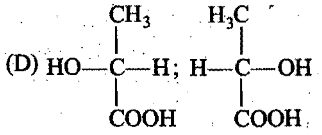
118. The alkene that exhibits geometrical isomerism is: **[AIEEE 2009]**
(a) propene ☐ (b) 2-methyl propene ☐
(c) 2-butene ☐ (d) 2-methyl-2-butene ☐

SET II : This set contains questions with one or more correct answers.

119. Match the list I and list II and select the correct answer using the code given below the lists:

	List I	**List II**
(i)	1. A pair of chain isomers	(A)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOC_2H_5;$ $CH_3-\overset{OH}{\overset{\vert}{C}}=CHCOOC_2H_5$
	2. A pair of position isomers	(B) $CH_3CH_2CH_2CHO; CH_3COCH_2CH_3$
	3. A pair of functional isomers	(C) $CH_3CH_2-C\equiv CH;$ $CH_3-C\equiv C-CH_3$
	4. A pair of tautomers	(D)  $CH_3CH_2CH_2CH_3; CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$

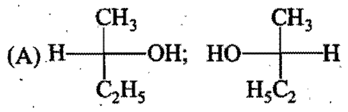
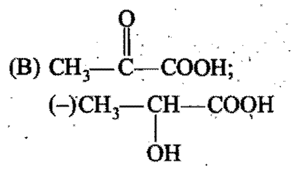
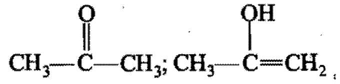
Codes : (a) 1-A, 2-B, 3-C, 4-D, (b) 1-D, 2-C, 3-B, 4-A
(c) 1-B, 2-D, 3-A, 4-C, (d) 1-C, 2-A, 3-D, 4-B

	List I	**List II**
(ii)	1. A pair of optical isomers	(A) 
	2. A pair of geometrical isomers	(B) 
	3. A pair of metamers	(C) $C_2H_5OC_2H_5; CH_3OC_3H_7$
	4. A pair of diastereomers	(D) 

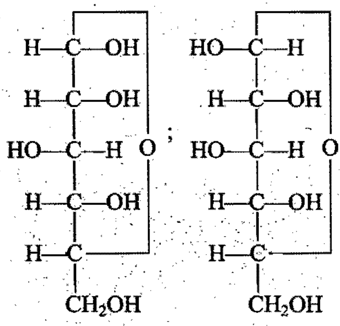
Codes : (a) 1-D, 2-A, 3-C, 4-B, (b) 1-A, 2-B, 3-D, 4-C
(c) 1-C, 2-D, 3-B, 4-A, (d) 1-B, 2-C, 3-A, 4-D

	List I	**List II**
(iii)	1. Conformation	(A) Polarimeter
	2. Meso form	(B) Optically inactive
	3. Specific rotation	(C) Eclipsed and staggered forms
	4. Non-superimposable mirror images	(D) Enantiomers

Codes : (a) 1-A, 2-D, 3-B, 4-C, (b) 1-D, 2-A, 3-C, 4-B
(c) 1-B, 2-C, 3-D, 4-A, (d) 1-C, 2-B, 3-A, 4-D

	List I	**List II**
(iv)	1. A pair of anomers	(A) 
	2. Enolisation	(B)  $CH_3-\overset{O}{\overset{\|}{C}}-COOH;$ $(-)CH_3-\underset{OH}{\underset{\vert}{CH}}-COOH$
	3. Asymmetric synthesis	(C)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3; CH_3-\overset{OH}{\overset{\vert}{C}}=CH_2$

4. Fischer projection (D)

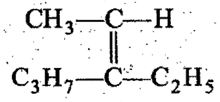


Codes : (a) 1-C, 2-A, 3-D, 4-B, (b) 1-A, 2-B, 3-C, 4-D
(c) 1-D, 2-C, 3-B, 4-A, (d) 1-B, 2-D, 3-A, 4-C

120. *Cis*-2-butene and *trans*-2-butene are :
(a) geometrical isomers ☐ (b) diastereomers ☐
(c) enantiomers ☐ (d) position isomers ☐

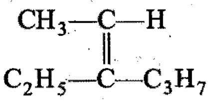
121. Which of the following can exist in 'syn' and 'anti' forms?
(a) $C_6H_5—N=N—OH$ ☐
(b) $C_6H_5—N=N—C_6H_5$ ☐
(c) $C_6H_5—CH=N—OH$ ☐
(d) $(C_6H_5)_2C=N—OH$ ☐

122. The *Z*-isomer among the following are:



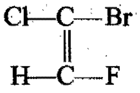
$\begin{array}{c} CH_3—C—H \\ \| \\ C_3H_7—C—C_2H_5 \end{array}$

(I)



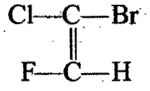
$\begin{array}{c} CH_3—C—H \\ \| \\ C_2H_5—C—C_3H_7 \end{array}$

(II)



$\begin{array}{c} Cl—C—Br \\ \| \\ H—C—F \end{array}$

(III)



$\begin{array}{c} Cl—C—Br \\ \| \\ F—C—H \end{array}$

(IV)

(a) (I) ☐ (b) (II) ☐
(c) (III) ☐ (d) (IV) ☐

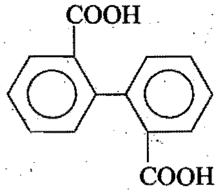
123. Keto-enol tautomerism is observed in :
(a) $C_6H_5—CHO$ ☐ (b) $C_6H_5COCH_3$ ☐
(c) $C_6H_5COC_6H_5$ ☐ (d) $C_6H_5COCH_2COCH_3$ ☐

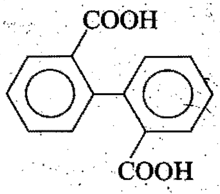
124. Which of the following statement(s) is/are correct about tautomers?
(a) They possess different electronic and atomic arrangements ☐
(b) They possess different electronic but same atomic arrangement ☐
(c) They have different atomic arrangements but same electronic arrangement ☐
(d) They exist in equilibrium ☐

125. The lowest molecular weight alkanes, which are optically active, are:
(a) 3-methylhexane ☐
(b) 2,3-dimethylpentane ☐
(c) 2,3,3-trimethylbutane ☐
(d) 2-methylhexane ☐

126. Which of the following compounds are chiral and resolvable?
(a) $[C_6H_5\overset{+}{N}(CH_2CH_2CH_3)(C_2H_5)(CH_3)]Br^-$ ☐
(b) $C_6H_5N(CH_3)(C_2H_5)$ ☐
(c) $CH_3CH_2CH(CH_3)N(CH_3)(C_2H_5)$ ☐

(d)



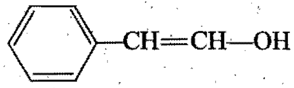


☐

127. Which of the following compounds will show geometrical isomerism?
(a) 2-Butene ☐ (b) Propene ☐
(c) 1-Phenyl propene ☐ (d) 2-Methyl-2-butene ☐

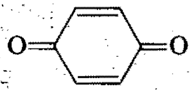
128. Tautomerism is exhibited by:

(a)



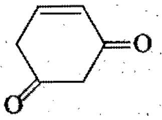
☐

(b)



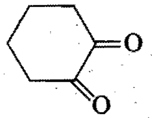
☐

(c)



☐

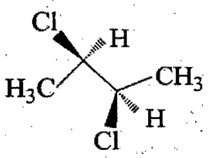
(d)



☐

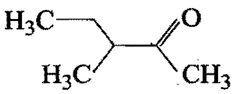
129. Geometrical isomerism is exhibited by: **[BHU (Mains) 2008]**
(a) 2-chlorobut-2-ene ☐ (b) but-2-ene ☐
(c) 3-methylpent-2-ene ☐ (d) 2-methyl but-2-ene ☐

130. The correct statement(s) about the compound given below is (are): **[IIT 2008]**

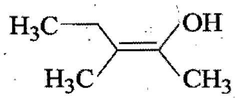


(a) the compound is optically active ☐
(b) the compound possesses centre of symmetry ☐
(c) the compound possesses plane of symmetry ☐
(d) the compound possesses axis of symmetry ☐

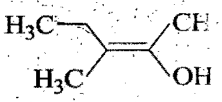
131. The correct statement(s) concerning the structures *E*, *F* and *G* is (are): **[IIT 2008]**



(*E*)



(*F*)



(*G*)

(a) *E*, *F* and *G* are resonance structures ☐
(b) *E*, *F* and *E*, *G* are tautomers ☐
(c) *F* and *G* are geometrical isomers ☐
(d) *F* and *G* are diastereomers ☐

132. The correct statement(s) about the compound $H_3C(HO)HC—CH=CH—CH(OH)CH_3$ (*X*) is (are) : **[IIT 2009]**
(a) the total number of stereoisomers possible for (*X*) is 6 ☐

(b) the total number of diastereomers possible for (*X*) is 3 ☐

(c) if the stereochemistry about the double bond in (*X*) is *trans*, the number of enantiomers possible for (*X*) is 4 ☐

(d) if the stereochemistry about the double bond in (*X*) is *cis*, the number of enantiomers possible for (*X*) is 2 ☐

ASSERTION-REASON TYPE QUESTIONS

Section A : IIT Type Questions

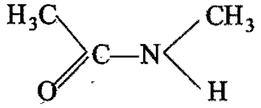
The questions given below consist of an **Assertion (A)** and **Reason (R).** Use the following keys to choose the correct answer:

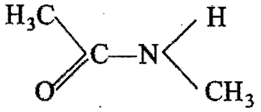
(a) If both assertion (A) and reason (R) are correct and reason (R) is correct explanation of assertion (A).
(b) If both assertion (A) and reason (R) are correct but reason (R) is not correct explanation of assertion (A).
(c) If assertion (A) is correct but reason (R) is incorrect.
(d) If assertion (A) is incorrect but reason (R) is correct.
(e) If both assertion (A) and reason (R) are incorrect.

1. (A) All compounds having C=C bond exhibit geometrical isomerism.
(R) Rotation about C=C bond is restricted.

2. (A) Diastereomers are not mirror image of each other.
(R) Diastereomers may be optically active.

3. (A) Following amide exist in two structural forms:


(I)


(II)

(R) Rotation about carbon nitrogen bond is restricted due to resonance.

4. (A) Dextro-isomers rotate the plane of polarised light towards right.
(R) Dextro-isomers are represented by putting (*D*) before their name.

5. (A) *Trans*-1-chloropropene has higher dipole moment than *cis*-1-chloropropene.
(R) The resultant of the two vectors in *trans*-1-chloro propene is more than in *cis*-1-chloropropene.

6. (A) Meso tartaric acid is optically inactive.
(R) Meso tartaric acid has plane of symmetry.

Section B : AIIMS Type Questions

Choose the correct answer:

(a) If both (A) and (R) are true and (R) is correct explanation of (A).
(b) If both (A) and (R) are true but (R) is not correct explanation of (A).
(c) If (A) is true but (R) is false.
(d) If both (A) and (R) are false.

7. (A) Alkanes containing more than three carbons exhibit chain isomerism.
(R) All the carbon atoms in alkanes are sp^3-hybridized.

8. (A) Lactic acid shows geometrical isomerism.
(R) It has a C=C double bond.

9. (A) Metamers can also be chain or position isomers :
(R) The term tautomerism was introduced to explain the reactivity of a substance according to two possible structures.

10. (A) All the hydrogen atoms in but-2-ene lie in one plane.
(R) All the carbon atoms in it are sp^2-hybridized.

11. (A) Benzaldehyde forms two oximes on reacting with NH_2OH.
(R) The two oximes arise due to geometrical isomerism around C=N bond.

12. (A) Cyclobutane is less stable than cyclopentane.
(R) Presence of 'bent bonds' causes loss of orbital overlap.

13. (A) Ethyl acetoacetate gives reddish violet colour on treatment with ferric chloride.
(R) 'Keto' form is dominant in it.

14. (A) The boiling point of *cis*-1,2-dichloroethene is higher than corresponding *trans*-isomer.
(R) The dipole moment of *cis*-1,2-dichloroethene is higher than *trans*-isomers.

15. (A) Molecules that are not superimposable on their mirror images are chiral. **[IIT 2007]**
(R) All chiral molecules have chiral centre.

ANSWERS

OBJECTIVE QUESTIONS

1. (c) **2.** (c) **3.** (b) **4.** (d) **5.** (a) **6.** (d) **7.** (b) **8.** (d) **9.** (c) **10.** (b)
11. (b) **12.** (a) **13.** (a) **14.** (c) **15.** (c) **16.** (c) **17.** (d) **18.** (a) **19.** (c) **20.** (c)
21. (a) **22.** (e) **23.** (a) **24.** (c) **25.** (d) **26.** (d) **27.** (d) **28.** (d) **29.** (b) **30.** (a)
31. (a) **32.** (d) **33.** (b) **34.** (b) **35.** (c) **36.** (c) **37.** (c) **38.** (d) **39.** (b) **40.** (a)
41. (b) **42.** (d) **43.** (a) **44.** (c) **45.** (a) **46.** (d) **47.** (b) **48.** (a) **49.** (d) **50.** (a)
51. (c) **52.** (b) **53.** (a) **54.** (c) **55.** (d) **56.** (b) **57.** (a) **58.** (b) **59.** (d) **60.** (a)
61. (b) **62.** (a) **63.** (c) **64.** (c) **65.** (b) **66.** (b) **67.** (b) **68.** (b) **69.** (b) **70.** (d)
71. (b) **72.** (c) **73.** (a) **74.** (c) **75.** (c) **76.** (d) **77.** (a) **78.** (c) **79.** (c) **80.** (d)
81. (b) **82.** (a) **83.** (d) **84.** (d) **85.** (d) **86.** (c) **87.** (c) **88.** (b) **89.** (b) **90.** (e)
91. (a) **92.** (a) **93.** (d) **94.** (a) **95.** (a) **96.** (c) **97.** (a) **98.** (c) **99.** (a) **100.** (b)
101. (b) **102.** (b) **103.** (c) **104.** (a) **105.** (d) **106.** (d) **107.** (b) **108.** (a) **109.** (c) **110.** (e)
111. (d) **112.** (c) **113.** (b) **114.** (d) **115.** (c) **116.** (d) **117.** (b) **118.** (c)
119. (i–b), (ii–a), (iii–d), (iv–c) **120.** (a,b) **121.** (a,b,c) **122.** (a,c) **123.** (b,d) **124.** (a,d) **125.** (a,b) **126.** (a,c)
127. (a,c) **128.** (a,c,d) **129.** (a,b,c) **130.** (a,d) **131.** (b,c,d) **132.** (a,d)

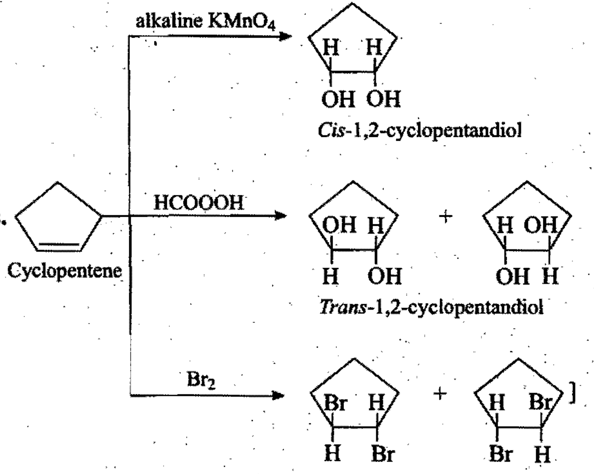
ASSERTION-REASON TYPE QUESTIONS

1. (d) **2.** (c) **3.** (a) **4.** (c) **5.** (a) **6.** (a) **7.** (c) **8.** (e) **9.** (b) **10.** (d)
11. (a) **12.** (a) **13.** (b) **14.** (a) **15.** (c)

BRAIN STORMING PROBLEMS

1. Give the stereoselective products, when cyclopentene is treated with (a) alkaline $KMnO_4$ (b) HCOOOH (c) Br_2

[Ans.

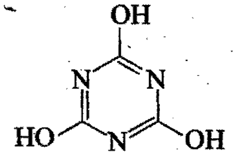


Cis-1,2-cyclopentandiol

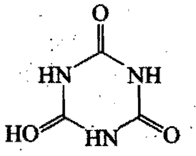
Trans-1,2-cyclopentandiol

Trans-1,2- dibromocyclopentane]

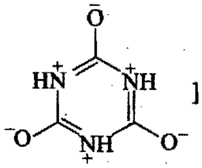
2. Write down tautomeric and resonating structures of the following compounds:



[Ans.



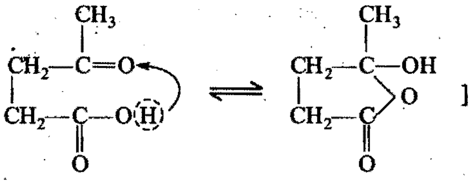
Tautomer



Resonating structure]

3. Give the ring-chain tautomers of 4-keto pentanoic acid (Laevulic acid):

[Ans.

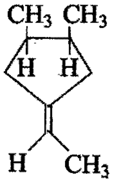


]

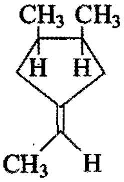
(Ring-chain tautomerism)

4. Identify enantiomers and diastereomers among the following:

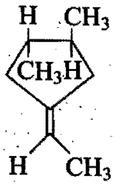
(i)



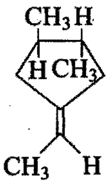
(ii)



(iii)



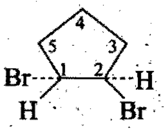
(iv)



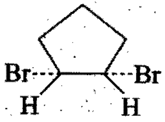
[Ans. (I), (II), (III), (IV)—Enantiomers
(I and III); (II and III); (I and IV),
(II and IV)—Diastereomers]

5. Indicate optical configuration in following compounds:

(a)



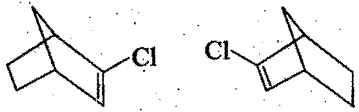
(b)



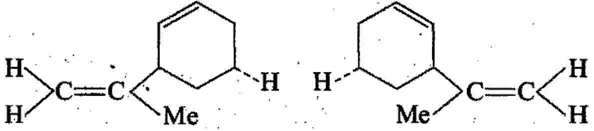
[Ans. (a) (1*R*, 2*R*) 1, 2-dibromocyclopentane
(b) (1*R*, 2*S*) 1, 2-dibromocyclopentane]

6. Specify chiral-enantiomers and achiral-identical pairs among the following:

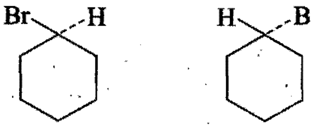
(i)



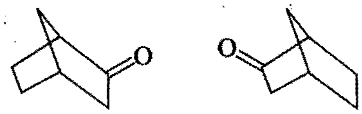
(ii)



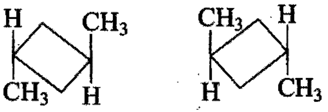
(iii)



(iv)



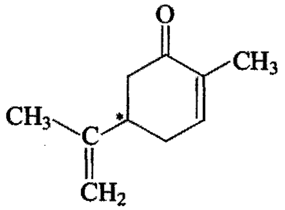
(v)



[Ans. (i) Chiral-enantiomers
(ii) Chiral-enantiomers
(iii) Achiral-identical
(iv) Chiral-enantiomers
(v) Achiral-identical]

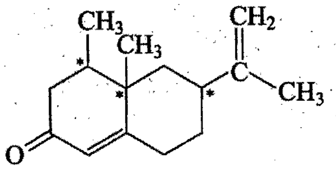
7. Put star mark to the chirality centre of the following compounds:

(a)



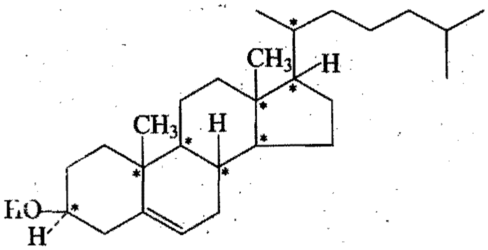
Carvone (Spearmint oil)

(b)



Noot katone (Grape fruit oil)

(c)

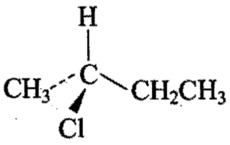


Cholesterol

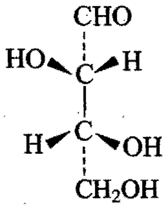
Note : Star marks are given in the figure of question.

8. Assign '*R*' and '*S*' configuration for the following:

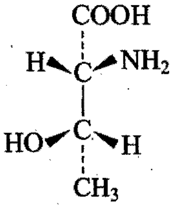
(a)



(b)



(c)



[**Ans.** (a) (*S*)-2-chlorobutane
(b) (2*S*, 3*R*)-2, 3, 4-trihydroxybutanal
(c) (2*R*, 3*S*)-2-amino-3-hydroxy butanoic acid]

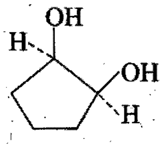
9. Assign Cahn-Ingold Prelog priorities to the following sets of substituents:

(a) —H, —Br, $-CH_2CH_3$, $-CH_2CH_2OH$
(b) —COOH, $-COOCH_3$, $-CH_2OH$, —OH
(c) —CN, $-CH_2NH_2$, $-CH_2NHCH_3$, $-NH_2$
(d) —Br, $-CH_2Br$, —Cl, $-CH_2Cl$

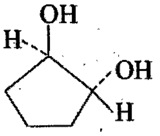
[**Ans.** (a) —Br > $-CH_2CH_2OH$ > $-CH_2CH_3$ > —H
(b) —OH > $-COOCH_3$ > —COOH > $-CH_2OH$
(c) $-NH_2$ > —CN > $-CH_2NHCH_3$ > $-CH_2NH_2$
(d) —Br > —Cl > $-CH_2Br$ > $-CH_2Cl$]

10. Which of the following structures represent 'meso' form?

(a)

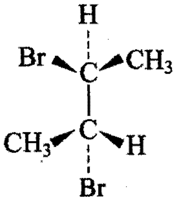


(b)



(c)

(d)



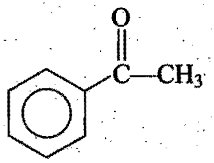
[**Ans.** (a) and (d) are meso forms.]

11. Which of the following have a 'meso' form?
(a) 2,3-Dibromobutane (b) 2,3-Dibromopentane
(c) 2,4-Dibromopentane

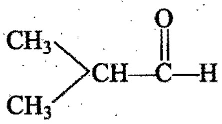
[**Ans.** (a) and (c) are meso forms
(Draw the projection forms to verify)]

12. Write down tautomeric structure of the following compounds:

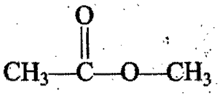
(a)



(b)

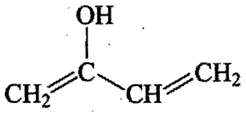


(c)



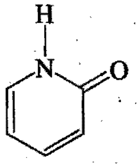
$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$$

(d)

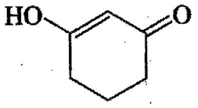


$$CH_2{=}\overset{OH}{\overset{|}{C}}-CH{=}CH_2$$

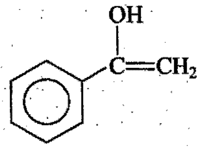
(e)



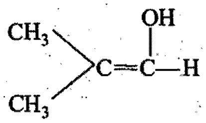
(f)



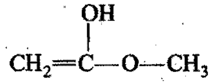
[**Ans.** (a)



(b)

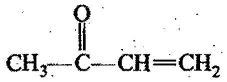


(c)



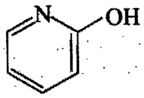
$$CH_2{=}\overset{OH}{\overset{|}{C}}-O-CH_3$$

(d)

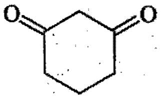


$$CH_3-\overset{O}{\overset{\|}{C}}-CH{=}CH_2$$

(e)



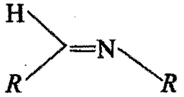
(f)

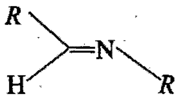


]

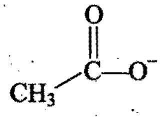
13. Specify whether the following pairs of compounds are identical, resonating structures or position isomers :

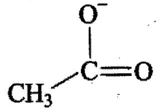
(a)



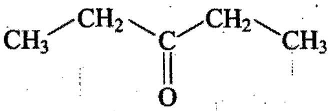


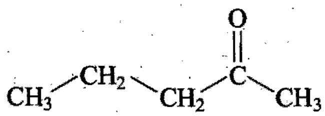
(b)



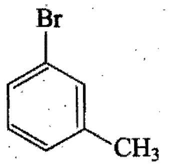


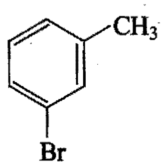
(c)

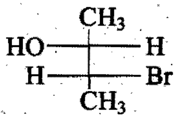
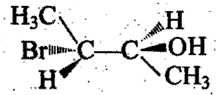




(d)



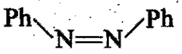
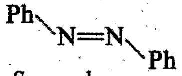


(d)  4.  (iv) (2*R*, 3*S*) -3-bromo 2-butanol

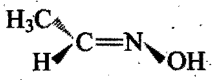
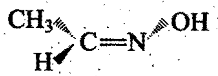
Codes :

(a) (A–1–i); (B–2–ii); (C–3–iii); (D–4–iv) ☐
(b) (A–4–iii); (B–3–iv); (C–2–ii); (D–1–i) ☐
(c) (A–4–iv); (B–3–iii); (C–2–ii); (D–1–i) ☐
(d) (A–3–iii); (B–4–ii); (C–2–i); (D–1–iv) ☐

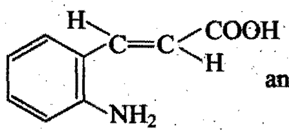
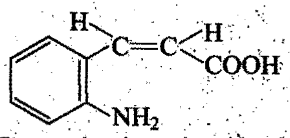
31. For which of the following pairs of compounds are the correct notations given?

(a)  and  ☐

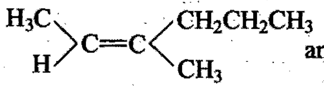
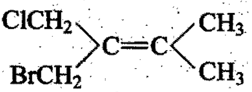
Anti-azobenzene *Syn*-azobenzene

(b)  and  ☐

Syn-acetaldoxime *Anti*-acetaldoxime

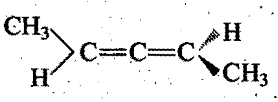
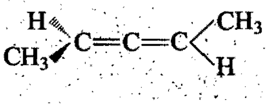
(c)  and 

Trans-*o*-aminocinnamic acid *Cis*-*o*-aminocinnamic acid ☐

(d)  and 

Z-isomer *E*-isomer ☐

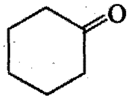
32. The molecules

 and 

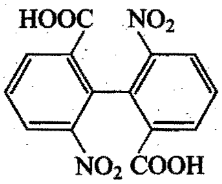
are:

(a) enantiomers ☐ (b) diastereomers ☐
(c) structural isomers ☐ (d) none of these. ☐

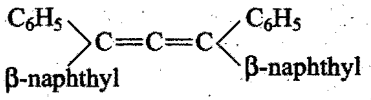
33. Which of the following compounds will exhibit geometrical isomerism?

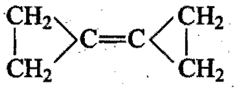
(a) $CH_3—CH=CH—COOH$ ☐
(b) $Br—CH=CH—Br$ ☐
(c) $C_6H_5—CH=NOH$ ☐
(d)  ☐

34. Which of the following compounds exhibits optical isomerism?

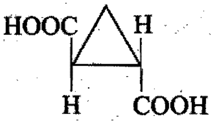
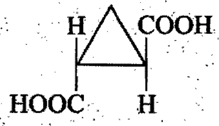
(a)  ☐

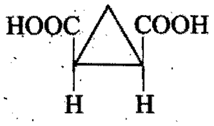
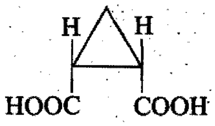
(b) $CH_2=C=CH_2$ ☐

(c)  ☐

(d)  ☐

35. Which of the following represents a pair of enantiomers?

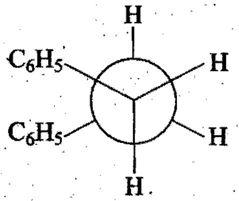
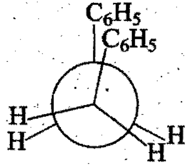
(a)  ☐ (b)  ☐

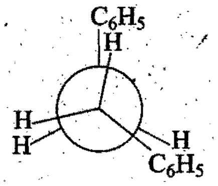
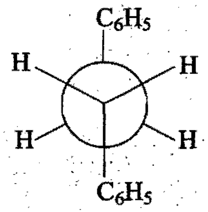
(c)  ☐ (d)  ☐

36. Which of the following cycloalkanes involves maximum torsional strain?

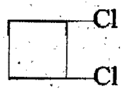
(a) Cyclopropane ☐ (b) Cyclobutane ☐
(c) Cyclopentane ☐ (d) Cyclohexane ☐

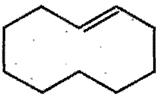
37. The most stable conformation of 1,2-diphenyl ethane is:

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

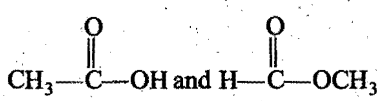
38. Which of the following can form geometrical isomer?

(a)  ☐ (b) $CH_3—CH=N—OH$ ☐

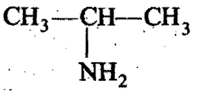
(c)  ☐ (d) All of these ☐

39. Which of the following is/are correct matchings?

Column 1 **Column 2**

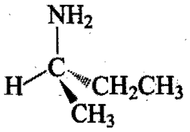
(a)  $CH_3—\overset{O}{\overset{\|}{C}}—OH$ and $H—\overset{O}{\overset{\|}{C}}—OCH_3$ metamers ☐

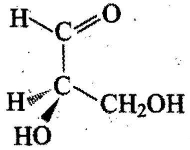
(b) $CH_3—CH_2—C \equiv CH$ and $CH_3—C \equiv C—CH_3$ position isomer ☐

(c) $CH_3CH_2CH_2NH_2$ and  $CH_3—\underset{NH_2}{\underset{|}{CH}}—CH_3$ tautomers ☐

(d) CH_3CH_2OH and $(CH_3)_2O$ functional isomer ☐

40. Consider the following structures and pick up the right statements:

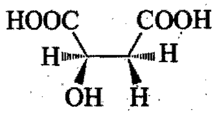

(I)

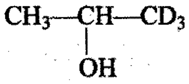

(II)

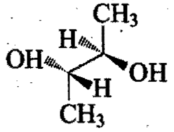

(III)

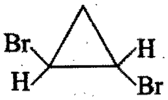
(a) I and II have *R*-configuration ☐
(b) I and III have *R*-configuration ☐
(c) only III has *S*-configuration ☐
(d) both (a) and (c) are correct ☐

41. Which of the following will not show optical activity?

(a)  ☐

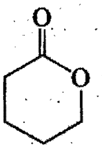
(b)  $CH_3-\underset{OH}{CH}-CD_3$ ☐

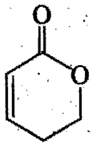
(c)  ☐

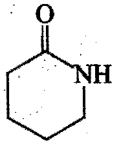
(d)  ☐

42. Which of the following compounds can not show tautomerism? **[PMT (Kerala) 2007]**

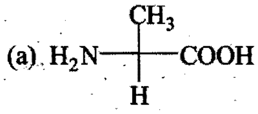
(a) HO—CH═CH_2 ☐

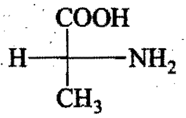
(b)  ☐

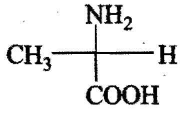
(c)  ☐

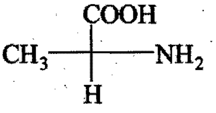
(d)  ☐

43. Among the following amino acids, the (*R*)-enantiomer is represented by:

(a)  $H_2N-\overset{CH_3}{\underset{H}{C}}-COOH$ ☐

(b)  $H-\overset{COOH}{\underset{CH_3}{C}}-NH_2$ ☐

(c)  $CH_3-\overset{NH_2}{\underset{COOH}{C}}-H$ ☐

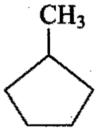
(d)  $CH_3-\overset{COOH}{\underset{H}{C}}-NH_2$ ☐

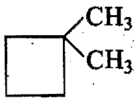
44. The IUPAC name of the compound,

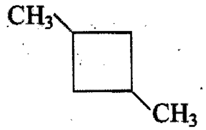
 is:

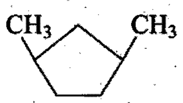
(a) (2*E*, 4*E*, 6*Z*)-octa-2,4,6-triene ☐
(b) (2*E*, 4*E*, 6*E*)-octa-2,4,6-triene ☐
(c) (2*Z*, 4*E*, 6*Z*)-octa-2,4,6-triene ☐
(d) (2*Z*, 4*Z*, 6*Z*)-octa-2,4,6-triene ☐

45. Which of the following cycloalkanes will show *cis-trans* isomerism?

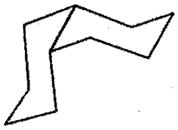
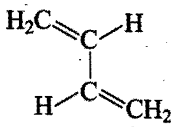
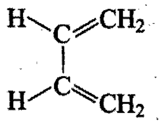
(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

46. Match **List I** with **List II** and select the answer from given codes:

List I **Structure of the compound**	**List II** **Name of geometrical isomer**
A. 	1. *S-cis*
B. 	2. *Trans*
C. 	3. *Cis*
D. 	4. *S-trans*

Codes :

	A	B	C	D
(a)	1	2	3	4
(b)	4	3	2	1
(c)	2	3	1	4
(d)	3	2	4	1

47. Which of the following is correctly matched?

Compound	**Number of geometrical isomers**
(a) $CH_3—CH═CH—CH═CH—C_2H_5$	4
(b) $CH_3—(CH═CH)_4—CH_3$	2
(c) $H_2C═CH—CH═CH_2$	$2^3+2^1=10$
(d) $CH_3(—CH═CH)_5—CH_3$	$2^4+2^2=20$

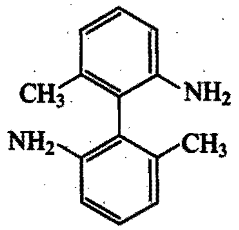
48. Match **List I** with **List II** and select the correct answer from the given codes:

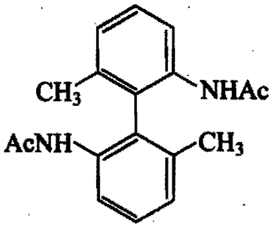
List I **Compound**	**List II** **Number or optical isomers**
A. A symmetrical compound with '*n*' chiral carbon.	1. 2^{n-1}
B. Symmetrical molecule with '*n*' chiral carbon when *n* is even.	2. $2^{n-1}-2^{\frac{n-1}{2}}$
C. Symmetrical molecule with '*n*' chiral carbon when *n* is odd.	3. 2^n

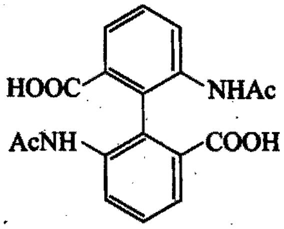
Codes :

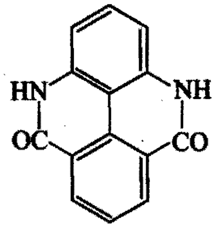
	A	B	C
(a)	1	2	3
(b)	3	2	1
(c)	3	1	2
(d)	2	3	1

49. Select the optically inactive compound among the following:

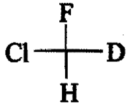
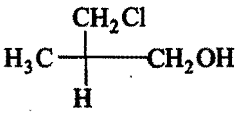
(a)  ☐

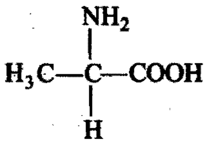
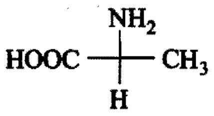
(b)  ☐

(c)  ☐

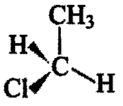
(d)  ☐

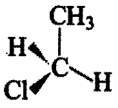
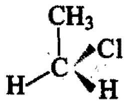
50. Identify, which of the following molecules does not have '*R*' configuration?

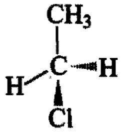
(a)  $\mathrm{Cl}-\overset{\mathrm{F}}{\underset{\mathrm{H}}{+}}-\mathrm{D}$ ☐ (b)  $\mathrm{H_3C}-\overset{\mathrm{CH_2Cl}}{\underset{\mathrm{H}}{+}}-\mathrm{CH_2OH}$ ☐

(c)  $\mathrm{H_3C}-\overset{\mathrm{NH_2}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{COOH}$ ☐ (d)  $\mathrm{HOOC}-\overset{\mathrm{NH_2}}{\underset{\mathrm{H}}{+}}-\mathrm{CH_3}$ ☐

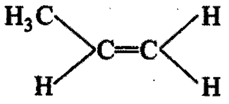
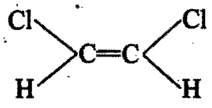
51. Which of the following is the enantiomer of the structure?

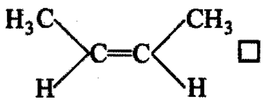
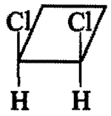


(a)  ☐ (b)  ☐

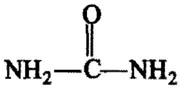
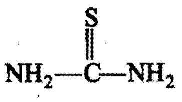
(c)  ☐ (d) It does not have an enantiomer ☐

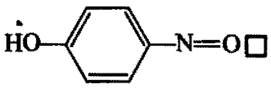
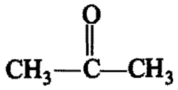
52. Which of the following will have a *trans* isomer?

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

53. Which of the following compounds shows tautomerism?

(a)  $\mathrm{NH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH_2}$ ☐ (b)  $\mathrm{NH_2}-\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH_2}$ ☐

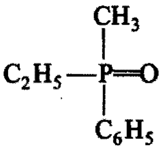
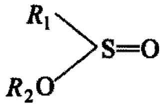
(c)  ☐ (d)  $\mathrm{CH_3}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_3}$ ☐

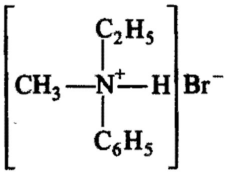
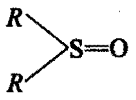
54. Increasing order of stability among the three main conformations (*i.e.*, eclipse, anti, gauche) of 2-fluoroethanol is: **[AIEEE 2006]**

(a) eclipse, gauche, anti ☐ (b) gauche, eclipse, anti ☐

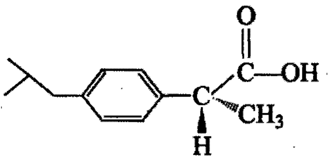
(c) eclipse, anti, gauche ☐ (d) anti, gauche, eclipse ☐

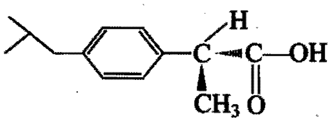
55. Which of the following is(are) optically active?

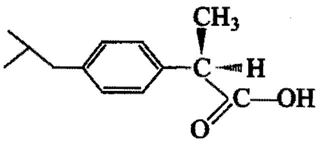
(a)  ☐ (b)  ☐

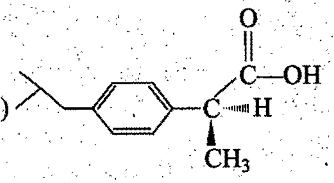
(c)  ☐ (d)  ☐

56. The *S*-ibuprofen is responsible for its pain relieving property. Which one of the structures shown is *S*-ibuprofen?

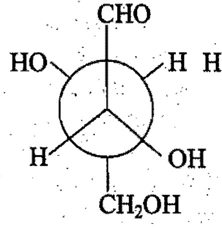
(a)  ☐

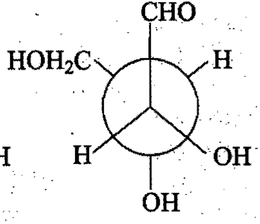
(b)  ☐

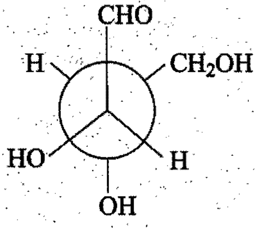
(c)  ☐

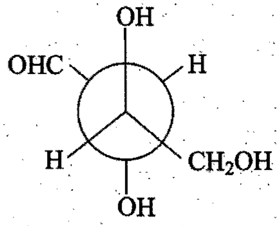
(d)  ☐

57. Four Newman projection formulae of compound $CH_2OH—CHOH—CHOH—CHO$ are shown below:


(I)


(II)

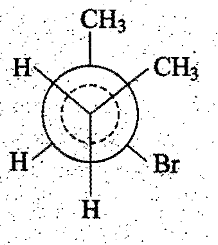
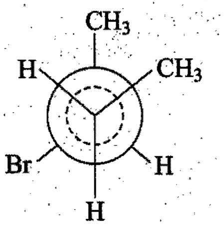

(III)

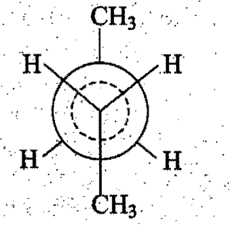
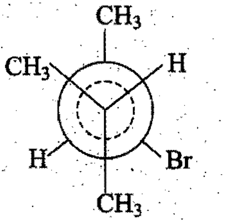

(IV)

Which of the above represents erythro isomer?

(a) I and III ☐ (b) I and IV ☐
(c) I and II ☐ (d) II and IV ☐

58. In the dehydrohalogenation of 2-bromobutane, which conformation leads to the formation of *cis*-2-butene?

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

59. The major product from the reaction of Br_2 with *Z*-3-hexene is:

(a) optically active ☐
(b) racemic mixture ☐
(c) meso form ☐
(d) both racemic mixture and meso form ☐

60. Which one of the following statement(s) is/are true for *threo*-butane-2,3-diol regarding their population of different conformers?

(a) The most populated conformer will have the hydroxyl groups of the *gauche* position. ☐
(b) The most populated conformer will have the hydroxyl groups at the *anti* position. ☐
(c) All staggered conformations will be equally populated. ☐
(d) Relative populations of different conformers is not predictable. ☐

[**Ans.** (a) Intramolecular hydrogen bonding is possible in *gauche* conformation which makes it more stable than *anti* form.]

ANSWERS : BRAIN STORMING PROBLEMS

18. (d)	**19.** (c)	**20.** (d)	**21.** (a)	**22.** (b)	**23.** (b)	**24.** (d)	**25.** (a)	**26.** (a,b)	**27.** (d)
28. (d)	**29.** (a)	**30.** (b)	**31.** (b,c,d)	**32.** (a)	**33.** (a,b,c)	**34.** (a,c)	**35.** (a,b)	**36.** (a)	**37.** (d)
38. (d)	**39.** (b,d)	**40.** (a)	**41.** (c)	**42.** (c)	**43.** (b)	**44.** (c)	**45.** (c,d)	**46.** (d)	**47.** (a,d)
48. (c)	**49.** (d)	**50.** (d)	**51.** (d)	**52.** (b,c,d)	**53.** (a,b,c,d)	**54.** (c)	**55.** (a,b,c)	**56.** (d)	**57.** (b)
58. (a)	**59.** (b)	**60.** (a)							

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Stereoisomers, which can be interconverted simply by rotation about sigma bonds, are conformational isomers while those, which can be converted only by breaking and remaking of bonds and not simply by rotation, are called configurational isomers.

The angle between C—C and C—H bonds on adjacent carbon atoms in any conformation is called dihedral angle.

The cyclic compounds most commonly found in nature containing six membered rings can exist in a conformation that is almost completely free of strain. The most stable conformation of cyclohexane is chair form.

According to Bayer strain theory, the greater deviation from the normal tetrahedral angle, greater is the angle strain or torsional strain and hence lesser is the stability of the cycloalkane.

Answer the following questions:

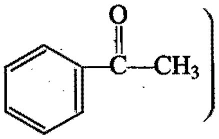
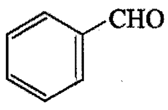
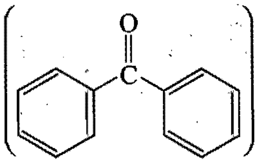
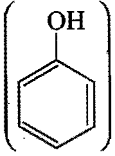
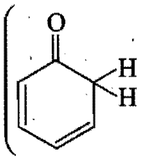
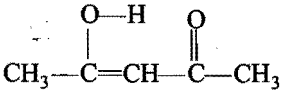
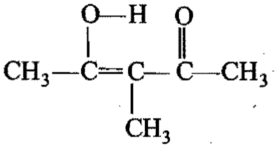
1. Dihedral angle in staggered and eclipsed conformations are:
   (a) 60° and 0° (b) 0° and 60°
   (c) 60°, 120° (d) 120°, 60°
2. Dihedral angle between two methyl groups of *n*-butane in the gauche and anti forms are:
   (a) 60°, 0° (b) 60°, 180°
   (c) 0°, 60° (d) 180°, 60°
3. Which among the following conformations of cyclohexane is the most stable form?
   (a) Chair form (b) Half chair form
   (c) Twist boat form (d) Boat form
4. Which of the following molecules has the highest deviation from tetrahedral bond angle?
   (a) Cyclopropane (b) Cyclobutane
   (c) Cyclopentane (d) Cyclohexane
5. The energy barrier between eclipsed and staggered forms is:
   (a) 44 kJ/mol (b) 6.7 kJ/mol
   (c) 12.55 kJ/mol (d) 29.7 kJ/mol
6. Select the correct sequence of decreasing order of stability:
   (a) gauche > staggered > partially eclipsed > fully eclipsed
   (b) staggered > gauche > partially eclipsed > fully eclipsed
   (c) fully eclipsed > partially eclipsed > gauche > staggered
   (d) partially eclipsed > fully eclipsed > staggered > gauche

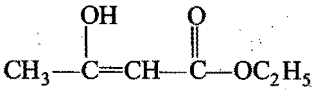
Passage 2

Tautomerism arises due to 1,3-migration of a proton from one polyvalent atom to the other within the same molecule. Two isomers thus obtained exist in dynamic equilibrium with each other are called tautomers and the phenomenon is called tautomerism or allelotropism or dynamic isomerism.

For an aldehyde or ketone to exhibit keto-enol tautomerism, it is essential that it must have at least one α-hydrogen atom. In simple aldehydes and ketones the 'enolic' form is negligibly small. This is due to greater stability of the 'keto' form with respect to 'enol' form. Strength of (C=O) bond in keto form has greater energy than (C=C) bond in enol form.

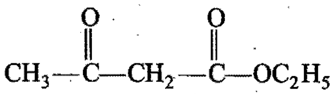
Answer the following questions:

1. The compound acetophenone () shows the 'keto' - 'enol' tautomerism.
   (a) True (b) False
   [**Hint :** Compounds having at least one hydrogen at α-position with respect to 'keto' group show the tautomerism.]
2. Benzaldehyde () and benzophenone () both possess tautomerism.
   (a) True (b) False
3. Phenol () is more stable than 2,4-cyclohexadiene-1-one ().
   (a) True (b) False
4. Acetylacetone ( $CH_3-\overset{\overset{O-H}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-CH_3$) is more stable than ( $CH_3-\overset{\overset{O-H}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$) α-methyl acetyl acetone.
   (a) True (b) False
5. 'Enol' form of acetoacetic ester is more stable than 'keto' form.



$CH_3-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-OC_2H_5$

(More stable)



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$

(Less stable)

(a) True (b) False

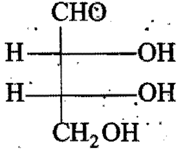
Hint : Enol form is stabilised by intramolecular hydrogen bond.]

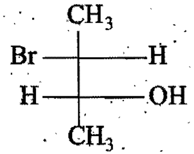
Passage 3

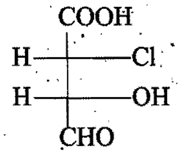
The prefixes 'erythro' and 'threo' are used for distinguishing a pair of enantiomers containing two chiral carbon atoms when two of the atoms or groups on each chiral carbon atom are the same while the third is different. The stereoisomer, in which the two identical groups are on the same side of the Fischer projection formula, is called the **erythro isomer** while the isomer, in which the two identical groups are on the opposite sides of the Fischer projection formula, is called the **threo isomer.**

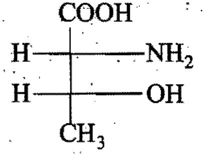
Answer the following questions :

1. Which among the following is a 'threo' isomer?

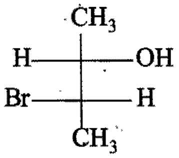
(a) 

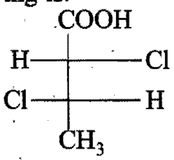
(b) 

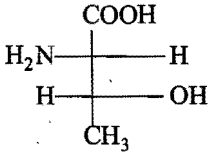
(c) 

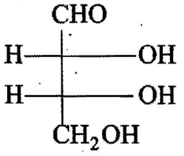
(d) 

2. Erythro isomer among the following is:

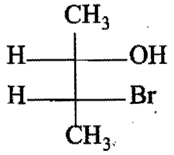
(a) 

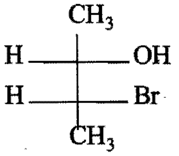
(b) 

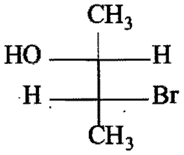
(c) 

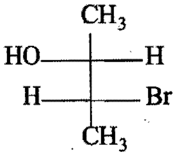
(d) 

3. Select the correct representation among the following:

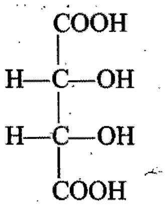
(a)  Threo-3-bromo-2-butanol

(b)  Erythro-3-bromo-2-butanol

(c)  Threo-3-bromo-2-butanol

(d)  Erythro-3-bromo-2-butanol

4. Select the correct statement about the following compound:



(a) It is optically active form
(b) It has two chiral carbons
(c) It is erythro isomer
(d) It has plane of symmetry

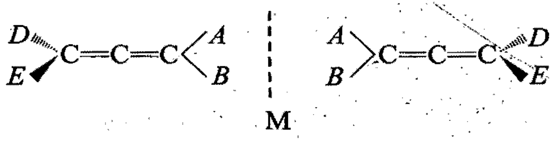
Passage 4

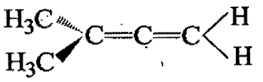
Allenes are the compounds which have the general structure

ABC=C=*CAB* OR *ABC*=C=*CDE*

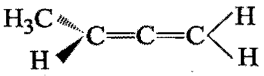
The examination of the space formula of allenes shows that the central carbon is *sp*-bonded. The remaining two *p*-orbitals of central atom are perpendicular to each other, and each overlaps with the *p*-orbital of one adjacent carbon atom, forcing the two remaining bonds of each carbon into perpendicular planes. Thus, the molecule and its mirror image are not superimposable, because the group *A* and *B* lie in the plane of paper and the group *D* and *E* in the plane perpendicular to the plane of the paper.

Identify whether the following statements are True or False:

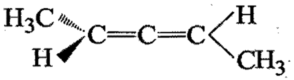


1.  It is optically active:

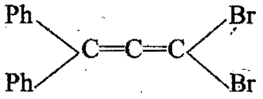
(a) True (b) False

2.  It is optically inactive form:

(a) True (b) False

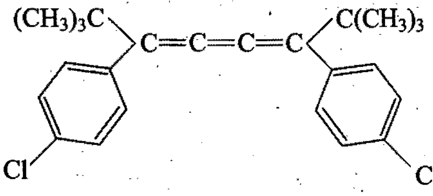
3.  It is optically inactive form:

(a) True (b) False

4. 

All the terminal groups of this molecule be in the same plane:

(a) True (b) False

5. 

All the terminal groups of it are in the same plane:
(a) True (b) False

[**Hint :** When odd no. of cumulative double bonds exists, orbital overlapping causes the four groups to occupy one plane and *cis-trans* isomerism is observed.]

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1.	**1.** (a)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (c)	**6.** (b)
Passage 2.	**1.** (a)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (a)	
Passage 3.	**1.** (b)	**2.** (d)	**3.** (b,c)	**4.** (b,c,d)		
Passage 4.	**1.** (b)	**2.** (a)	**3.** (a)	**4.** (b)	**5.** (a)	

5

MECHANISM OF ORGANIC REACTIONS

5.1 INTRODUCTION

A chemical equation is a symbolic representation of a chemical change. It indicates the initial reactants and final products involved in a chemical change. Reactants generally consist of two species:

1. One which is being attacked; it is called a **substrate.**
2. Other which attacks the substrate; it is referred to as a **reagent.** These two interact to form products.

$$\text{Substrate} + \text{Reagent} \longrightarrow \text{Products}$$

Most of the reactions are complex and take place *via* intermediates which may or may not be isolated. The intermediates are generally very reactive. They react readily with other species present in the environment to form the final products. **The detailed step by step description of a chemical reaction is called its mechanism.**

$$\text{Substrate} \longrightarrow \text{Intermediates} \longrightarrow \text{Products}$$

Mechanism is only a hypothesis which explains various facts regarding a chemical change.

Most of the attacking reagents carry either a positive or a negative charge. The positively charged reagents attack the substrate at the points where electron density is high while the negatively charged reagents attack the points of low electron density. The reactions of organic compounds essentially involve changes in the existing covalent bonds present in their molecules. These changes may involve electronic displacements in the bonds, breaking of the bonds, energy changes accompanying the cleavage and formation of new bonds. To understand clearly the mechanism of various organic reactions, it is thus essential to have knowledge about the following well established concepts:

(i) Electronic displacements in covalent bonds,
(ii) Cleavage (fission or breaking) of covalent bonds,
(iii) Nature of attacking reagents.

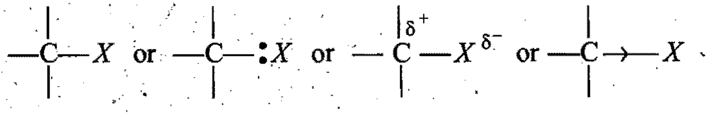
5.2 ELECTRONIC DISPLACEMENT IN COVALENT BONDS

The electronic displacements in covalent bonds may occur either due to the presence of some atom or group in the molecule or under the influence of attacking reagent. As a result of these electron displacements, centres of different electron densities are created and these centres are susceptible to attack by the reagents. The factors which create the centres of different electron densities in the substrate are mainly:

1. Inductive effect
2. Electromeric effect
3. Resonance and Mesomeric effect
4. Hyperconjugation

1. Inductive effect : A covalent bond is formed on account of the equal contribution of electrons by two atoms. In case two atoms are similar, the electron pair occupies a central position between the two nuclei of the atoms and such a bond is known as non-polar covalent bond. For example, the bonds between H_2 molecule (H : H), chlorine molecule (Cl : Cl), carbon and carbon $-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-(-\underset{|}{\overset{|}{C}}:\underset{|}{\overset{|}{C}}-)$ are non-polar covalent bonds as the influence of the electron pair is same on both the atoms.

In a covalent bond between two dissimilar atoms (having different electronegativities), the electron pair does not remain in the centre but is attracted towards the more electronegative atoms. The bond becomes somewhat polar due to unequal sharing of the electron pair. For example, in the bond $-\overset{|}{\underset{|}{C}}-X$ if X is more electronegative than C, the electron pair is attracted towards X. With the result of this shifting, X acquires a partial negative charge denoted by δ^- and C attains a partial positive charge denoted by δ^+



$$-\overset{|}{\underset{|}{C}}-X \quad\text{or}\quad -\overset{|}{\underset{|}{C}}-\!:\!X \quad\text{or}\quad -\overset{|\delta^+}{\underset{|}{C}}-X^{\delta^-} \quad\text{or}\quad -\overset{|}{\underset{|}{C}}\rightarrow\!\!-X$$

The polarity thus produced in the molecule as a result of higher electronegativity of one atom compared to other is termed inductive effect. It is important to note that the electron pair, although permanently displaced or simply shifted, but remains in the same valence shell. The inductive effect is always transmitted along a chain of carbon atoms. Whenever an electron withdrawing atom such as halogen (X) or group ($-NO_2$, $-CN$, $-COOH$, etc.) is attached to the end of a carbon chain, the σ electrons of the C—X bond are slightly displaced towards the more electronegative halogen atom. However, its intensity decreases as distance from the source atoms increases.

$$-C_4 \longrightarrow\!\!- C_3^{\delta\delta\delta^+} \longrightarrow\!\!- C_2^{\delta\delta^+} \longrightarrow\!\!- C_1^{\delta^+} \rightarrow\!\!- Cl^{\delta^-}$$

The positive charge on C_1 attracts the electron pair shared between C_1 and C_2 towards itself. This will cause C_2 to acquire a small positive charge but this charge on C_2 will be smaller than on C_1. Similarly, C_3 will acquire positive charge that will be still smaller. This effect is still relayed further. In fact, inductive effect tends to be insignificant beyond the second carbon atom. **It is a permanent effect in the molecule** and can be observed practically in the form of dipole moment. "This type of electron displacement along a carbon chain due to the presence of a source is called **Inductive effect** or **Transmission effect.**" This effect is represented by an arrow head in the middle of covalent bond pointing in the direction of electron displacement ($\rightarrow\!\!-$).

The carbon-hydrogen bond is used as a standard for comparing the tendency of electron attraction and repulsion. There are two types of inductive effects, *i.e.*, **–*I* effect** and **+*I* effect**: (i) The atom or group which has more power to attract electrons in comparison to hydrogen is said to have **–*I* effect.** The σ electrons are displaced towards the substituent X. (ii) The atom or group which has less power to attract the electrons than hydrogen is said to have **+*I* effect.** The σ electrons are displaced away from the substituent Y.

$$-C_3^{\delta\delta\delta^-} \leftarrow\!\!- C_2^{\delta\delta^-} \leftarrow\!\!- C_1^{\delta^-} \leftarrow\!\!- Y^{\delta^+}$$

The first type is referred to as electron attracting or electron withdrawing while the second type electron repelling or electron releasing atom or group (Ingold convention).

Some common atoms or groups which cause –*I* and + *I* effects are shown below in decreasing orders:

–*I* Effect : Atoms or groups **(Electron-attracting or withdrawing)** in the decreasing order is:

$NR_3 > -NO_2 > -SO_2R > -CN > -COOH > -F$
$> -Cl > -Br > -I > -OR > -COR > -OH$
$> -C_6H_5 > -CH{=}CH_2 > -H$

+*I* Effect : Groups **(Electron-releasing or repelling)** in the decreasing order is:

$(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > CH_3- > D > H$

Important Features of Inductive Effect

(i) It is a permanent effect in the molecule or ion.

(ii) The shared pair of electrons although permanently shifted towards more electronegative atom, yet remains in the same valence shell.

(iii) As a result of electron shifting, the more electronegative end acquires partial negative charge and the other acquires partial positive charge.

(iv) The inductive effect is not confined to the polarisation of one bond but is transmitted along a chain of carbon atoms through σ-bonds. However, the effect is insignificant beyond second carbon in the chain.

(v) Inductive effect brings changes in physical properties such as dipole moment, solubility, etc. It affects the rates of the reaction.

(vi) Carbon-hydrogen bond is taken as a standard of inductive effect. Zero effect is assumed for this bond. Atoms or groups which have a greater electron-withdrawing capacity than hydrogen are said to have –*I* effect whereas atoms or groups which have a greater electron releasing power are said to have +*I* effect.

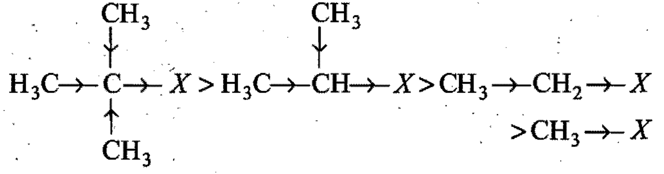
The phenomenon of inductive effect is very important in organic chemistry as it is helpful in explaining a number of facts. Some of them are discussed below:

(a) Reactivity of alkyl halides : The presence of halogen atom in the molecule of alkyl halide creates a centre of low electron density which is readily attacked by the negatively charged reagents. For example, CH_3Cl is more reactive than CH_4 as inductive effect is present in CH_3Cl and no inductive effect in methane.

$$H_3C\rightarrow\!\!-Cl \quad\text{or}\quad H_3\underset{\uparrow}{\overset{\delta^+}{C}}-\overset{\delta^-}{Cl}$$

Site for the attack by
electron-rich reagent

The activity also increases from primary to secondary and from secondary to tertiary halides as the +*I* effect of methyl groups enhances –*I* effect of the halogen atom by repelling the electrons towards the tertiary carbon atom. The reactivity order for alkyl halides is:



$$H_3C\rightarrow\!\!-\overset{\overset{CH_3}{\downarrow}}{\underset{\underset{CH_3}{\uparrow}}{C}}\rightarrow\!\!-X > H_3C\rightarrow\!\!-\overset{\overset{CH_3}{\downarrow}}{CH}\rightarrow\!\!-X > CH_3\rightarrow\!\!-CH_2\rightarrow\!\!-X > CH_3\rightarrow\!\!-X$$

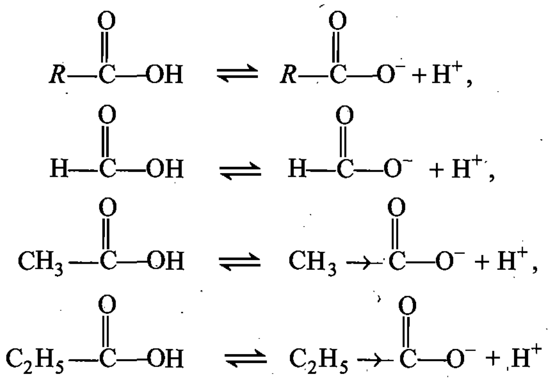
Tertiary > Secondary > Primary > Methyl

(b) Dipole moment : As the inductive effect increases, the dipole moment increases.

$$\underset{1.64\,D}{CH_3 \rightarrow I} \qquad \underset{1.79\,D}{CH_3 \rightarrow Br} \qquad \underset{1.83\,D}{CH_3 \rightarrow Cl}$$

$$\xrightarrow[\text{Inductive effect increases}]{\qquad\qquad\qquad\qquad\qquad}$$

(c) Relative strength of the acids (Acidic nature of —COOH) : An acid may be defined as a species that has the tendency to lose proton. Furthermore, the strength of an acid depends on the tendency to release proton when the acid is dissolved in water.



$$R-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-O^- + H^+,$$

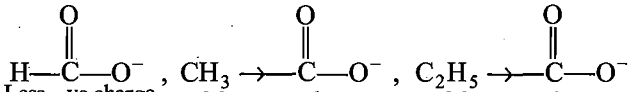
$$H-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons H-\overset{O}{\overset{\|}{C}}-O^- + H^+,$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons CH_3 \rightarrow \overset{O}{\overset{\|}{C}}-O^- + H^+,$$

$$C_2H_5-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons C_2H_5 \rightarrow \overset{O}{\overset{\|}{C}}-O^- + H^+$$

So, (i) stronger is acid, weaker is its conjugate base.

(ii) More negative is the charge on carboxylate ion, the more is its reactivity and more is basic nature, *i.e.*, lesser is acidic nature.



$$H-\overset{O}{\overset{\|}{C}}-O^-, \quad CH_3 \rightarrow \overset{O}{\overset{\|}{C}}-O^-, \quad C_2H_5 \rightarrow \overset{O}{\overset{\|}{C}}-O^-$$

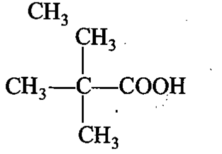
Less – ve charge (Most acidic) | More – ve charge (Less acidic) | Most – ve charge (Least acidic)

Thus, acidic nature is:

$$HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH > C_4H_9COOH$$

$$\xrightarrow[\text{(+ Inductive effect increases, so acid strength decreases)}]{\qquad\qquad\qquad\qquad\qquad}$$

Among isomeric carboxylic acid, acidity decreases with increase in branching of alkyl group attached to carboxylic group. $CH_3CH_2CH_2CH_2COOH > CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCOOH >$

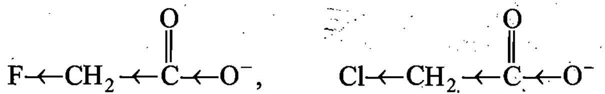


$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-COOH$$

Any group or atom showing +*I* effect decreases the acid strength as it increases the negative charge on the carboxylate ion which holds the hydrogen firmly. Alkyl groups have +*I* effect.

Further, the halogenated fatty acids are much stronger acids than the parent fatty acids and the acidity is increased almost proportionately with the increase in electronegativity of the halogen present which helps in repelling the proton from the hydroxy group of acid.

$$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$$



$$F \leftarrow CH_2 \leftarrow \overset{O}{\overset{\|}{C}} \leftarrow O^-, \qquad Cl \leftarrow CH_2 \leftarrow \overset{O}{\overset{\|}{C}} \leftarrow O^-$$

Less – ve charge (More acidic) | More – ve charge (Less acidic)

Furthermore, the inductive effect in di- and tri-halogeno substituted acids is still more marked with the result that these acids are progressively more stronger than the corresponding monohalogeno substituted acids. Thus, acidic nature decreases in the order:

$$\underset{\text{Trichloro acetic acid}}{CCl_3COOH} > \underset{\text{Dichloro acetic acid}}{CHCl_2COOH} > \underset{\text{Monochloro acetic acid}}{CH_2ClCOOH} > \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\xrightarrow[\text{(– Inductive effect increases, so acid strength increases)}]{\qquad\qquad\qquad\qquad\qquad}$$

Thus, the group or atom having –*I* effect increases the strength as it decreases the negative charge on the carboxylate ion. Greater is the number of such atoms or groups (having –*I* effect), greater is the acid strength.

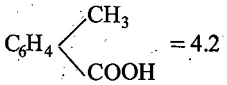
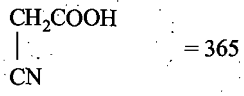
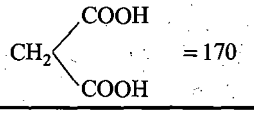
Since, the inductive effect decreases with increase in distance of halogen atom from the carboxylic group (source), the strength of the acid is proportionally decreased. Thus, the chlorobutyric acids follow the following acidity order:

$$\underset{\substack{\alpha\text{-Chlorobutyric acid} \\ K_a \times 10^5 = (14.0)}}{CH_3CH_2CH(Cl)COOH} > \underset{\substack{\beta\text{-Chlorobutyric acid} \\ (8.2)}}{CH_3CH(Cl)CH_2COOH}$$

$$> \underset{\substack{\gamma\text{-Chlorobutyric acid} \\ (3.0)}}{CH_2(Cl)CH_2CH_2COOH} > \underset{\substack{n\text{-Butyric acid} \\ (1.5)}}{CH_3CH_2CH_2COOH}$$

This fact can be shown by the following table that higher the K_a values (dissociation constants), more stronger will be the acid.

Measurement of Acid Strength
(K_a values of some acids × 10^{-5})

$HCOOH = 17.7$	$C_6H_5COOH = 6.35$
$CH_3COOH = 1.76$	 $C_6H_4\langle^{CH_3}_{COOH} = 4.2$
$CH_3CH_2COOH = 1.60$	
$(CH_3)_2CHCOOH = 1.38$	 $\underset{CN}{\underset{\mid}{CH_2COOH}} = 365$
$(CH_3)_3CCOOH = 0.89$	
$ClCH_2COOH = 136$	
$Cl_2CHCOOH = 5330$	$HOOC—COOH = 5400$
$Cl_3CCOOH = 23200$	 $CH_2\langle^{COOH}_{COOH} = 170$
$FCH_2COOH = 217$	

The relative strength of acids are measured in their ionisation constants (K_a or pK_a values).

$$\underset{\text{Acid}}{HA} \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

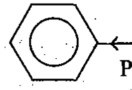
Greater the value of K_a or lower the value of pK_a, stronger will be the acid.

pK_a values of some acids are:

$HCOOH = 3.77$	$\begin{array}{l}CH_2COOH\\ \vert \\ CN\end{array} = 2.47$
$CH_3COOH = 4.76$	
$C_2H_5COOH = 4.88$	
$C_6H_5COOH = 4.17$	$ClCH_2COOH = 2.86$
$NO_2CH_2COOH = 1.68$	$Cl_2CHCOOH = 1.29$
	$ICH_2COOH = 3.16$

(See also Section **12.6,** the acidity of carboxylic acids)

K_a (ionisation constant of acid)


$\leftarrow OH > H—OH > CH_3 \rightarrow OH$

Phenol Water Methyl alcohol

As compared to water, phenol is more acidic (*–I* effect) but methyl alcohol is less acidic (*+I* effect).

The decreasing order of acid strength in alcohols is also due to *+I* effect of alkyl groups.

CH_3OH	>	CH_3CH_2OH	>	$(CH_3)_2CHOH$	>	$(CH_3)_3COH$
Methyl alcohol		Ethyl alcohol		Iso-propyl alcohol		*Tert*-butyl alcohol

Acidity of some important inorganic acids used in organic chemistry are given below:

$HF < HCl < HBr < HI$ (Acidity)

$F^- > Cl^- > Br^- > I^-$ (Basicity)

$H_2O < H_2S < H_2Se$ (Acidity)

$OH^- > SH^- > SeH^-$ (Basicity)

$CH_4 < NH_3 < H_2O < HF$ (Acidity)

Relative acidity of hydrocarbons may be given as:

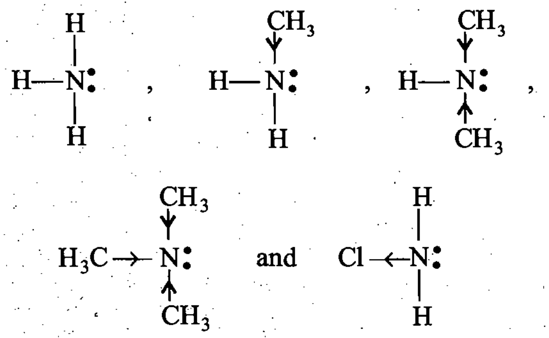
$$HC\equiv CH > CH_2=CH_2 > CH_3—CH_3$$
$$pK_b = \quad 25 \qquad 44 \qquad 50$$

As the hybridisation changes from sp^3 in ethane to sp^2 in ethene and to sp in ethyne, the acidity increases and the pK_a decreases. This is because of the relative stability of the unshared electrons in the conjugated bases of each of these compounds. In other words, energy of hybrid orbitals is in the order: $sp < sp^2 < sp^3$.

Or being the most electronegative, the *sp*-hybridized carbon atom in ethyne polarizes its C—H bond to the greatest extent, causing its hydrogens to be most positive. Therefore, ethyne donates a proton to a base more readily. Relative basicity of corresponding carbanions is given below:

$$CH_3—\bar{C}H_2 > CH_2=\bar{C}H > CH\equiv\bar{C}$$

(d) Strength of bases : A compound is said to be basic in nature, if it is capable of accepting a proton. Base strength is defined as the tendency to donate an electron pair for sharing. The difference in base strength in various amines can be explained on the basis of inductive effect. The *+I* effect increases the electron density while *–I* effect decreases. The amines* are stronger bases than NH_3 as the alkyl groups increase electron density on nitrogen due to *+I* effect while $ClNH_2$ is less basic due to *–I* effect. "So, more is the tendency to donate electron pair for coordination with proton, the more is basic nature, *i.e.*, more is the negative charge on nitrogen atom (due to *+I* effect of alkyl group), the more is basic nature".



Thus, the basic nature decreases in the order:

$(C_2H_5)_2NH$	>	$CH_3CH_2NH_2$	>	CH_3NH_2	>	NH_3	>	$ClNH_2$
Diethyl amine		Ethyl amine		Methyl amine		Ammonia		Chloro amine

The order of basicity is as given below:

Alkyl groups (*R*—)	**Relative base strength**
(i) CH_3	$R_2NH > RNH_2 > R_3N > NH_3$
(ii) C_2H_5	$R_2NH > R_3N > RNH_2 > NH_3$

Note: (i) In gas phase, tertiary amines are more basic than secondary amines which are more basic than primary amines.

(ii) In aqueous medium basicity of ethyl amine is:

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

The relative strengths of bases are measured as K_b or pK_b values.

$$\underset{\text{Base}}{BOH} \rightleftharpoons B^+ + OH^-$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$pK_b = -\log K_b$$

Greater the value of K_b or lower the value of pK_b, stronger will be the base.

Amine	$(CH_3)_2NH$	CH_3NH_2	$(CH_3)_3N$
pK_b	3.23	3.32	4.2

(See also Sec. **16.13**)

K_b (ionisation constant of base)

$$CH_3NH_2 > NH_3 > C_6H_5NH_2 > (C_6H_5)_2NH > (C_6H_5)_3N$$

As compared to ammonia, methyl amine is more basic (*+I* effect) but aniline is less basic and diphenylamine is still more weaker (*–I* effect).

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* It is important to note that the relative basic character of amines is not in total accordance with inductive effect ($t > s > p$) but it is in the following order: Secondary > Primary > Tertiary

The reason is believed to be steric factor.

The decreasing order of base strength in alcohols is due to +*I* effect of alkyl groups.

$$\underset{(3^\circ)}{(CH_3)_3COH} > \underset{(2^\circ)}{(CH_3)_2CHOH} > \underset{(1^\circ)}{CH_3CH_2OH} > \underset{\text{methyl}}{CH_3OH}$$

In Lucas test of making distinction between three types (1°, 2° and 3°) of monohydric alcohols,

$$\left[\underset{\text{(Base)}}{R{-}OH} + \underset{\text{(Acid)}}{HCl(conc.)} \xrightarrow{\text{Anhyd. } ZnCl_2} \underset{\text{(White ppt.)}}{R{-}Cl} + H_2O\right]$$

the basic character of alcohols is in the order, benzyl >3°>2°>1° and hence, the strongest base (3°) will be reacting fastest with conc. HCl in presence of anhydrous $ZnCl_2$ (Lucas reagent) and gives white turbidity immediately.

2. Electromeric effect : It is a **temporary effect.** It comes into play instantaneously at the demand of the attacking reagent and as soon as the attacking reagent is removed the original condition is restored.

A multiple bond (double or triple) consists of sigma and π-bonds. The electrons of the π-bond are loosely held and easily polarisable. When a compound having a multiple bond is approached by a charged reagent, the π-electrons of the bond are completely polarised, *i.e.*, shifted towards one of the constituent atoms. Thus,

$$>C{=}C< \underset{\text{Reagent removed}}{\overset{\text{Reagent added}}{\rightleftharpoons}} >\overset{+}{C}{-}\overset{-}{\ddot{C}}<$$

The atom which acquires the electron pair becomes negatively charged while the other atom gets the positive charge.

The effect involving the complete transfer of a shared pair of electrons to one of atoms joined by a multiple bond (double or triple) at the requirement of attacking reagent is known as electromeric effect. It is indicated by *E* and represented by a **curved** arrow (↷) showing the shifting of electron pair.

Direction of the shift of electron pair : The direction of the shift of electron pair can be decided on the basis of following points:

(i) When the groups linked to a multiple bond are similar, the shift can occur to either direction. For example, in ethylene the shift can occur to any one of the carbon atoms.

$$\left.\begin{array}{l} H_2C{=}CH_2 \longrightarrow H_2\overset{+}{C}{-}\overset{-}{\ddot{C}}H_2 \\ H_2C{=}CH_2 \longrightarrow H_2\overset{-}{\ddot{C}}{-}\overset{+}{C}H_2 \end{array}\right\} \text{Both are similar}$$

(ii) When the dissimilar groups are linked on the two ends of the double bond, the shift is decided by the direction of inductive effect. For example, in propylene the shift can be shown in the following ways:

$$CH_3{-}CH{=}CH_2 \longrightarrow CH_3{-}\overset{+}{C}H{-}\overset{-}{\ddot{C}}H_2 \qquad \ldots(i)$$

$$CH_3{-}CH{=}CH_2 \longrightarrow CH_3{-}\overset{-}{\ddot{C}}H{-}\overset{+}{C}H_2 \qquad \ldots(ii)$$

Due to electron repelling nature of methyl group, the electronic shift occurs according to eq. (i) way and not by eq. (ii) way.

$$CH_3 \rightarrow \underset{\text{Pent-2-ene}}{CH{=}CH} \leftarrow\!\leftarrow CH_2CH_3 \longrightarrow CH_3\overset{-}{C}H{-}\overset{+}{C}H{-}CH_2CH_3$$

+*I* effect of CH_3CH_2— is larger than that of CH_3—, hence π-electron transfer is from C_3 to C_2.

In the case of carbonyl group, the shift is always towards oxygen, *i.e.*, more electronegative atom.

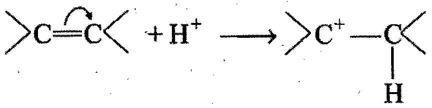
$$>C{=}O \longrightarrow >\overset{+}{C}{-}\overset{-}{\ddot{O}}$$

[In cases where inductive effect and electromeric effect simultaneously operate, usually electromeric effect predominates.]

Since, the electromeric effect takes place only at the time of attacking reagent, it always facilitates the reaction and never inhibits it. This effect is of common occurrence during addition of polar reagents on $>C{=}C<$ and $>C{=}O$ bonds.

There are two types of electromeric effects, *i.e.*, **+*E* effect** or **–*E* effect.**

(a) When the transfer of electrons takes place towards the attacking reagent, the effect is called **+*E* effect**, *e.g.*, the addition of acids to alkenes.



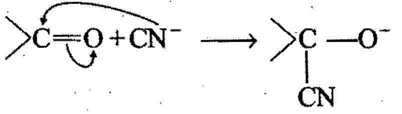
$$>C{=}C< + H^+ \longrightarrow >C^+{-}\underset{\underset{H}{|}}{C}<$$

$$CH_3 \rightarrow \underset{\text{Propene}}{CH{=}CH_2} + H^+ \longrightarrow CH_3{-}\overset{+}{C}H{-}CH_3$$

Since, —CH_3 group is electron repelling, the electrons are transferred in the direction shown.

The attacking reagent is attached to that atom on which electrons have been transferred.

(b) When the transfer of electrons takes place away from the attacking reagent, the effect is called **–*E* effect.** For example, the addition of cyanide ion to carbonyl compounds.



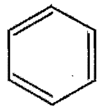
$$>C{=}O + CN^- \longrightarrow >\underset{\underset{CN}{|}}{C}{-}O^-$$

The attacking reagent does not get attached to that atom on which electrons have been transferred.

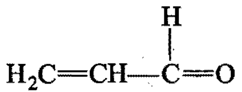
3. Resonance and Mesomeric effect : For resonance (See **section 1.12**). If the single and double bonds are present alternately in a molecule, it is said to contain double bonds in conjugation and the molecule is called a **conjugated molecule.** For example, butadiene is a conjugated molecule.

$$CH_2{=}CH{-}CH{=}CH_2$$

Following are some of the conjugated systems:

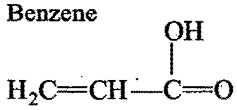


Benzene



$H_2C{=}CH{-}\overset{H}{C}{=}O$

Acrolein



$H_2C{=}CH{-}\overset{OH}{C}{=}O$

Acrylic acid

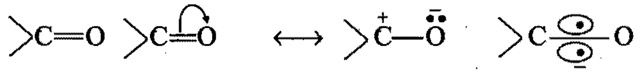
$H_2C{=}CH{-}\ddot{\underset{\cdot\cdot}{Cl}}:$

Vinyl chloride

(lone pair on Cl behaves like a π-bond thus it also makes vinyl chloride a conjugated system.)

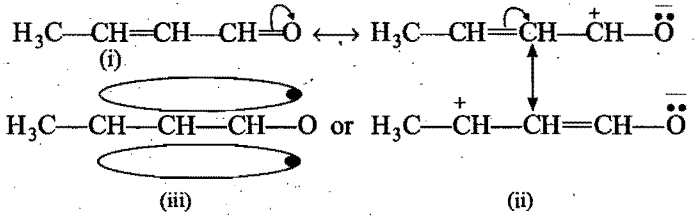
In such compounds, the π-electrons are delocalised and polarity in the molecule is developed. The same thing also happens when an atom or group with lone pair of electrons is situated in conjugation with a conjugated double bond. **The mesomeric effect refers to the polarity produced in a molecule as a result of interaction between two π-bonds or a π-bond and lone pair of electrons.** The effect is transmitted in the chain in a similar manner as the inductive effect.

In a carbonyl group (>C=O), the oxygen atom is more electronegative than carbon atom. The π-electrons of the double bond get displaced towards the oxygen atom. The shifting of electrons is shown by a curved arrow (↷). This will give an ionic structure. The actual structure seems to lie in between the structures (i) and (ii) which can be best represented as structure (iii) in which π-electrons are drawn preferentially towards oxygen.

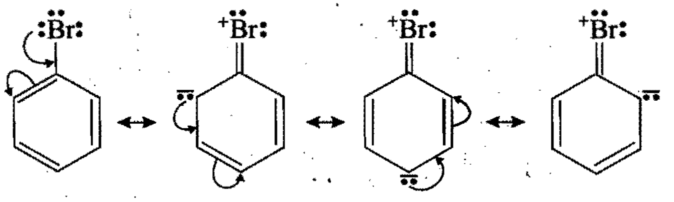


(i) (ii) (iii)

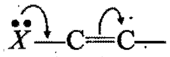
Now if the carbonyl group is conjugated with C=C type system, the above polarisation is transmitted further through π-electrons.



The polarisation also occurs when an atom or group having lone pair of electrons is present in conjugation with the double bond (conjugated system) as in bromobenzene.



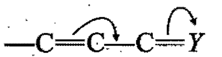
Like inductive effect, mesomeric effect may be $+M$ or $-M$. It is $+M$ when the transference of electrons is away from the atom or group and $-M$ when transference of electrons is towards atom or group (but away from conjugate system). In general,



$\ddot{X}{-}C{=}C{-}$

$+M$ effect

and



$-C{=}C{-}C{=}Y$

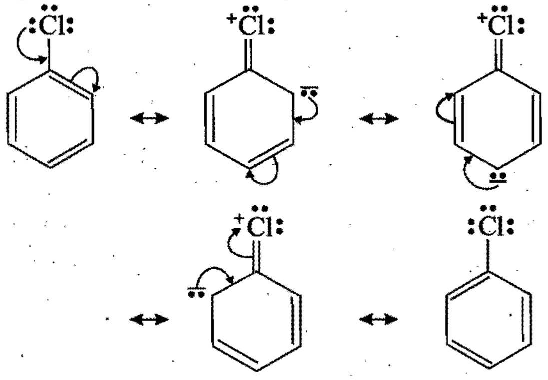
$-M$ effect

Some common atoms or groups which cause $+M$ or $+R$ and $-M$ or $-R$ effects are listed below:

+M or +R effect groups:

$-Cl, -Br, -I, -NH_2, -NHR, -NR_2, -OH, -OR, -SR, -SH, -OCH_3$, etc.

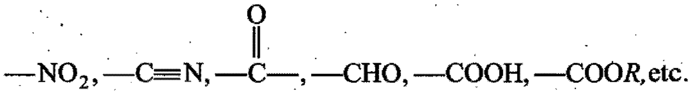
For example, $+M$ effect of halogen atom in vinyl and allyl halides explain their low reactivity.



This effect extends the degree of delocalization and imparts stability to the molecule. Phenoxide ion gets stabilized by resonance (See **section 16.15**). Lone pair on nitrogen in aniline gets delocalized and thus the basic nature of aniline is less than that of NH_3 (See **section 16.13**). Thus, $+M$ effect activates benzene nucleus for electrophilic substitution (S_E) reaction at *o*- and *p*-position.

Note: $-X$ ($-Cl, -Br, -I$) groups are *ortho-para* directing due to ($+M$) effect but these groups are deactivating due to ($-I$) effect.

−M or −R effect groups:



$-NO_2, -C\equiv N, -\overset{O}{\overset{\|}{C}}-, -CHO, -COOH, -COOR$, etc.

For example, in $-M$ effect the π-electron displacement takes place towards such groups ($-NO_2$, $-CHO$, $-COOH$). So, electrophile attacks at the *m*-position in nitrobenzene (See **section 16.12**). Thus, $-M$ effect deactivates benzene nucleus for S_E but activates for S_N reaction.

Salient Features of Mesomeric Effect

(i) π-electrons and lone pair of electrons are involved. This effect operates through conjugative mechanism.

(ii) It is a permanent effect present in the molecule in the ground state.

(iii) It affects the physical properties such as dipole moment, solubility, etc. Rate of reaction of the substance is also affected.

(iv) It is denoted by M. Groups which have the capacity to increase the electron density of the rest of the molecule are said to have $+M$ effect. Such groups possess lone pairs of electrons. Groups which decrease the electron density of the rest of the molecule by withdrawing electron pairs are said to have $-M$ effect, *e.g.*,

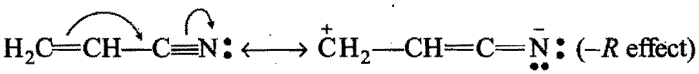
(a) The groups which donate electrons to the double bond or to a conjugated system are said to have **+M effect** or **+R effect.** For example,

$H_2C{=}CH{-}\ddot{Cl}: \longleftrightarrow \bar{C}H_2{-}CH{=}\overset{+}{Cl}:$ (+*R* effect)

Vinyl chloride

In vinyl chloride, C—Cl bond has double bond character due to resonance.

(b) The groups which withdraw electrons from the double bond or from a conjugated system towards itself due to resonance are said to have **–*M* effect** or **–*R* effect.** For example,



$H_2C{=}CH{-}C{\equiv}\ddot{N}: \longleftrightarrow \overset{+}{C}H_2{-}CH{=}C{=}\overset{-}{\ddot{N}}:$ (–*R* effect)

Vinyl cyanide

Similarities between Inductive and Mesomeric Effects

(i) Both are permanent effects.

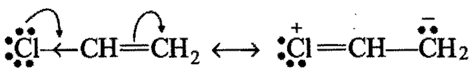
(ii) Both affect the physical properties of the molecule.

(iii) Both can either hinder or facilitate a particular reaction. Both affect the rates of reaction, the strength of acids and bases, the reactivity of halides and the substitution of different aromatic species.

The two effects differ in the following points:

Inductive effect	Mesomeric effect
1. It is operative in saturated compounds.	1. It is operative in unsaturated compounds especially having conjugated systems.
2. It involves electrons of sigma bonds.	2. It involves electrons of π-bonds or lone pair of electrons.
3. The electron pair is slightly displaced from its position and thus partial charges are developed.	3. The electron pair is completely transferred and thus full positive and negative charges are developed.
4. It is transmitted over a quite short distance. The effect becomes negligible after second carbon atom in the chain.	4. It is transmitted from one end to other end of the chain provided conjugation is present.

The inductive and mesomeric effects, when present together, may act in the same direction or oppose each other. The mesomeric effect is more powerful than the former. For example, in vinyl chloride due to –*I* effect the chlorine atom should develop a negative charge but on account of mesomeric effect it has positive charge.



$:\ddot{\underset{..}{Cl}}{-}CH{=}CH_2 \longleftrightarrow :\overset{+}{\underset{..}{Cl}}{=}CH{-}\overset{-}{\ddot{C}}H_2$

4. Hyperconjugation : The inductive effect (+*I*) of the alkyl group follows the order of tertiary > secondary > primary > methyl. But the effect has been found in reverse order when an unsaturated system ($>C{=}C<$) is attached with the alkyl group. In such cases, alkyl group is electron releasing but different from inductive effect and the magnitude of the two effects changes in opposite direction in passing along a series of alkyl groups.

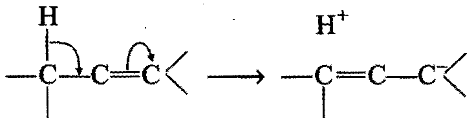
$$\underset{\text{Decreasing hyperconjugation}}{\overset{\text{Increasing inductive effect}}{\xrightarrow{\hspace{8cm}}}}$$

CH_3—, CH_3CH_2—, $(CH_3)_2CH$—, $(CH_3)_3C$—

Increasing inductive effect

Decreasing hyperconjugation

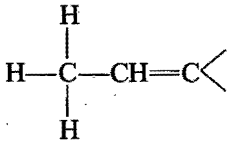
Baker and Nathan suggested that alkyl groups with atleast one hydrogen atom on the α-carbon atom, attached to an unsaturated carbon atom, (*i.e.*, having $>C{=}C<$) or positive charge (as in carbonium ion) or a negative charge (as in carbanion) or odd electrons (as in free radical, etc.) are able to release electrons by a mechanism similar to that of electromeric effect, *e.g.*,



$-\overset{H}{\underset{|}{C}}{-}C{=}C< \;\longrightarrow\; -\overset{H^+}{\underset{|}{C}}{=}C{-}\bar{C}<$

This type of electron release by alkyl group attached to the unsaturated system (H—C—C=C) is known as **hyperconjugation** (involving delocalization of σ and π-bond orbitals, *i.e.*, **σ- π conjugation**) or the kind of delocalization involving sigma bond orbital is called **hyperconjugation.**

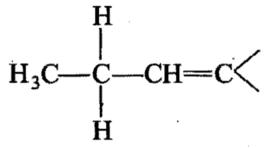
There should be atleast one H-atom at α-carbon with respect to sp^2-hybrid carbon (C=C) and greater the number of C—H bonds at α-carbon to the unsaturated system, greater will be the electron release and thus greater the hyperconjugation effect. Thus, electron release due to the presence of three alpha H—C bonds in methyl group is greater than that by an ethyl group (CH_3CH_2—) in which there are only two alpha H—C bonds. Similarly, the effect is still smaller in case of isopropyl group $(CH_3)_2CH$— having only one alpha H—C bond and the effect is zero in *tert.* butyl as it has no hyperconjugated H—C bond.



$H{-}\overset{H}{\underset{H}{C}}{-}CH{=}C<$

Methyl compound

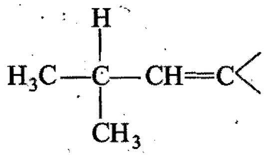
(Containing three H—C hyperconjugated bonds)



$H_3C{-}\overset{H}{\underset{H}{C}}{-}CH{=}C<$

Ethyl compound

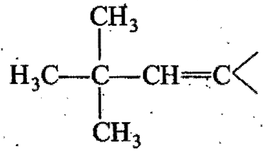
(Containing two H—C hyperconjugated bonds)



$H_3C{-}\overset{H}{\underset{CH_3}{C}}{-}CH{=}C<$

Iso-propyl compound

(Containing one H—C hyperconjugated bond)

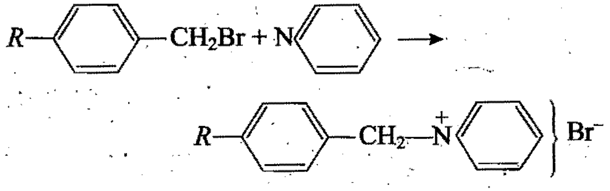


$H_3C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH{=}C<$

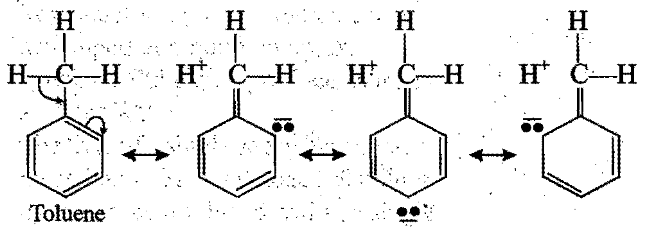
Tert. butyl compound

(Containing no H—C hyperconjugated bond)

The phenomenon of hyperconjugation, as originally observed by Baker and Nathan, that the rate of reaction of *p*-alkyl substituted benzyl bromide with pyridine was opposite to that expected from inductive electron release.



This was called as **Baker-Nathan effect** and they explained it by considering that hyperconjugative forms contribute to the actual structure of toluene.



Another example where the effect operates in the reverse direction:

$$Cl{-}C{-}C{=}C \longleftrightarrow Cl^{-}{-}C{=}C{-}C^{+}$$

Evidences for hyperconjugation

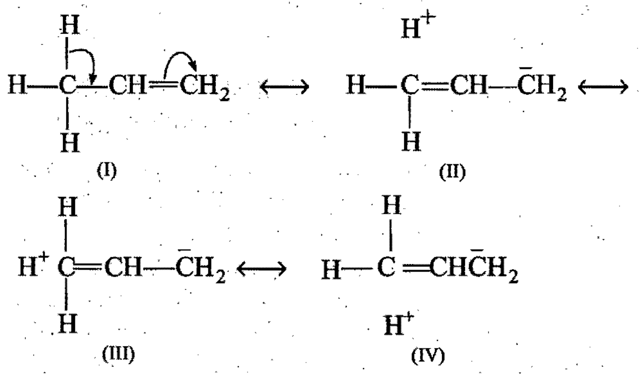
(i) Heat of hydrogenation : It is the heat evolved/mol in the addition of hydrogen to form a saturated hydrocarbon.

$$\rangle C{=}C\langle + H_2 \longrightarrow \rangle CH{-}CH\langle \;+ E\text{ (kcal)}$$

where E is the heat of hydrogenation.

Heats of hydrogenation show that greater the number of alkyl groups attached to the doubly bonded carbon atoms, greater is the stability (*i.e.*, lower is the heat of hydrogenation) of the alkene or lesser the heat of hydrogenation, lesser is the internal energy and more is stability of the system. Hyperconjugation decreases the heat of hydrogenation. For ethene it is 32.8 kcal/mol, for propene, 30.1 kcal/mol, *cis*-but-2-ene is 28.6 kcal/mol, *trans*-but-2-ene is 27.6 kcal/mol, 2-methyl but-2-ene is 26.9 kcal/mol and so on. *Trans*-but-2-ene is, however, more stable than *cis*-but-2-ene in which the two methyl groups are closed together and hence their electronic clouds repel each other.

(ii) Stability of alkenes : Propene may be regarded as the resonance hybrid of the following structures:



In the resonating structures II, III and IV, there is no definite bond between one of the carbon atoms and one of the hydrogen atoms, hence hyperconjugation is also known as **No-Bond Resonance.**

So, propene is more stable than ethene, because in propene there are three H—C hyperconjugated bonds and none in ethene thus the σ electrons of C—H bonds can delocalize over three different II, III and IV resonating structures.

Further the more substituted alkenes are more stable; thus, larger the number of methyl groups linked to C—C double bond, more is the number of hyperconjugative C—H bonds and greater is the stability of alkene. So, the stability of alkenes is:

$$\underset{\substack{\text{2,3-Dimethyl but-2-ene}\\ \text{(I)}}}{(CH_3)_2C{=}C(CH_3)_2} > \underset{\substack{\text{2-Methyl but-2-ene}\\ \text{(II)}}}{(CH_3)_2C{=}CHCH_3} > \underset{\substack{\text{2-Methyl propene}\\ \text{(III)}}}{(CH_3)_2C{=}CH_2} >$$

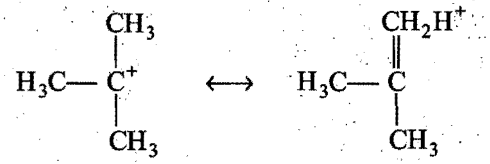
$$\underset{\substack{\text{But-1-ene}\\ \text{(IV)}}}{CH_3CH_2CH{=}CH_2} > \underset{\substack{\text{Propene}\\ \text{(V)}}}{CH_3CH{=}CH_2}$$

This order of stability is because of greater number of contributing structures, causing larger delocalization and hence stability of alkenes. For example, alkene (I) has 12α-hydrogen atoms while alkene (II) has 9α-hydrogen atoms and so on. Therefore, there will be larger hyperconjugation in alkene (I) and will be more stable than alkene (II).

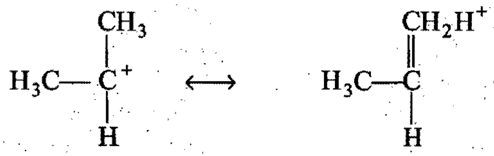
(iii) Stability of carbocations :

Tert. alkyl > *Sec.* alkyl > *Pri.* alkyl > Methyl

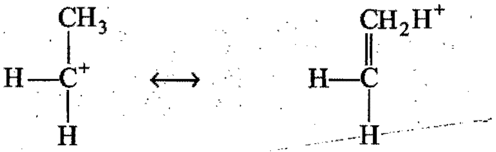
In general, the greater the number of H-atoms present on the carbon atoms α- to unsaturation, the more resonating forms are possible due to hyperconjugation and thus greater is the stability of carbocation.



Tertiary carbocation (9-equivalent forms)



Secondary carbocation (6-equivalent forms)



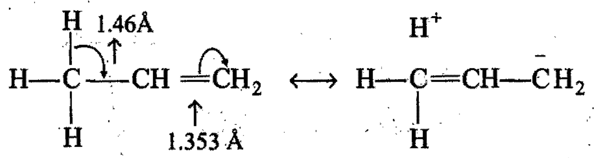
Primary carbocation (3-equivalent forms)

(iv) Stability of alkyl free radicals : In the same order

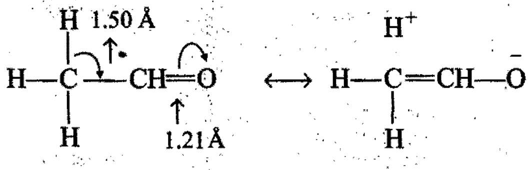
$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$, *i.e.*, more the number of hyperconjugative structures, the greater is its stability.

But in methyl carbonium ion ($\overset{+}{C}H_3$), the carbon is even more electron deficient than that in a radical (with seven electrons), hence, stability of alkyl carbonium ions due to **hyperconjugation** is greater than that of radicals.

(v) Bond lengths (Shortening of C—C single bonds adjacent to multiple bonds): Hyperconjugation, like conjugation and resonance, also affects bond length, *e.g.*, the $H_3C{-}C$ bond length in propene is 1.46 Å in contrast to normal 1.54 Å (in propane). It is due to the partial double bond character acquired and hence a little shorter. Similarly, the C=C bond length is 1.353 Å as compared to 1.334 Å due to partial single bond character acquired.

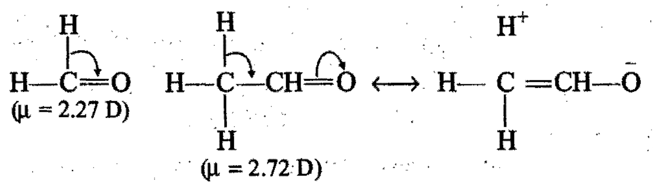


Similarly, hyperconjugation accounts for shortening of C—C bond in acetaldehyde.

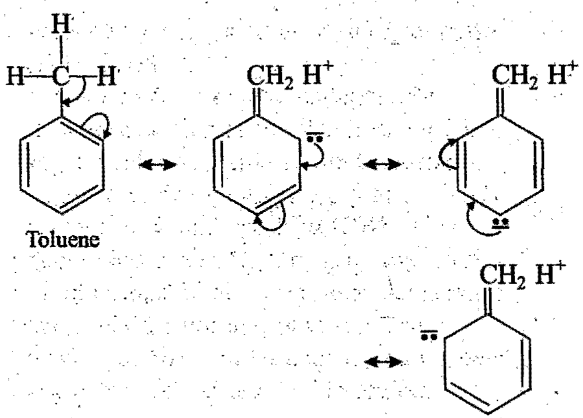


(vi) Dipole moment : Since, hyperconjugation causes the development of charges, it also affects the dipole moment in the molecule.

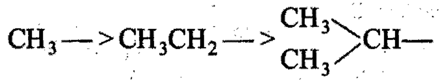
The increase in dipole moment, when hydrogen of formaldehyde ($\mu = 2.27$ D) is replaced by methyl group, *i.e.*, acetaldehyde ($\mu = 2.72$ D) can be referred to hyperconjugation, which leads to development of charges.



(vii) Orienting influence of alkyl group in *o, p*- positions and of $—CCl_3$ group in *m*- position : *Ortho-, para-* directing property of methyl group in toluene is partly due to +*I* effect and partly due to hyperconjugation.



The electron donating power of alkyl group depends on the number of α-hydrogens of the alkyl group.



$$CH_3— > CH_3CH_2— > \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!> CH—$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Among the following which acid is strongest?
   (a) Acetic acid (b) Monochloro acetic acid
   (c) Dichloroacetic acid (d) Trichloroacetic acid
   [Ans. (d)]
   [Hint : Due to –*I* effect.]
2. Which of the following acid is strongest?
   (a) HCOOH (b) CH_3COOH
   (c) CH_3CH_2COOH (d) $CH_3CH_2CH_2COOH$
   [Ans. (a)]
   [Hint : Due to +*I* effect.]
3. Which of the following groups has highest inductive effect?
   (a) $CH_3—$ (b) $CH_3CH_2—$
   (c) $(CH_3)_2CH—$ (d) $(CH_3)_3C—$
   [Ans. (d)]
4. Considering the following alkenes:
   $CH_3CH_2CH{=}CH_2$, But-1-ene (I); $(CH_3)_2C{=}C(CH_3)_2$, 2,3-Dimethyl but-2-ene (II)
   $(CH_3)_2C{=}CHCH_3$, 2-Methyl but-2-ene (III); $(CH_3)_2C{=}CH_2$, 2-Methyl propene (IV)
   The correct decreasing order of stability is:
   (a) I > II > III > IV (b) II > III > IV > I
   (c) IV > III > II > I (d) III > IV > I > II
   [Ans. (b)]
   [Hint : More substituted alkene has the greater number of hyperconjugative C—H bonds and so greater is the stability of alkenes.]
5. The decreasing order of basic strength in
   $C_6H_5NH_2$ (I), $(C_6H_5)_2NH$ (II), CH_3NH_2 (III), NH_3 (IV) is:
   (a) IV > III > II > I (b) I > II > III > IV
   (c) III > IV > I > II (d) II > I > III > IV
   [Ans. (c)]
   [Hint : As compared to ammonia, methylamine is more basic (+*I* effect) but aniline is less basic and diphenylamine is still more weaker (–*I* effect).]

5.3 FISSION OR CLEAVAGE OR BREAKING OF A COVALENT BOND

Organic compounds are mostly made up of covalent bonds. A covalent bond consists of a pair of electrons which is being shared by two atoms. It can be represented as $A{:}B$. Organic reactions invariably involve fission or breaking of covalent bonds. When the two atoms joined by a covalent bond are separated, the process is termed **fission** or **cleavage of bond.** The fission or cleavage or breaking of a covalent bond can take place in two ways depending upon the nature of the given compound, the nature of attacking reagent and the reaction conditions.

(i) Homolytic fission or homolysis,
(ii) Heterolytic fission or heterolysis.

(i) Homolytic fission : This involves the breaking of a covalent bond in such a way that each atom separates with one electron of the shared pair, *i.e.*, each atom acquires its initial configuration.

$$A{:}B \longrightarrow A^{\bullet} + {}^{\bullet}B$$
$$Cl{:}Cl \longrightarrow Cl^{\bullet} + {}^{\bullet}Cl$$
$$H{:}H \longrightarrow H^{\bullet} + {}^{\bullet}H$$
$$H_3C{:}H \longrightarrow H_3C^{\bullet} + {}^{\bullet}H$$

Such atoms or fragments are electrically neutral and have one or more unpaired electron. These atoms or fragments are called **free radicals.** So, free radicals may be defined as "atoms or group of atoms having unpaired electron and obtained by the homolytic fission of a covalent bond."

Bond dissociation energy for some bonds in alkane are tabulated below:

Bond Dissociation Energies for Some Alkanes

Compound	*DH*° (kcal mol^{-1})	Compound	*DH*° (kcal mol^{-1})
$CH_3—H$	105	$C_2H_5{+}CH_3$	89
$C_2H_5—H$	101	$C_2H_5{+}C_2H_5$	88
$C_3H_7—H$	101	$(CH_3)_2CH{+}CH_3$	88
$(CH_3)_2CHCH_2—H$	101	$(CH_3)_3C{+}CH_3$	87
$(CH_3)_2CH—H$	98.5	$(CH_3)_2CH{+}CH(CH_3)_2$	85.5
$(CH_3)_3C—H$	96.5	$(CH_3)_3C{+}C(CH_3)_3$	78.5
$CH_3—CH_3$	90		

Bond dissociation energy of various *A*—*B* bonds in kcal mol^{-1} are given below :

	B* in *A*—*B						
A* in *A*—*B	**—H**	**—F**	**—Cl**	**—Br**	**—I**	**—OH**	**—NH_2**
H—	104	136	103	87	71	119	108
CH_3—	105	110	85	70	57	93	84
CH_3CH_2—	101	111	84	70	56	94	85
$CH_3CH_2CH_2$—	101	110	85	70	56	92	84
$(CH_3)_2CH$—	98.5	111	84	71	56	96	86
$(CH_3)_3C$—	96.5	110	85	71	55	96	85

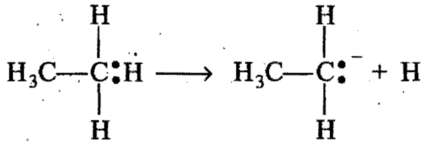
Such a fission usually occurs in non-polar bonds when both the atoms linked by the covalent bond have nearly the same electronegativity. Homolytic fission is most common mode of fission in vapour phase and generally initiated by high temperature, ultraviolet (UV) radiations and by the presence of organic peroxides or catalysts.

(ii) Heterolytic fission : This involves the breaking of a covalent bond in such a way that both the electrons of the shared pair are carried away by one of the atoms. This type of fission occurs when the two atoms differ considerably in their electronegativities. The electron pair is carried away by the atom which is more electronegative in comparison to other.

$$A{:}B \longrightarrow \overset{-}{A}{:} + \overset{+}{B} \quad [A \text{ is more electronegative than } B]$$
$$A{:}B \longrightarrow \overset{+}{A} + {:}\overset{-}{B} \quad [B \text{ is more electronegative than } A]$$

Heterolytic fission leads to the formation of charged or ionic species, one having a positive charge and other a negative charge. This type of fission occurs most readily in polar covalent bonds and is favoured by polar solvents like water or alcohol and is influenced by the presence of ions due to acid and base catalyst. Quite often the ionic species formed by heterolytic fission bear the positive or negative charge on carbon atom. Such ionic species are known as carbocations or carbanions according to the charge which the carbon atom carries (positive or negative).

$$CH_3{:}Cl \longrightarrow \underset{\text{Carbocation}}{H_3C^+} + {:}\overset{-}{Cl}$$



$$H_3C—CH_2{:}H \longrightarrow H_3C—CH_2{:}^- + H^+$$

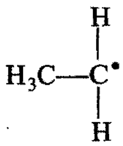
Carbanion

5.4 REACTION INTERMEDIATES

Short lived (10^{-6} seconds to a few seconds) and highly reactive fragments called reaction intermediates result from homolytic and heterolytic bond fission. The important reaction intermediates are free radicals, carbocations, carbanions, carbenes, nitrenes and benzyne.

(i) Free radicals : A free radical may be defined as an atom or group of atoms having an odd or unpaired electron. These result on account of homolytic fission of a covalent bond and are denoted by putting a dot (•) against the symbol of atom or group of atoms.

$Cl^{\bullet}$ Chlorine free radical ; $H^{\bullet}$ Hydrogen free radical ; $H_3C^{\bullet}$ Methyl free radical ;



$H_3C—CH_2^{\bullet}$

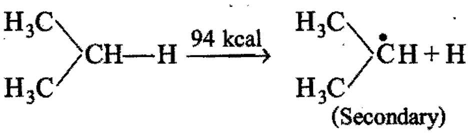
Ethyl free radical

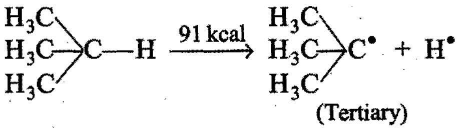
The formation of free radical is initiated by heat, light or catalysts.

(a) $Cl\!:\!Cl \xrightarrow[\text{sunlight}]{\text{Energy}} Cl^{\bullet} + Cl^{\bullet}$

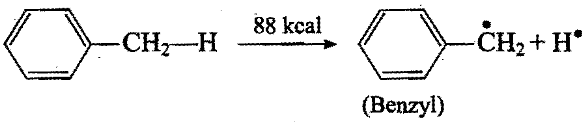
(b) $H_3C\!:\!H \xrightarrow{\text{102 kcal}} H_3C^{\bullet} + H^{\bullet}$

(c) $H_3C—CH_2—H \xrightarrow{\text{97 kcal}} H_3C—\dot{C}H_2 + H^{\bullet}$ (Primary)

(d)


(e)


(f) $H_2C{=}CH—CH_2—H \xrightarrow{\text{86 kcal}} H_2C{=}CH—\dot{C}H_2 + H^{\bullet}$ (Allyl)

(g)


(h) $CH_3—NH_2 \xrightarrow{\text{Heat/light}} \dot{C}H_3 + \dot{N}H_2$

Chemical reaction which takes place in the presence of **HELPR** [H : Heat (≥ 500°C), E : Electricity, L : Light (sun light, *hv*), P : Peroxide, R : Radical] is known as free radical reaction.

Characteristics of Free Radicals

(i) Free radicals are generally electrically neutral.

(ii) They are highly unstable.

(iii) They are short-lived and highly reactive on account of the presence of odd electrons. They readily try to pair up the odd electrons. Three types of reactions are observed in free radicals.

(a) The mutual combination of free radicals forms neutral molecules.

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2\ (Cl\!:\!Cl)$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3\!:\!CH_3\ \text{(Ethane)}$$

(b) The reaction between free radical and a neutral molecule gives a new radical.

$$CH_4 + Cl^{\bullet} \longrightarrow \dot{C}H_3 + HCl$$

(c) A free radical can lose a neutral molecule to form a new radical.

$$\underset{\text{Acetate radical}}{CH_3COO^{\bullet}} \longrightarrow \underset{\text{Methyl radical}}{\dot{C}H_3} + CO_2$$

(iv) Free radicals are paramagnetic in nature.

(v) Free radicals are generally formed either in presence of UV/visible light or in presence of peroxides.

Reactions Involving Free Radicals

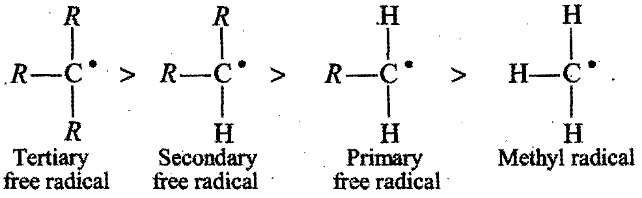
(i) Wurtz reaction giving alkanes.

(ii) Substitution reactions of alkanes.

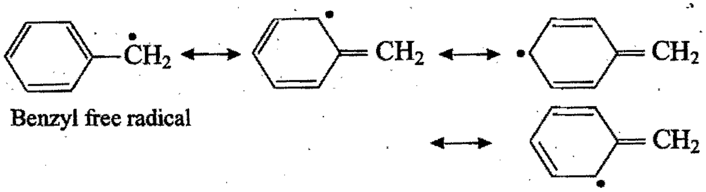
(iii) Kolbe's electrolytic reaction giving alkanes, alkenes and alkynes.

(iv) Anti-Markownikoff's addition or peroxide effect or Kharasch effect.

Relative stabilities of free radicals : The tertiary alkyl free radicals are most stable and methyl free radical is least stable, *i.e.*, the free radical formed easily has greater stability.



Benzyl and allyl free radicals are resonance stabilized hence are more stable than alkyl free radicals.

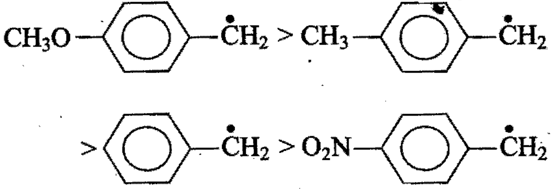

Benzyl free radical

$$CH_2{=}CH—\dot{C}H_2 \longleftrightarrow \dot{C}H_2—CH{=}CH_2\ \text{(Allyl)}$$

Relative stability of free radicals are:

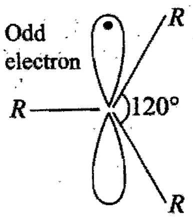
(i) 3° > Benzyl > allyl > 2° > 1° > methyl > vinyl

(ii) $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > (CH_3)_3\dot{C} > C_6H_5\dot{C}H_2 > CH_2{=}CH—\dot{C}H_2 > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3 > HC{\equiv}\dot{C}$

(iii)


The stability of various free radicals can be compared from their bond dissociation energies (the energy required for the homolytic cleavage of the covalent bond in the molecule to form two radicals). In general, the smaller the amount of energy required for bond breaking, the more stable is the radical.

Structure of alkyl free radicals: The carbon atom of alkyl free radicals which is bonded to only three atoms or groups of atoms is sp^2-hybridized. Thus, free radicals have a planar structure with odd electron situated in the unused p-orbital at right angles to the plane of hybrid orbitals.



However, in the substituted alkyl radicals the '*s*' character of these orbitals has been found to increase, thus, tending to the pyramidal shape.

$$\dot{C}H_3 < \dot{C}H_2F < \dot{C}HF_2 < \dot{C}F_3$$

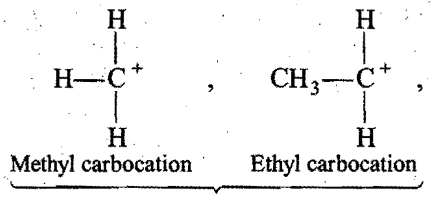
So, CF_3 is essentially pyramidal in shape.

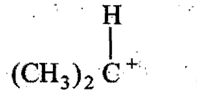
(ii) Carbocations (Carbonium ions) : When a covalent bond, in which carbon is linked to a more electronegative atom or group, breaks up by heterolytic fission, the more electronegative atom takes away the electron pair while carbon loses its electron and thus acquires a positive charge.

Such organic ions carrying a positive charge on carbon atom are known as carbocations or carbonium ions.

Carbocation

Carbocations are named by adding the words 'carbocation' to the parent alkyl group. These are also termed as primary, secondary, tertiary, depending upon the nature of the carbon atom bearing positive charge.





$$(CH_3)_2\overset{+}{C}H$$

Isopropyl carbocation (Secondary)

$(CH_3)_3C^+$ *Tert.* butyl carbocation (Tertiary)

Formation of Carbocations

(a) By heterolysis : They are formed by heterolysis of halogen compounds.

$$(CH_3)_3C\overset{\curvearrowright}{-}Cl \longrightarrow (CH_3)_3\overset{+}{C} + \overset{-}{Cl}$$

(b) By protonation of alkenes or alcohols :

$$H_2C{=}CH_2 \xrightleftharpoons{H^+} \overset{+}{C}H_2{-}CH_3$$

$$R{-}O{-}H \xrightleftharpoons{H^+} R{-}\overset{+}{O}H_2 \xrightleftharpoons{-H_2O} R^+ + H_2O$$

(c) By decomposition of diazo compounds :

$$C_6H_5{-}N_2{-}Cl \xrightarrow{-Cl} C_6H_5\overset{+}{N}_2 \xrightarrow{-N_2} \overset{+}{C}_6H_5 + N_2$$

Characteristics of Carbocation

(a) Carbon atom carrying positive charge has six electrons in its valence shell, *i.e.*, 2 electrons less than octet.

(b) The positively charged carbon atom in the carbocation is in sp^2 state of hybridization (trigonal planar). The three hybridized orbitals which lie in the same plane are involved in the formation of three σ- bonds with other atoms or groups while the unhybridized p-orbital remains vacant. The carbocation has a **planar structure.**

Reactions Involving Carbocations

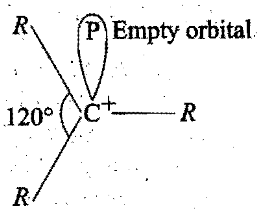
(i) Elimination reactions (E_1) to form alkenes from alkyl halides and alcohols.

(ii) Electrophilic addition reaction of alkenes, alkynes and alkadienes.

(iii) S_N1 reactions of alkyl halides and diazonium salts.

(iv) Molecular pinacol-pinacolone rearrangement.

Structure of Carbocations



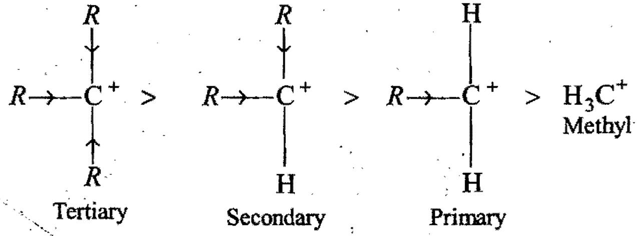
The only difference from free radicals which have odd electron.

Carbocations are very reactive as they have a carbon atom having a vacant p-orbital (6 electrons in valence shell). The positively charged carbon atom tries to complete its octet and hence, these ions react readily with those species which can release two electrons for the formation of fourth bond, *i.e.*, they react with nucleophilic reagents.

Usually the order of reactivity of any chemical species is reverse to that of its stability. Therefore, the order of reactivity of ions is:

Primary (1°) > Secondary (2°) > Tertiary (3°)

Stability : The stability of alkyl carbocations is influenced by resonance, hyperconjugation and inductive effects. An alkyl group has an electron releasing inductive effect. An alkyl group attached to the positively charged carbon of a carbocation tends to release electrons towards that carbon. In doing so it reduces positive charge on the carbon. In other words, the positive charge gets dispersed as the alkyl group becomes somewhat positively charged itself. **This dispersal of the charge stabilizes the carbocation.** More the number of alkyl groups, the greater the dispersal of positive charge and, therefore, more the stability of carbocation is observed.



Stability decreases as +*I* decreases (dispersal of positive charge decreases).

$$CH_3CH_2CH_2\overset{+}{C}H_2 > CH_3CH_2\overset{+}{C}H_2 > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

Stability decreases as molecular mass decreases or +*I* effect decreases.

If α-hydrogen with respect to carbocationic carbon has one or more than one lone pair of electrons, then lone pair of electrons strongely stabilises a carbocation due to the delocalization.

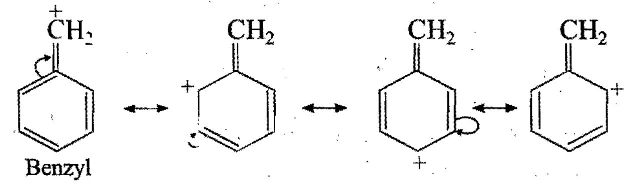
Amino ($-NH_2$) and alkoxy ($-OR$) groups are important substituents for such type of carbocations.

$$(CH_3)_2\ddot{N}-\overset{+}{C}H_2 \text{ and } CH_3-\ddot{O}-\overset{+}{C}H_2 \text{ are more stable}$$

than $R_3-\overset{+}{C}$.

Allyl and benzyl carbocations are much more stable as these are stabilized by resonance, while propylium ($CH_3CH_2\overset{+}{C}H_2$) ion has no resonance.

$$H_2C=CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH_2 \text{ (Allyl)}$$



Benzyl carbocation

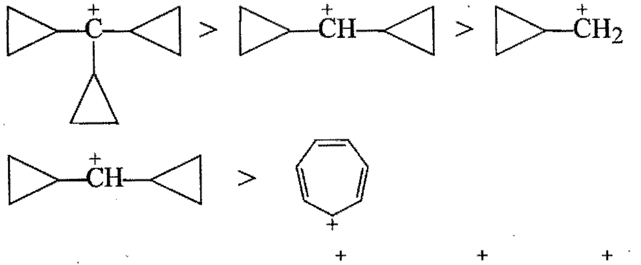
Allyl and benzyl carbocations are conjugated species, hence their stability can be compared by the number of resonating structures.

$H_2C=CH-\overset{+}{C}H_2$ (Allyl has two resonating structures)

$C_6H_5\overset{+}{C}H_2$ (Benzyl has four resonating structures)

So, benzyl carbocation is more stable than the allyl carbocation. But experimentally it has been found that the stabilities of both carbocations is almost same.

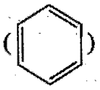
Cyclopropyl methyl carbocations are more stable than benzyl carbocations and their stability increases with an additional cyclopropyl group. Thus, decreasing order of stability is:



$$> (C_6H_5)_3\overset{+}{C} > (C_6H_5)_2\overset{+}{C}H > C_6H_5\overset{+}{C}H_2$$

Note : Stability of benzyl, allyl and tertiary alkyl carbocations are almost same in solutions. The order of stability of different compounds in decreasing order is as follows:

Aromatic compounds > Conjugated non-aromatic compounds >

() ($H_2C=CH-CH=CH-CH=CH_2$)

non-conjugated compounds > antiaromatic compounds ($H_2C=CH-CH_2-CH=CH_2$)

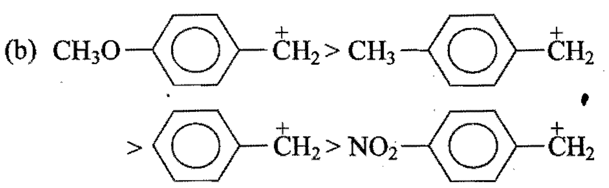
Relative stability of carbocations are:

(a) Triphenyl > 3° > benzyl > allyl > 2° > 1° > methyl

$$(C_6H_5)_3\overset{+}{C} > (C_6H_5)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C} > C_6H_5\overset{+}{C}H_2$$

$$> CH_2=CH-\overset{+}{C}H_2 > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

$$> H_2C=\overset{+}{C}H > HC\equiv\overset{+}{C} > \overset{+}{C}_6H_5$$

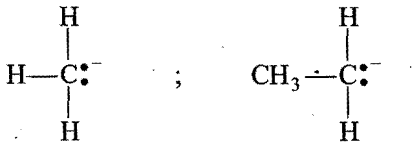
(b) 

The groups like $-NO_2$, $-CN$ and $-Br$ (electron attracting) which have $-I$ effect reduce the stability of carbocations.

(iii) Carbanions: When a covalent bond, in which carbon is attached to a lesser electronegative atom, breaks up by heterolysis the atom leaves without taking away the bonding pair of electrons and thus the carbon atom acquires a negative charge due to an extra electron.

$$>C:Y \longrightarrow \underset{\text{Carbanion}}{>\overset{-}{C}:} + \overset{+}{Y}$$

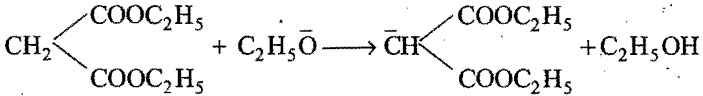
Such organic ions which contain a negatively charged carbon atom are called carbanions. These are named after the parent alkyl group and adding the word carbanion.



Methyl carbanion ; Ethyl carbanion

These are also termed as primary, secondary and tertiary depending on the nature of carbon atom bearing the negative charge.

Organic compounds which possess a labile or acidic hydrogen have the tendency to produce carbanions as in the case of reactive methylene compounds which lose proton in presence of sodium ethoxide (C_2H_5ONa).



Malonic ester

Characteristics of Carbanions

(a) The carbon carrying the negative charge contains 8 electrons in the valence shell, *i.e.*, complete octet.

(b) They are highly reactive because in them the carbon carrying the negative charge is electron rich and can donate its non-bonding pair of electrons to some other group for sharing. Hence, carbanions behave as nucleophiles and readily attacked by electrophiles.

(c) The negatively charged carbon is in a state of sp^3-hybridization. The hybrid orbitals are directed towards the corners of a tetrahedron. Three of hybrid orbitals are involved in the formation of single covalent bonds with other atoms while the fourth hybrid orbital contains a lone pair of electrons. Thus, carbanions have a **pyramidal structure** similar to NH_3 molecule.

(d) Carbanions are diamagnetic.

Reactions Involving Carbanions

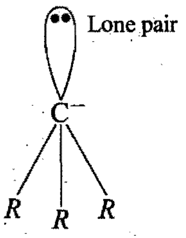
(i) Aldol condensation of aldehydes having α-H atoms.

(ii) Cannizzaro's reaction of aldehydes without α-H atoms.

(iii) Perkin's reaction involves the formation of carbanions as intermediate.

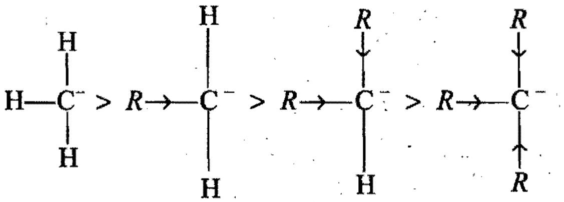
(iv) Knoevenagel reaction involves the formation of carbanions as intermediate.

Structure of Carbanions :



(Pyramidal shape)

Stability : The stability of carbanions is influenced by resonance, inductive effect and *s*-character of orbitals. The groups having +*I* effect decrease the stability while groups having −*I* effect increase the stability of carbanions.



$$\mathrm{H{-}\overset{H}{\underset{H}{C^-}}} > R\rightarrow\overset{H}{\underset{H}{C^-}} > R\rightarrow\overset{\overset{R}{\downarrow}}{\underset{H}{C^-}} > R\rightarrow\overset{\overset{R}{\downarrow}}{\underset{\underset{R}{\uparrow}}{C^-}}$$

Stability decreases as + *I* effect increases
(Methyl > 1° > 2° > 3° carbanion)

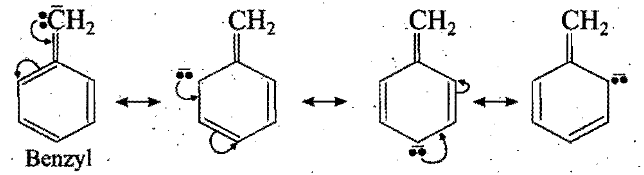
So, this order of stability can be explained on the basis of electron releasing inductive effect (+*I*) of the alkyl groups. Greater the number of alkyl groups on the carbon atom carrying the negative charge, greater would be the intensity on the negative charge on carbon and hence, less stable would be the carbanion. Primary (1°) carbanion with only one alkyl group is maximum stable, followed by secondary (2°) with two alkyl groups and tertiary (3°) with three alkyl groups.

The groups having +*I* effect decrease the stability while groups having −*I* effect increase the stability of carbanions.

Order of reactivity of carbanions is reverse the order of stability, *i.e.*, 3° > 2° > 1°

Allyl and benzyl carbanions are stabilized due to resonance.

$$H_2C{=}CH{-}\bar{C}H_2 \longleftrightarrow \bar{C}H_2{-}CH{=}CH_2 \quad \text{(Allyl)}$$



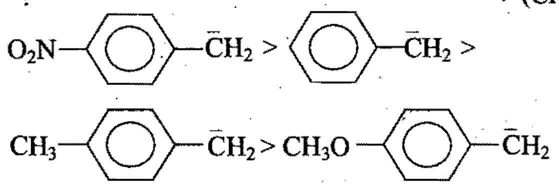
Benzyl carbanion

Relative stability of carbanions are:

Aromatic > benzyl > allyl > $HC\equiv\bar{C} > H_2C{=}\bar{C}H >$ alkyl (*p*- > *sec*- > *tert*-).

(i) $(C_6H_5)_3\bar{C} > (C_6H_5)_2\bar{C}H > C_6H_5\bar{C}H_2 > CH_2{=}CH{-}\bar{C}H_2 > HC\equiv\bar{C} > H_2C{=}\bar{C}H > \bar{C}H_3 > CH_3\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

(ii)



Stability of carbanion increases with increase in *s*-character of orbitals.

$$\underset{50\%\ s\text{-character}}{R{-}C\equiv\bar{C}} > \underset{33\%\ s\text{-character}}{R_2C{=}\bar{C}H} > \underset{25\%\ s\text{-character}}{R_3C{-}\bar{C}H_2}$$

The groups like $-NO_2$, $-CN$, $-COOC_2H_5$, $>C{=}O$, halogens and C_6H_5-(electron attracting) increase the stability of carbanions.

Difference between Free Radicals and Ions (Carbocations and Carbanions)

	Free radicals	Ions
1. Nature	Neutral in nature Examples: $\dot{C}H_3$, $\dot{C}l$, $CH_3{-}\dot{C}H_2$ etc.	Carry either positive or negative charge. Examples: $\overset{+}{C}H_3$, $:\bar{C}H_3$, $:\bar{C}l$, etc.
2. Configuration	One unpaired electron is present in valence shell.	Paired electrons are present in the valence shell. Carbocations—The carbon carrying positive charge has six valence electrons. Carbanions—The carbon carrying negative charge has eight electrons.
3. Magnetic nature	Paramagnetic	Diamagnetic.
4. Formation	Homolytic fission	Heterolytic fission.

(iv) Carbenes : The carbenes $:CH_2$ (or **methylene**) are highly reactive, short-lived, diagonal in geometry and neutral species in which carbon atom has six electrons in the outer shell (electron deficient), out of which two constitute a lone pair and two are shared. So, they are divalent carbon species containing two unpaired electrons and possess no charge.

Thus, in short, carbenes are sp^2 as well as sp-hybridized, neutral, transitory reaction intermediate containing a carbon atom with two bonds and two electrons. They can be formed:

(A) By the photochemical decomposition or pyrolysis of aliphatic diazo compounds or ketenes.

$$(i)\quad \underset{\text{Diazo methane}}{CH_2N_2} \xrightarrow[\text{(UV)}]{h\nu \text{ or Heat}} \underset{\text{Carbene}}{:CH_2} + N_2$$

$$R{-}CHN_2 \xrightarrow{h\nu \text{ or Heat}} \underset{\text{Alkyl carbene}}{RCH:} + N_2$$

$$RCO{-}CHN_2 \xrightarrow{h\nu \text{ or Heat}} \underset{\text{Acyl carbene}}{RCO{-}CH:} + N_2$$

Substituted carbenes are simply named as derivative of carbenes. For example:

$$\underset{\text{Dialkyl carbene}}{R{-}\overset{\bullet\bullet}{C}{-}R} \qquad \underset{\text{Phenyl carbene}}{C_6H_5{-}\overset{\bullet\bullet}{C}H} \qquad \underset{\text{Dichloro carbene}}{:CCl_2}$$

$$(ii)\quad \underset{\text{Ketene}}{H_2C{=}C{=}O} \longrightarrow \underset{\text{Carbene}}{:CH_2} + CO$$

(B) By the action of a base on suitable polyhalogen compound.

$$(i)\quad \underset{\text{Chloroform}}{CHCl_3} + C_2H_5ONa \longrightarrow \underset{\text{Dichlorocarbene}}{:CCl_2} + C_2H_5OH + NaCl$$

$$(ii)\quad CHCl_3 + \underset{\textit{Tert.}\text{ butoxide ion}}{(CH_3)_3CO^-} \rightleftharpoons (CH_3)_3C{-}OH + :CCl_3 \longrightarrow :CCl_2 + Cl^-$$

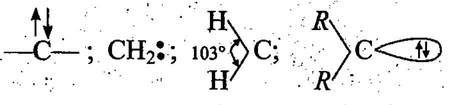
$$CHX_3 \xrightarrow[\Delta]{\text{KOH (alc.)}} \overset{-}{C}X_3 + H^+$$

$$\overset{-}{C}X_3 \longrightarrow :CX_2 + X^-$$

So, carbenes are related to carbanions through the α-elimination reaction.

sp^2-hybrid carbene is of two types:

(a) Singlet : When both the electrons go into one orbital and have opposite spin (antiparallel), *i.e.*, the unshared electrons are paired in one orbital and has a **bent** structure.

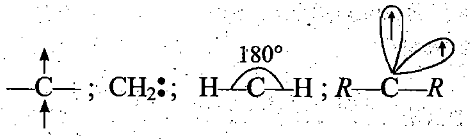


The singlet state is actually found to have H—C—H bond angle 103° (between 90° to 120°) and a C—H bond length of 1.12 Å. It is generally considered as the less stable and highly reactive. It is also known as **hot methylene.**

Singlet state has single spin multiplicity.

Spin multiplicity = $(2\Sigma s + 1) = 2 \times \{(+½) + (-½)\} + 1 = 1$

(b) Triplet : When the two electrons go into different orbitals and have same spin (parallel), *i.e.*, the unshared electrons are not paired. Such carbene would have a permanent magnetic moment and would exist in three closely grouped energy state, if it were placed in a magnetic field. Such a state is called **triplet state** and is believed to be a **linear** molecule, so sp-hybrid carbene is always a triplet carbene,



With H—C—H bond angle 180° and a C—H bond length of 1.03 Å, it might be considered as a free diradical and is more stable. It is also known as **cold methylene** (carbene).

The decreasing order of stability of different types of singlet carbenes are as follows:

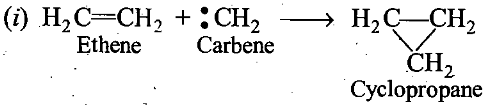
$$:CH_2 > :CF_2 > :CCl_2 > :CBr_2 > :Cl_2$$

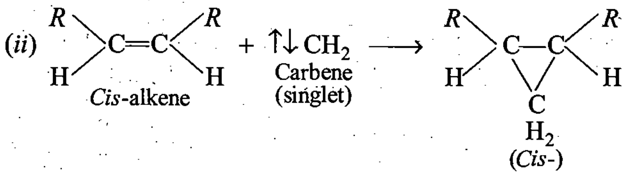
Triplet state has three spin multiplicity.

Spin multiplicity = $(2\Sigma s + 1) = 2\{(+½) + (+½)\} + 1 = 3$

Reactions : Carbenes undergo several important reactions.

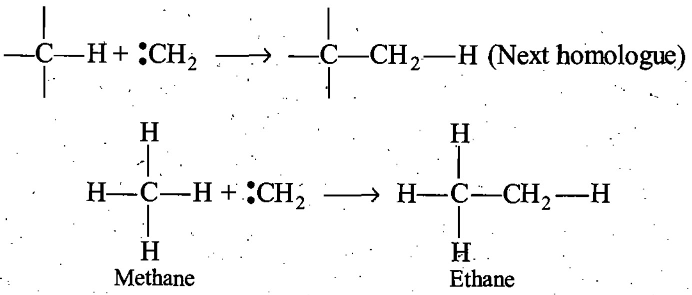
(a) Addition to alkenes : Formation of cycloalkane derivatives, *e.g.*,





Addition reaction of singlet carbenes with alkenes or alkynes is known as chelotropic addition.

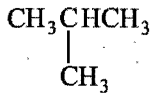
(b) Insertion reactions : Carbenes are also used in its insertion between the C—H bond, *e.g.*,



Further it can be inserted in all the possible positions (*pri.*, *sec.*, *tert.*).

$$\underset{\text{Propane}}{CH_3CH_2CH_2H} + :CH_2 \longrightarrow \underset{n\text{-butane}}{CH_3CH_2CH_2CH_3}$$

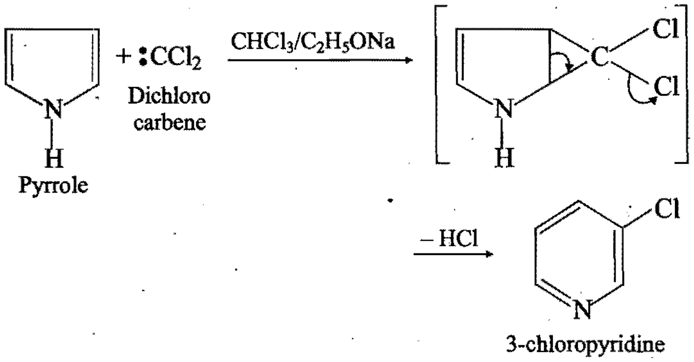
and



$$CH_3\underset{\underset{CH_3}{|}}{C}HCH_3$$

Iso-butane

(c) Ring expansion reactions : These involve the addition of a halogeno carbene across a double bond followed by rearrangement.



Carbenes have important synthetic applications and are the reactive intermediates in some well known reactions like Carbylamine reaction, Reimer-Tiemann reaction, Wittig reaction and Wolff rearrangement, etc.

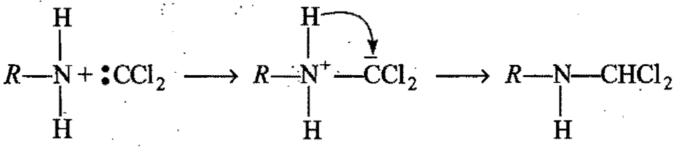
Carbenes as reaction intermediates:

(a) Carbylamine reaction : By heating a mixture of primary amine and chloroform with ethanolic potassium hydroxide to form isocyanide (carbylamine) is known as carbylamine reaction.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$$

Mechanism:

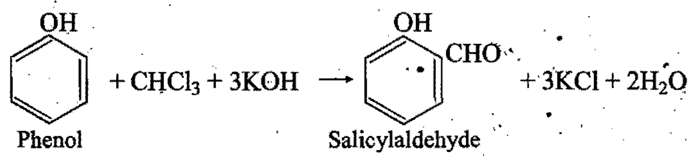
$$CHCl_3 \xrightarrow[(-H_2O)]{OH^-} :\bar{C}Cl_3 \longrightarrow \underset{\text{Dichlorocarbene}}{:CCl_2} + Cl^-$$



$$R-\overset{H}{\underset{H}{\overset{|}{\underset{|}{N}}}} + :CCl_2 \longrightarrow R-\overset{H}{\underset{H}{\overset{|}{\underset{|}{N^+}}}}-\bar{C}Cl_2 \longrightarrow R-\underset{H}{\underset{|}{N}}-CHCl_2$$

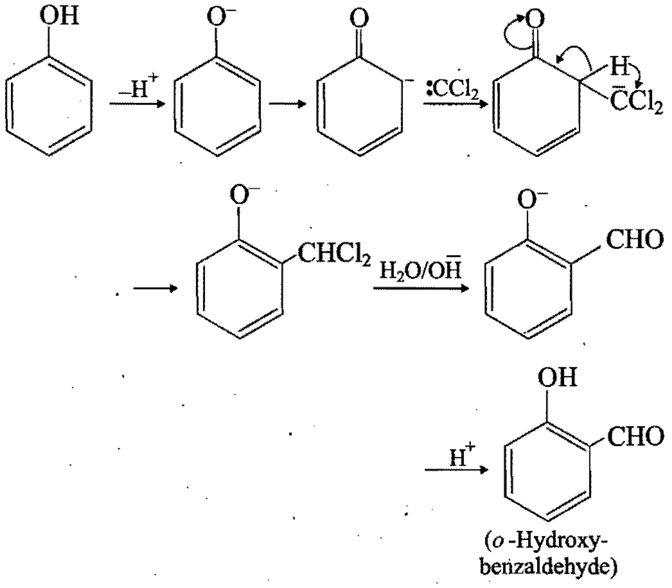
$$\xrightarrow{-HCl} R-N{=}CHCl \xrightarrow{-HCl} R-\overset{+}{N}{=}\overset{-}{C} \text{ (Alkyl isocyanide)}$$

(b) Reimer-Tiemann reaction : Phenol on heating with chloroform and aqueous alkali followed by acid hydrolysis to yield salicylaldehyde is known as Reimer-Tiemann reaction.



Mechanism:

$$CHCl_3 + OH^- \longrightarrow H_2O + :\bar{C}Cl_3 \longrightarrow :\bar{C}Cl_2 + Cl^-$$

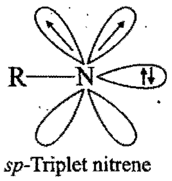


(v) Nitrenes or Imidogenes

Nitrenes are the organic species having the general formula, $R-\ddot{\underset{\cdot\cdot}{N}}$. These are the nitrogen similar to carbenes and neutral univalent nitrogen intermediates (with one bond and two nonbonded electron pairs, *i.e.*, $-\ddot{\underset{\cdot\cdot}{N}}$). These are defined as *'the electron deficient species in which nitrogen has a sextet of electrons'* (six electrons in the outermost shell). They are highly reactive and act as strong **electrophiles** as they need a pair of electrons to complete the octet. The parent species is $\ddot{\underset{\cdot\cdot}{N}}-H$ (known as **nitrene** or **imidogene** or **azene** or **imine**). It is difficult to be formed because it tends to polymerise to $(NH)_n$ as soon as it is formed. Hence, substituted nitrenes have received the much attention.

Nitrenes can exist in the **singlet** and **triplet** states just as in the case of carbenes with one of the covalent bonds replaced by nitrogen lone pair. The triplet state is the ground state and most nitrenes exist in this state.

In general nitrenes obey Hunds rule and are ground state triplet with two degenerate *sp*-orbitals containing a single electron each.



sp-Triplet nitrene

Nomenclature: The nomenclature of nitrenes is also similar to that of the carbenes. For example,

$\ddot{N}Ph$ is called phenyl nitrene, $\ddot{N}-\overset{\overset{O}{\|}}{C}-R$ is acyl nitrene and

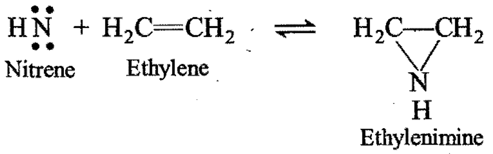
$\ddot{N}Et$ is called ethyl nitrene, and so on.

Formation of Nitrenes

(a) The simplest nitrene ($\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}-H$) is formed when hydrazoic acid (N_3H) is irradiated with UV light in aromatic solvents which forms a small amount of primary aromatic amines.

$$\underset{\text{Hydrazoic acid}}{N_3H} \xrightarrow{hv} N_2 + \underset{\text{Nitrene}}{H\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}} \xrightarrow{C_6H_5CH_3} \underset{p\text{-Toluidine}}{p\text{-}H_2N-C_6H_4-CH_3}$$

In the presence of ethylene, nitrene is trapped to form ethylenimine (a cyclic product).



(b) Alkyl, aryl and acyl nitrenes may be prepared by the photolysis of alkyl azides, alkyl isocyanates or acyl azides respectively.

$$\underset{\text{Alkyl azide}}{R-N_3} \xrightarrow{\text{Light}} \underset{\text{Alkyl nitrene}}{R-\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}} + N_2$$

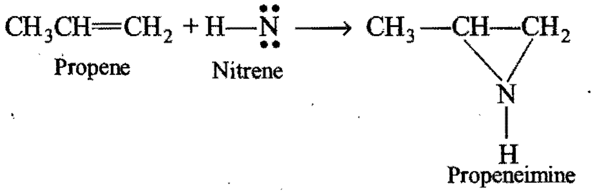
$$\underset{\text{Methyl azide}}{CH_3-N_3} \xrightarrow{\text{Light}} \underset{\text{Methyl nitrene}}{CH_3-\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}} + N_2$$

$$\underset{\text{Phenyl azide}}{C_6H_5-N_3} \xrightarrow{\text{Light}} \underset{\text{Phenyl nitrene}}{C_6H_5-\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}} + N_2$$

$$\underset{\text{Acetyl azide}}{CH_3CON_3} \xrightarrow{\text{Light}} \underset{\text{Acetyl nitrene}}{CH_3CO\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}} + N_2$$

Reactions: Nitrenes are highly reactive unstable compounds and give the following reactions.

1. Addition to alkenes: Nitrenes add on alkenes to form corresponding alkeneimine, a cyclic product.



2. Addition to alkanes: Acetyl nitrene reacts with isobutane to form acetyl tert. butylamine.

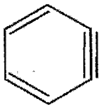
$$\underset{\text{2-Methylpropane}}{(CH_3)_3CH} + \underset{\text{Acetyl nitrene}}{CH_3CO\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}} \longrightarrow \underset{\text{Acetyl tert. butylamine}}{(CH_3)_3CNHCOCH_3}$$

Also photolysis of phenyl nitrene (on dimerization) forms azobenzene.

$$\underset{\text{Phenyl nitrene}}{2C_6H_5-\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}} \xrightarrow{\text{Light}} \underset{\text{Azobenzene}}{C_6H_5-N=N-C_6H_5}$$

Applications: Nitrenes have important synthetic applications particularly acyl nitrene ($R-\overset{\overset{O}{\|}}{C}-\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}$), has been proposed as possible intermediate in the Hofmann, Curtius and Lossen rearrangements.

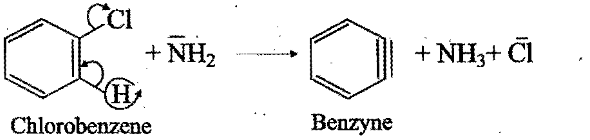
(vi) Benzyne (1,2-Dehydrobenzene or Aryne)

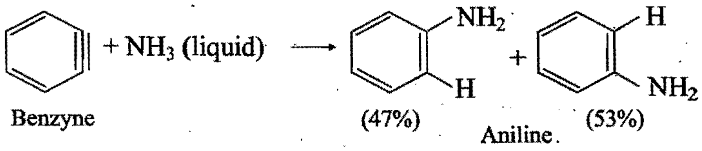

, (C_6H_4)

"Benzyne is a neutral, highly reactive reaction intermediate in which the aromatic character has not been markely disturbed". It is formed as an intermediate during nucleophilic substitution of aromatic compounds. It contains Carbon-Carbon triple bond in the benzene ring involving the formation of a new weaker C—C bond by sideways overlapping of sp^2-hybridized orbitals of two adjacent carbon atoms.

Formation of Benzyne

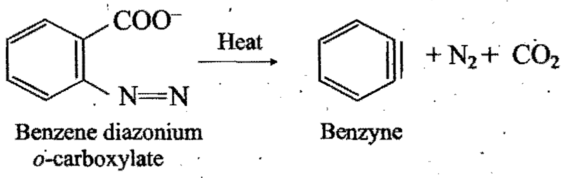
(a) When arylhalides are treated with very strong bases such as sodamide, $NaNH_2$ or certain metal alkoxides such as potassium tert. butoxide, Me_3COK, they eliminate HX from vicinal carbons to produce a species called **benzyne** which then undergoes reaction with the available nucleophile, $\bar{N}H_2$ (liquid ammonia) rapidly to form aromatic compound, aniline.

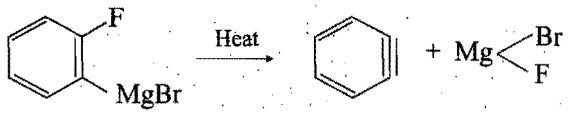




Experimentally both products are formed, hence, elimination addition mechanism is followed. Further, in this reaction, there occurs vicinal rearrangement in which the entering group occupies the *ortho*-position to the leaving group. Therefore, this reaction is also known as **cine-substitution.**

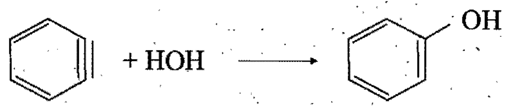
(b) Benzyne can also be obtained by the decomposition of benzene diazonium *o*-carboxylate or *o*-fluorophenyl magnesium bromide.



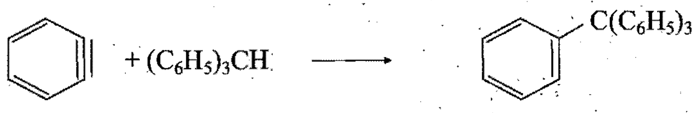


o-Fluorophenyl magnesium bromid   Benzyne

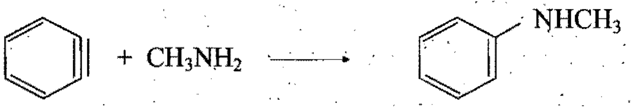
Benzyne reacts w nucleophilic reagents and form addition products.



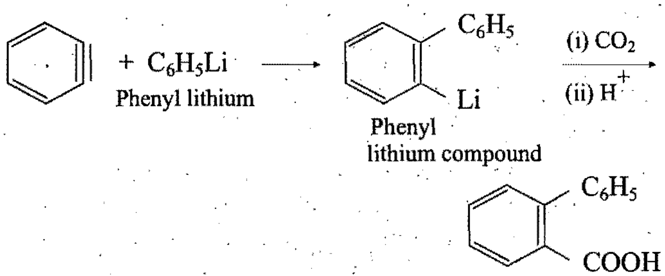
Benzyne   Phenol



Benzyne   Triphenylmethylbenzene (Tetraphenylmethane)



Benzyne   *N*-Methylaniline



Phenyl lithium compound

Biphenyl 2-carboxylic acid

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

6. Benzyne is:
(a) 1,2-dihydrobenzene
(b) 1,2-dehydrobenzene
(c) 1,2,3,4-tetrahydrobenzene
(d) imidogenes
[**Ans.** (b)]

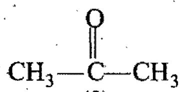
7. Which of the following is true about the cycloheptatrienyl free radical?
(a) it is an isolated stable free radical
(b) it is an aromatic free radical
(c) it has $4n + 2\pi$ electrons
(d) none of the above
[**Ans.** (d)]

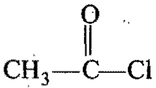
8. Heterolysis of propane gives:
(a) methyl and ethyl free radicals
(b) methylium ion and ethyl anion
(c) methyl anion and ethylium ion
(d) methylium and ethylium ions
[**Ans.** (c)]

9. Which of the following pairs of ions is more stable?
(a) $CH_3CH_2O^{\ominus}$ (I) and $CH_2=CH-O^{\ominus}$ (II)
(b) $(CH_3)_2\overset{\ominus}{C}-CH=O$ (I) and $(CH_3)_2\overset{\ominus}{C}-CH=CH_2$ (II)
(c) $Me_2\ddot{N}-CH=CH-CH=\overset{\oplus}{N}Me_2$ (I)
and $Me\underset{\bullet\bullet}{\ddot{O}}-CH=CH-CH=\overset{\oplus}{N}Me_2$ (II)
[**Ans.** (a) (II), (b) (I), (c) (I)]

10. Which among the following compounds behave both as an electrophile as well as a nucleophile?

$CH_2=CH_2$ (1) $CH_2=CH-\overset{+}{C}H_2$ (2)

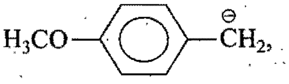

$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$
(3)


$CH_3-\overset{\overset{O}{\|}}{C}-Cl$
(4)

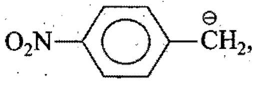
Answer using the following codes:
(a) only (1)
(b) (1) and (2)
(c) (3) and (4)
(d) (2), (3) and (4)
[**Ans.** (c)]

11. Which of the following species is an ambident nucleophile?
(a) $CH_3\overset{\ominus}{C}H_2$
(b) $H_2C=CH_2$
(c) $\overset{\ominus}{O}-\ddot{N}=O$
(d) $\overset{\ominus}{N}H_2$
[**Ans.** (c)]

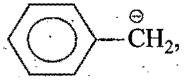
12. Consider the following carbanions:



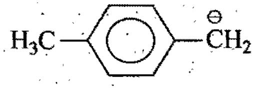
(I)



(II)



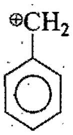
(III)

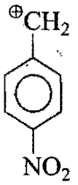


(IV)

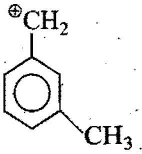
Correct decreasing order of stability is:
(a) II > III > I > IV
(b) III > IV > I > II
(c) IV > I > II > III
(d) I > II > III > IV
[**Ans.** (a)]

13. Which one of the following carbocations are most stable?

(a)


(b)


(c)


(d)


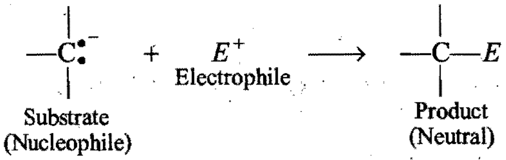
[**Ans.** (c) because $+R$ group present at *p*- (or *o*-) position increases the stability of benzyl carbocation and $-R$ group decreases stability.]

5.5 NATURE OF ATTACKING REAGENTS

Most of the attacking reagents carry either a positive or a negative charge. The positively charged reagents attack the regions of high electron density in the substrate molecule while the negatively charged reagents will attack the regions of low electron density in the substrate molecule. The fission of the substrate molecule to create centres of high or low electron density is influenced by attacking reagents. Most of the attacking reagents can be classified into two main groups:

(i) Electrophiles or electrophilic reagents
(ii) Nucleophiles or nucleophilic reagents

(i) Electrophiles : Electrophiles or electrophilic reagents are electron loving species (*Electro* = Electron, *philic* = loving). These species carry either positive charge or neutral molecules with electron deficient centre. So, a reagent which can accept an electron pair in a reaction, is called an electrophile. These contain, generally, two electrons less than the octet and attack regions of high electron density (negative centre) in the substrate molecule as to complete the octet and act as electrophiles.



Some common electrophiles are listed below:

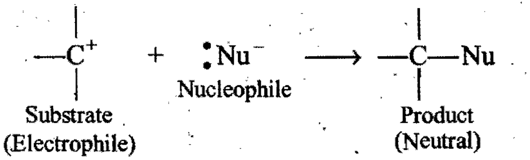
Positively charged	**Neutral molecules**
$H^+ (H_3^+O)$, Cl^+, Br^+,	SO_3, BF_3, $AlCl_3$
I^+, NO_2^+, NO^+, $\overset{+}{S}O_3H$	$ZnCl_2$, $\overset{*}{I}Cl$, PCl_5
	$BeCl_2$, $FeCl_3$, $SnCl_4$
R^+, R_3C^+ and other	$R\overset{*}{C}OCl$, $(R\overset{*}{C}O)_2O$
carbocations, CH_3CO^+,	CO_2, CS_2, CX_4
NH_4^+, $C_6H_5N_2^+$	$R-MgX$
	$:CCl_2$ (Carbene)
	$:\ddot{N}COOC_2H_5$ (Nitrene)
	$>C=O$

The star (*) indicates the atom that accepts electrons from the substrate.

Further, **cation carriers,** *e.g.,* $Br-Br$, $H-Br$, $Cl-OH$, O_2N-OH, etc., and oxidising agents such as Fe^{3+}, O_3, $R-O-O-R$, etc., also act as electrophilic reagents.

Since, electrophiles are capable of accepting electron pair, they act as **Lewis acids.** The reactions involving the attack of electrophiles are known as electrophilic reactions.

(ii) Nucleophiles : Nucleophiles or nucleophilic reagents are electron donating species. The name nucleophile means nucleus loving. Nucleophiles are electron rich, *i.e.,* they normally possess an unshared electron pair which they can donate. They are either negative ions or neutral molecules with free electron pairs to donate. They attack regions of low electron density (positive centres) in the substrate molecule.



The common nucleophiles are listed below:

Negatively charged	**Neutral molecules**
Cl^-, Br^-, I^-,	$:NH_3$, $R-\underset{\underset{H}{\vert}}{\ddot{N}}-H$,
R^-, H^-, S^-, NO_2^-,	$H-\ddot{\underset{\bullet\bullet}{O}}-H$,
NH_2^-, RNH^-, R_2N^-,	$R-\ddot{\underset{\bullet\bullet}{O}}-H$, $R-\ddot{\underset{\bullet\bullet}{O}}-R$,
	$R-\ddot{\underset{\bullet\bullet}{S}}-H$,
$[CH(COOC_2H_5)_2]^-$,	$R-\ddot{\underset{\bullet\bullet}{S}}-R$, $H-\ddot{\underset{\bullet\bullet}{S}}-H$,
$[CH_3COCHCOOEt]^-$,	$R_2-\underset{\underset{H}{\vert}}{N}:$, $R_3-N:$
R_3C^-, $CH_3COCH_2^-$, OH^-,	$LiAl\overset{*}{H}_4$, $(C_6H_5)_3P:$, $R_3P:$
OR^-, COO^-, $RCOO^-$,	$\overset{*}{R}-MgX$, $R-Li$,
CN^-, N_3^-, SH^-, HSO_3^-	$\ddot{P}H_3$, $R\ddot{P}H_2$, $R_2\ddot{P}H$
Carbanions	

The star (*) indicates the atom that donates electrons to the substrate.

In addition, **anion carriers,** *e.g.,* $\overset{\curvearrowright}{H-}H$, $\overset{\curvearrowright}{R-}MgX$, $H-H_3AlLi$, $>C=C<$, $H_2C=CH-CH=CH_2$, $\overset{\curvearrowright}{H-}C_6H_5$, etc., and reducing agents such as Fe^{2+}, $[Fe(CN)_6]^{4-}$, etc., also act as nucleophilic reagents.

Since, nucleophiles are capable of donating electron pairs, they act as **Lewis bases.** The reactions involving the attack of nucleophiles are known as nucleophilic reactions.

The effect of the attacking nucleophile (nucleophilicity *versus* basicity)

(i) A nucleophile with a negative charge is always more powerful nucleophile than its conjugate acid. Thus, OH^- is more powerful than H_2O and NH_2^- is more powerful than NH_3, etc.

(ii) If the nucleophilic atoms are from the same periodic table, nucleophilicity is roughly in the order of basicity, though basicity is thermodynamically controlled while nucleophilicity is kinetically controlled. So, an approximate order of nucleophilicity is:

$$\bar{N}H_2 > R\bar{O} > OH^- > R_2NH > Ar\bar{O} > NH_3 > \text{pyridine} >$$

$F^- > H_2O > Cl\bar{O}_4$, and another is $R_3C^- > R_2N^- > RO^- > F^-$.

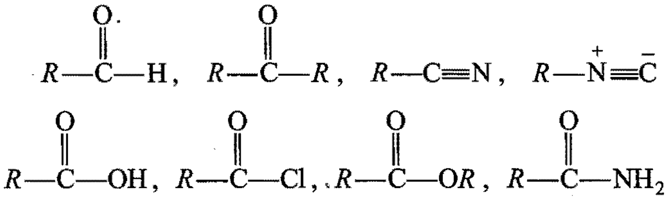
(iii) Going down the periodic table, nucleophilicity increases, though basicity decreases. Thus, the usual order of halide nucleophilicity is $I^- > Br^- > Cl^- > F^-$ (this order is solvent dependent), and sulphur nucleophile is more powerful than its oxygen analogue and the same is true for P *vs* N. The overall decreasing nucleophilicity order for S_N2 reaction in protic solvent is as follows:

$$RS^- > ArS^- > I^- > CN^- > OH^- > N_3^- > Br^- > ArO^-$$
$$> Cl^- > \text{pyridine} > CH_3COO^- > H_2O$$

(iv) The decreasing order of ionising power of solvents (for S_N1 reaction) is as follows:

$$CF_3COOH > HCOOH > H_2O > CH_3OH > CH_3COOH$$
$$> C_2H_5OH—H_2O(80\%) > (CH_3)_2SO > CH_3CN$$
$$> HCON(CH_3)_2 > Ac_2O > \text{pyridine} > CH_3COCH_3$$
$$> (C_2H_5)_2O > CHCl_3 > C_6H_6 > \text{alkanes}$$

Organic compounds in which carbon is bonded with electronegative atom (O, N, S) by multiple bond/(s) behaves as **electrophile as well as nucleophile:**



$R—\overset{O}{\overset{\|}{C}}—H$, $R—\overset{O}{\overset{\|}{C}}—R$, $R—C{\equiv}N$, $R—\overset{+}{N}{\equiv}\overset{-}{C}$

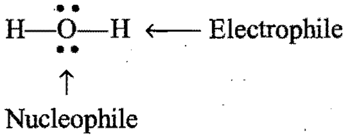
$R—\overset{O}{\overset{\|}{C}}—OH$, $R—\overset{O}{\overset{\|}{C}}—Cl$, $R—\overset{O}{\overset{\|}{C}}—OR$, $R—\overset{O}{\overset{\|}{C}}—NH_2$

Note : During the course of chemical reaction, electrophile reacts with nucleophile.

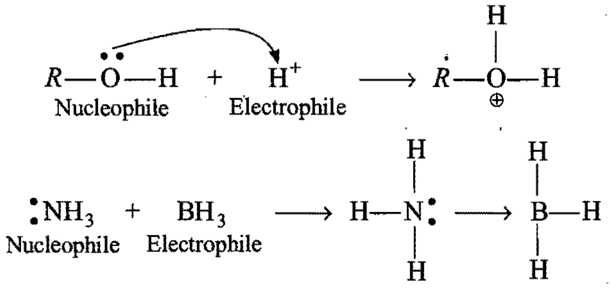
Comparison between Electrophiles and Nucleophiles

Nucleophiles	Electrophiles
(i) Electron rich, generally anions.	(i) Electron deficient, generally cations.
(ii) Act as Lewis bases, possess an unshared electron pair which they can donate.	(ii) Act as Lewis acids, possess an empty orbital which can accommodate an electron pair.
(iii) Attack regions of low electron density.	(iii) Attack regions of high electron density.
(iv) Can be represented by a general symbol Nu:	(iv) Can be represented by a general symbol E^+.

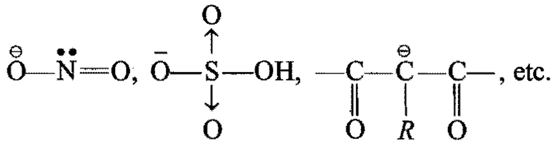
(iii) Ambiphile (Ambident) : They behave both like electrophiles (electron attracting) and nucleophiles (electron repelling) sites and hence, have dual (amphoteric) nature, *e.g.*, HOH, R—OH, RPH_2, CH_3CN and $H_2C{=}O$, etc.



Nucleophiles attack electrophiles during the course of the reaction.



The nucleophiles which can attack through two or more different ways to give different products are called **ambident nucleophiles.** For example, CN^- can attack through N or C to give cyanide (RCN) or isocyanide (RNC), and anions from compounds having reactive methylene group like malonic ester, β-keto ester, β-diketones, etc., are resonance stabilized.



$\overset{\ominus}{O}—\ddot{N}{=}O$, $\bar{O}—\overset{O}{\overset{\uparrow}{S}}—OH$ (with $\downarrow$ O below S), $—\underset{O}{\underset{\|}{C}}—\underset{R}{\underset{|}{\overset{\ominus}{C}}}—\underset{O}{\underset{\|}{C}}—$, etc.

5.6 TYPES OF ORGANIC REACTIONS

The reactions of organic compounds can be classified into four main types:

(i) Substitution or displacement reactions
(ii) Addition reactions
(iii) Elimination reactions
(iv) Rearrangement reactions

(i) Substitution or displacement reactions : Substitution or displacement reactions are those reactions in which an atom or group of atoms attached to a carbon atom in a substrate molecule is replaced by another atom or group of atoms. During the reaction, no change occurs in the carbon skeleton, *i.e.*, no change in the saturation or unsaturation of the initial organic compound. Depending on the mechanism, the substitution reactions are further classified into three types:

(a) Free radical substituting reactions
(b) Electrophilic substituting reactions
(c) Nucleophilic substituting reactions

Some of the examples of substitution reactions are:

(*i*) $$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow[\text{light}]{\text{UV}} CH_3Cl + HCl$$

(Hydrogen atom is replaced by chlorine)

(*ii*) $$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + NaOH \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + NaBr$$

(Bromine atom is replaced by hydroxyl group)

(*iii*) $$\underset{\text{Methyl alcohol}}{CH_3OH} + HBr \longrightarrow \underset{\text{Methyl bromide}}{CH_3Br} + H_2O$$

(Hydroxyl group is replaced by bromine)

(*iv*) $\underset{\text{Benzene}}{C_6H_6} + \underset{\text{(Conc.)}}{HNO_3} \xrightarrow{H_2SO_4\text{ (conc.)}} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$

(Hydrogen is replaced by NO_2 group)

(*v*) $\underset{\text{Propylene}}{CH_3CH=CH_2} + Cl_2 \xrightarrow{500°C} \underset{\text{Allyl chloride}}{ClCH_2CH=CH_2} + HCl$

(Hydrogen is replaced by chlorine)

(*vi*) $\underset{\text{Benzene}}{C_6H_6} + Cl_2 \xrightarrow{FeCl_3} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl$

(Hydrogen is replaced by chlorine)

(ii) Addition reactions : Addition reactions are those in which the attacking reagent adds up to the substrate molecule without elimination. Such reactions are given by those compounds which possess double or triple bonds (π-bonded). In the process a triple bond may be converted into double bond or single bonds and a double bond is converted into single bonds. For each π-bond of the molecule two sigma bonds are formed and the hybridization state of carbon atoms changes from sp to sp^2 and sp^2 to sp^3.

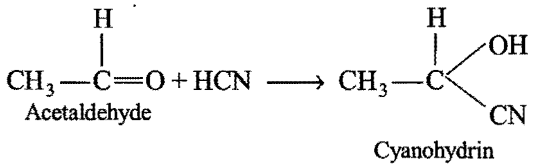
Like substitution reactions, addition reactions are also of three types:

(a) Free radical addition reactions
(b) Nucleophilic addition reactions
(c) Electrophilic addition reactions

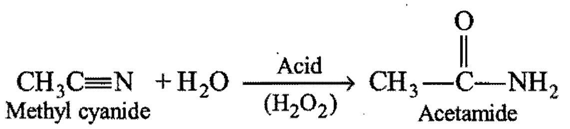
Some of the examples of addition reactions are:

(*i*) $\underset{\text{Acetylene}}{HC\equiv CH} + H_2 \xrightarrow[140°C]{Ni} \underset{\text{Ethylene}}{H_2C=CH_2} \xrightarrow[200°C]{H_2/Ni} \underset{\text{Ethane}}{CH_3-CH_3}$

(*ii*) $\underset{\text{Ethylene}}{H_2C=CH_2} + Br_2 \longrightarrow \underset{\text{1,2-Dibromoethane}}{CH_2Br-CH_2Br}$
(Ethylene bromide)

(*iii*)


$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{H}{|}}{C}=O} + HCN \longrightarrow \underset{\text{Cyanohydrin}}{CH_3-\overset{\overset{H}{|}}{C}\begin{smallmatrix}OH\\CN\end{smallmatrix}}$$

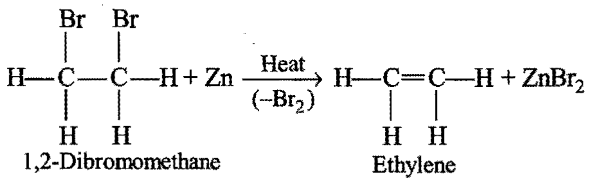
(*iv*)


$$\underset{\text{Methyl cyanide}}{CH_3C\equiv N} + H_2O \xrightarrow[(H_2O_2)]{\text{Acid}} \underset{\text{Acetamide}}{CH_3-\overset{\overset{O}{||}}{C}-NH_2}$$

(*v*) $\underset{\text{Acetylene}}{HC\equiv CH} + HBr \rightarrow \underset{\text{Vinyl bromide}}{CH_2=CHBr} \xrightarrow{HBr} \underset{\text{1,1-Dibromoethane}}{CH_3CHBr_2}$
(Ethylidine bromide)

(iii) Elimination reactions : The reverse of addition reactions are termed as elimination reactions. In these reactions generally atoms or groups from two adjacent carbon atoms (α, β) in the substrate molecule are removed and multiple (double or triple) bond is formed. In the process two sigma bonds are lost and a new π-bond is formed, *i.e.*, state of hybridization of carbon atom changes from sp^3 to sp^2 and sp^2 to sp. This reaction is known as **β-elimination.**

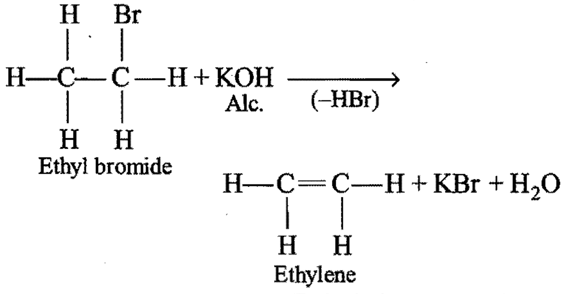
Some examples are:

(a)


$$\underset{\text{1,2-Dibromomethane}}{H-\overset{\overset{Br}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{Br}{|}}{\underset{\underset{H}{|}}{C}}-H} + Zn \xrightarrow[(-Br_2)]{\text{Heat}} \underset{\text{Ethylene}}{H-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-H} + ZnBr_2$$

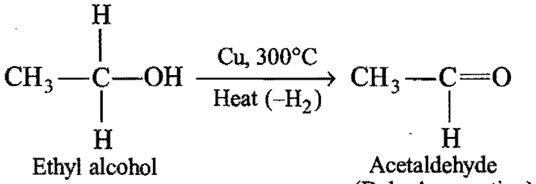
(Dehalogenation)

Base catalysed dehydrohalogenation of alkyl halides

(b)


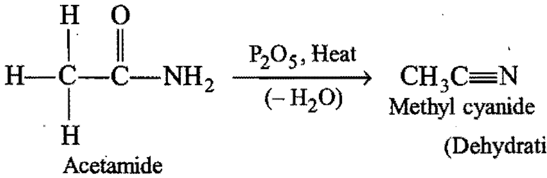
$$\underset{\text{Ethyl bromide}}{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{Br}{|}}{\underset{\underset{H}{|}}{C}}-H} + \underset{\text{Alc.}}{KOH} \xrightarrow{(-HBr)} \underset{\text{Ethylene}}{H-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-H} + KBr + H_2O$$

(Dehydrohalogenation)

(c)


$$\underset{\text{Ethyl alcohol}}{CH_3-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH} \xrightarrow[\text{Heat }(-H_2)]{Cu,\ 300°C} \underset{\text{Acetaldehyde}}{CH_3-\underset{\underset{H}{|}}{C}=O}$$

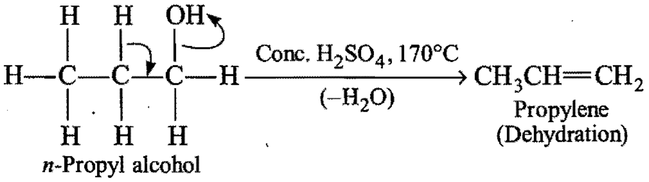
(Dehydrogenation)

(d)


$$\underset{\text{Acetamide}}{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{O}{||}}{C}-NH_2} \xrightarrow[(-H_2O)]{P_2O_5,\text{ Heat}} \underset{\text{Methyl cyanide}}{CH_3C\equiv N}$$

(Dehydration)

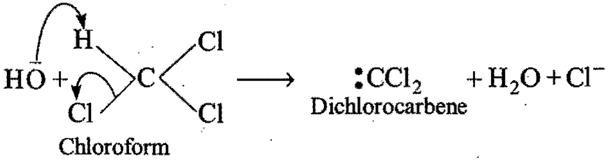
Acid catalysed dehydration of alcohols



$$\underset{n\text{-Propyl alcohol}}{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-H} \xrightarrow[(-H_2O)]{\text{Conc. }H_2SO_4,\ 170°C} \underset{\text{Propylene}}{CH_3CH=CH_2}$$

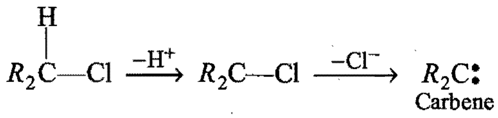
(Dehydration)

Another type of elimination is **α-elimination.** It is the removal of two atoms or groups from the same carbon atom of the substance and produces a carbene, if this atom is carbon.



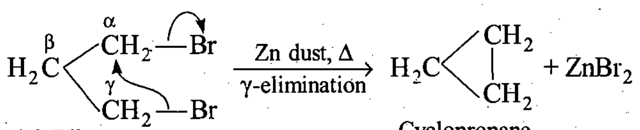
$$HO^- + \underset{\text{Chloroform}}{Cl_3CH} \longrightarrow \underset{\text{Dichlorocarbene}}{:CCl_2} + H_2O + Cl^-$$

Dichlorocarbene is the reactive intermediate involved in **carbylamine reaction** and **Reimer-Tiemann reaction.**



$$R_2\overset{\overset{H}{|}}{C}-Cl \xrightarrow{-H^+} R_2\overset{-}{C}-Cl \xrightarrow{-Cl^-} \underset{\text{Carbene}}{R_2C:}$$

In **γ-elimination,** it is removal of two atoms or groups from α-and γ-positions (other than from adjacent atoms or same atom) and produces a ring, *e.g.*,

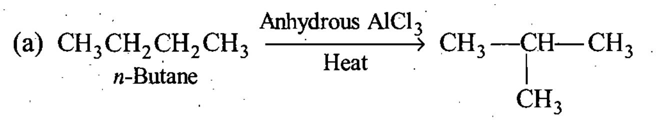


1,3-Dibromopropane Cyclopropane

This reaction is called **Freund reaction** and is extensively used for the synthesis of three membered rings.

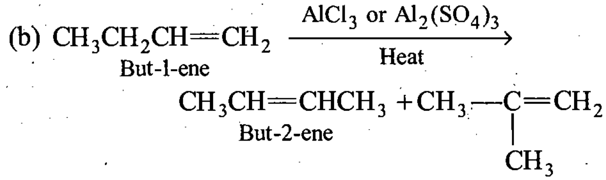
(iv) Rearrangement reactions : The reactions which involve the migration of an atom or group from one site to another within the molecule (nothing is added from outside and nothing is eliminated) resulting in a new molecular structure are known as rearrangement reactions. The new compound is actually the structural isomer of the original one.

Some of the examples are:



(a) $CH_3CH_2CH_2CH_3 \xrightarrow[\text{Heat}]{\text{Anhydrous } AlCl_3} CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_3$

n-Butane Isobutane

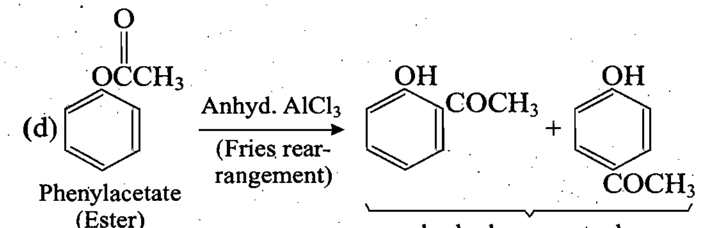


(b) $CH_3CH_2CH{=}CH_2 \xrightarrow[\text{Heat}]{AlCl_3 \text{ or } Al_2(SO_4)_3} CH_3CH{=}CHCH_3 + CH_3—\underset{\underset{CH_3}{|}}{C}{=}CH_2$

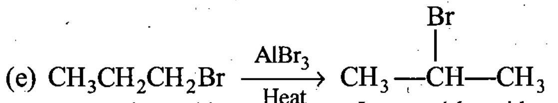
But-1-ene But-2-ene 2-Methylpropene

(c) $NH_4CNO \xrightarrow{\text{Heat}} NH_2—CO—NH_2$

Ammonium cyanate Urea

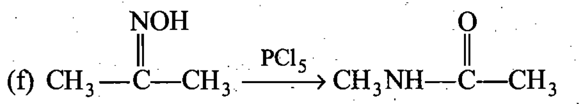


Phenylacetate (Ester) o- and p-hydroxy acetophenone



(e) $CH_3CH_2CH_2Br \xrightarrow[\text{Heat}]{AlBr_3} CH_3—\overset{\overset{Br}{|}}{CH}—CH_3$

n-Propyl bromide Isopropyl bromide



(f) $CH_3—\overset{\overset{NOH}{\|}}{C}—CH_3 \xrightarrow{PCl_5} CH_3NH—\overset{\overset{O}{\|}}{C}—CH_3$

Acetoxime N-Methyl acetamide

It is an example of **Beckmann rearrangement.**

5.7 TYPES OF MECHANISM

Reaction mechanisms are classified mainly into two classes:

(i) Free radical mechanism
(ii) Ionic or polar mechanism

(i) Free radical mechanism : This type of mechanism explains those reactions in which homolytic bond fission occurs. The homolytic bond fission is favoured by the following factors:

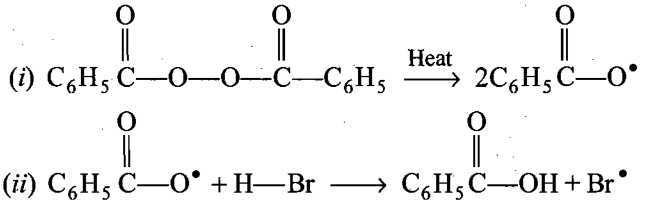
(a) Gaseous state of reactants, (b) Non-polar solvents, (c) Presence of energy in the form of UV, sunlight, heat, etc., (d) Presence of substances like peroxides which form free radicals readily on decomposition.

The mechanism of reactions involving the attack of free radicals on the substrate molecule is referred to free radical mechanism. The mechanism of free radical reactions involves three steps—initiation, propagation and termination. Each of these steps, in turn, may involve two or more steps.

Initiation step : This step involves the production of free radicals by irradiation or heating the reagent or by carrying out the reaction in the presence of an initiator such as peroxide. The production of free radical may be a one or two step process. For example, the formation of bromine-free radical from bromine during substituting reaction is a one step process.

$$Br : Br \xrightarrow{h\nu} 2Br^\bullet$$

A two-step process is involved in the formation of bromine radical from hydrogen bromide during addition of HBr on propylene in the presence of benzoyl peroxide.



(i) $C_6H_5\overset{\overset{O}{\|}}{C}—O—O—\overset{\overset{O}{\|}}{C}—C_6H_5 \xrightarrow{\text{Heat}} 2C_6H_5\overset{\overset{O}{\|}}{C}—O^\bullet$

(ii) $C_6H_5\overset{\overset{O}{\|}}{C}—O^\bullet + H—Br \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}—OH + Br^\bullet$

Propagation step : The free radical formed in the first step may generate a new free radical when it attacks the substrate. The new free radical may react with attacking reagent to form free radical or may react with free radical to form product.

This process may continue in an indefinite number of ways until there occurs an end of the chain of propagation.

$$Br^\bullet + CH_3—CH_3 \longrightarrow CH_3—\dot{C}H_2 + HBr$$

$$CH_3\dot{C}H_2 + Br_2 \longrightarrow CH_3CH_2Br + Br^\bullet$$

Termination step : In this step, there occurs destruction of free radicals, either by combination of two free radicals (same or different) or by disproportionation.

$$CH_3—\dot{C}H_2 + \dot{C}H_2—CH_3 \longrightarrow CH_3CH_2CH_2CH_3$$

(Coupling)

$$2CH_3\dot{C}H_2 \longrightarrow CH_3—CH_3 + CH_2{=}CH_2$$

(Disproportionation)

It is also possible to terminate chain reaction of free radicals by adding inhibitors like benzoquinone, phenols, amines, nitric oxide, etc.

(ii) Ionic or polar mechanism : This type of mechanism applies to those reactions in which heterolytic bond fission occurs. The heterolytic bond fission is favoured by the following factors:

(a) Liquid state of reactants, (b) Presence of polar solvents (acids or bases), (c) Inductive, mesomeric or electromeric effects which displace electrons in the substrate, (d) Absence of peroxides.

The heterolytic bond fission produces positive or negative centres in the substrate, *i.e.*, carbonium ions or carbanions come into existence. These centres are attacked by nucleophiles or electrophiles. **The mechanism of reactions involving the attack of nucleophilic or electrophilic reagents on polar substrate molecules is referred to as polar or ionic mechanism.**

A polar mechanism may be illustrated in the following way:

$$\underset{\text{Substrate}}{AB} \longrightarrow A^+ + B^-$$

A^+ is attacked by nucleophilic reagent.

B^- is attacked by electrophilic reagent.

The ionic reactions occur either in two stages or in one stage. For example, an OH^- ion may react with alkyl halide in either of the following two ways:

(*i*) $R\,|\,{:}X \xrightarrow[\text{bond fission}]{\text{First step}} R^+ + {:}X^-$ (Slow step)

Then, $R^+ + {:}OH^- \xrightarrow[\text{bond formation}]{\text{Second step}} R{:}OH$ (Fast step)

R^+ is an intermediate species which has a very short life time. The rate of reaction depends on the first step which is a slow one. In this step one molecule is involved and, thus, it is **unimolecular reaction** (First order change).

(*ii*) $\underset{\underset{{:}OH^-}{\uparrow}}{R}\,|\,{:}X \xrightarrow[\text{formation simultaneously}]{\text{Bond fission and}} R{:}OH + {:}X^-$

An intermediate 'transitory state' is formed in which the old bond is broken first and then only a new bond is formed at the same time. Such transitory state can be represented as below:

$$\overset{\delta-}{HO{:}} \to ---R \to ---\overset{\delta-}{{:}Cl}$$

Since, in this mechanism, two molecules are involved in the formation of transition state, the reaction is **bimolecular reaction** (Second order change).

5.8 MECHANISM OF SUBSTITUTION REACTIONS

As already defined, a substitution reaction involves the replacement of an atom or group attached to a carbon atom by another atom or group. These reactions may follow free radical, nucleophilic or electrophilic mechanism. Some typical examples are considered to explain the three types of mechanism.

(i) Free radical substitution reactions :

(a) Chlorination of methane : The chlorination of methane in the presence of ultraviolet light is an example of free radical substitution (HOMOLYSIS).

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow[h\nu]{520\text{-}670K} \underset{\substack{\text{Methyl}\\\text{chloride}}}{CH_3Cl} + HCl$$

The reaction does not stop with the formation of methyl chloride (CH_3Cl) but the remaining hydrogen atoms are replaced one by one with chlorine atoms to give rise chain reaction.

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$
$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

Mechanism :

Initiation step: The reaction is initiated by the breaking of chlorine molecule into chlorine-free radicals in presence of UV light.

$Cl_2 \xrightarrow[h\nu \text{ or heat}]{\text{Homolytic fission}} Cl^\bullet + Cl^\bullet$ (Chain initiation) . . . (i)

Propagation step: The chlorine-free radicals attack methane molecule ($Cl^\bullet$ is a substituent).

$CH_4 + Cl^\bullet \longrightarrow \dot{C}H_3 + HCl$ (Chain propagation) . . . (ii)

Each of the methyl-free radicals, in turn, reacts with chlorine molecule to form methyl chloride and at the same time chlorine-free radical is produced.

$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + Cl^\bullet$ (Chain propagation)

The chlorine-free radical can react with fresh methane molecule as in step (ii) or methyl chloride.

$Cl^\bullet + CH_3Cl \longrightarrow \dot{C}H_2Cl + HCl$ (Chain propagation)

The $\dot{C}H_2Cl$ free radical would react with another molecule of chlorine to form dichloro methane. This process may extend further till all the replaceable hydrogen atoms in the methane have been substituted by chlorine atoms.

$\dot{C}H_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^\bullet$ (Chain propagation)

$Cl^\bullet + CH_2Cl_2 \longrightarrow \dot{C}HCl_2 + HCl$ (Chain propagation)

$\dot{C}HCl_2 + Cl_2 \longrightarrow CHCl_3 + Cl^\bullet$ (Chain propagation)

$Cl^\bullet + CHCl_3 \longrightarrow \dot{C}Cl_3 + HCl$ (Chain propagation)

$\dot{C}Cl_3 + Cl_2 \longrightarrow CCl_4 + Cl^\bullet$ (Chain propagation)

For thermodynamic data of halogenation, the tabulated values are given below:

Enthalpies of the propagation steps in the halogenation of methane (kcal mol^{-1})					DH° values for the elemental halogens	
Reaction	**F**	**Cl**	**Br**	**I**	**Halogen**	DH° **(kcal mol^{-1})**
$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}\cdot + CH_4 \longrightarrow \cdot CH_3 + H\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:$	–31	+2	+18	+34	F_2	38
$\cdot CH_3 + X_2 \longrightarrow CH_3\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}: + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}\cdot$	–72	–27	–24	–21	Cl_2	58
$CH_4 + X_2 \longrightarrow CH_3\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}: + H\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:$	–103	–25	–6	+13	Br_2	46
					I_2	36

Termination step:

The chain of reactions initiated and propagated as shown above may be terminated if free radicals combine amongst themselves without giving rise to any new radicals.

$$\dot{C}l + \dot{C}l \longrightarrow Cl_2 \quad \text{(Chain termination)} \quad \ldots \text{(iii)}$$

$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl \quad \text{(Chain termination)}$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3—CH_3 \quad \text{(Chain termination)}$$

Reactivity of the halogens for free radical substitution is in the order:

$$F_2 > Cl_2 > Br_2 > I_2$$

Evidence in favour of free radical mechanism :

(*i*) The reaction does not occur in dark but requires energy to initiate the process.

(*ii*) It has been observed that addition of substances that are sources of free radicals can initiate the reaction in the dark and even at low temperature. For example, in the presence of 0.02% of tetraethyl lead $[(C_2H_5)_4Pb]$, the chlorination of methane can take place in dark at 140°C.

(*iii*) It has been observed that oxygen acts as an inhibitor in this reaction. This is due to the fact that methyl radical combines with oxygen to form much less reactive peroxy methyl radical, $CH_3COO^\bullet$.

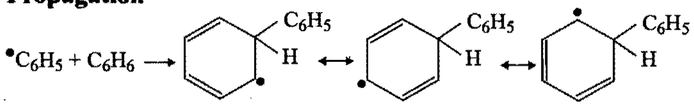
(b) Arylation of aromatic compounds (Gomberg reaction) : The reaction of benzene diazonium halide with benzene gives diphenyl by a free radical substitution reaction.

$$C_6H_5—H + \underset{\text{Benzene diazonium halide}}{C_6H_5N_2X} \xrightarrow{\text{Alkali}} \underset{\text{Diphenyl}}{C_6H_5—C_6H_5} + N_2 + HX$$

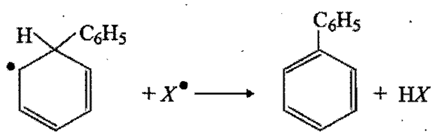
The **mechanism** of the reaction is as follows:

Initiation $\underset{\text{(In neutral or basic medium)}}{C_6H_5—N{=}N—X} \longrightarrow \dot{C}_6H_5 + N_2 + \dot{X}$

Propagation



Termination



(c) Wurtz reaction : Ethyl bromide on treatment with metallic sodium forms butane, ethane and ethylene by involving free radical mechanism.

$$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{Ether}} C_2H_5C_2H_5 + 2NaBr$$

$$C_2H_5Br + Na \longrightarrow \dot{C}_2H_5 + NaBr$$

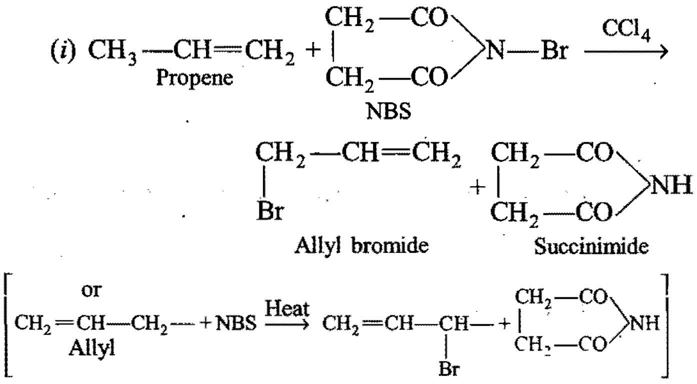
$$\dot{C}_2H_5 + \dot{C}_2H_5 \longrightarrow C_2H_5—C_2H_5 \quad \text{(Butane)}$$

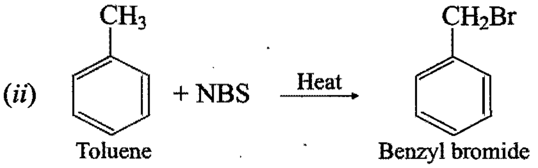
$$2CH_3\dot{C}H_2 \xrightarrow{\text{Disproportionation}} \underset{\text{Ethane}}{CH_3CH_3} + \underset{\text{Ethylene}}{H_2C{=}CH_2}$$

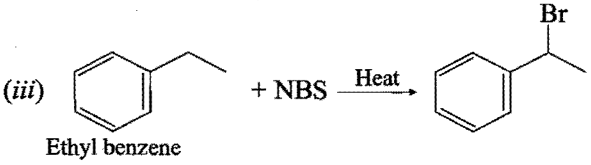
Other examples are:

(d) Allylic bromination by NBS (N-Bromosuccinimide)

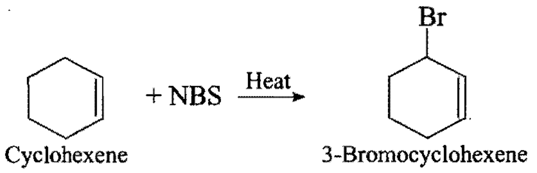
NBS is a selective brominating agent and it normally brominates the ethylenic compounds in the allylic $(CH_2{=}CH—CH_2—)$ position. This type of reaction involving substitution at the alpha carbon atom with respect to the double bond is termed **Allylic substitution**. It is also used for benzylic bromination. Some examples are:



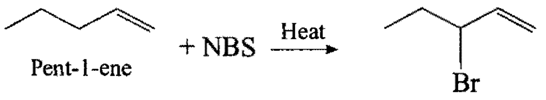




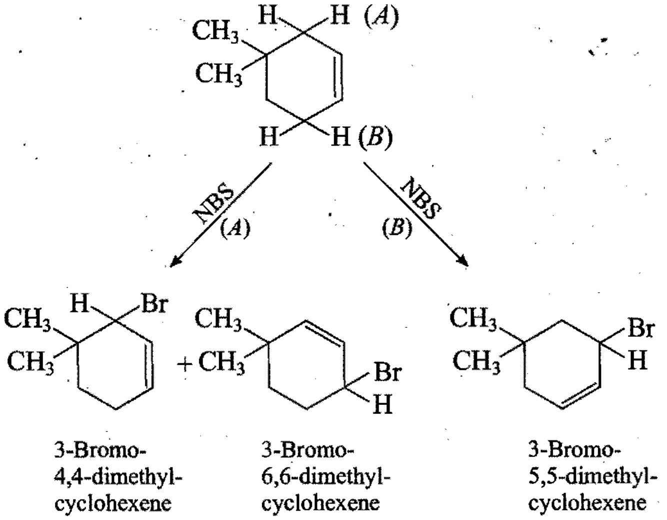
(iv)



(v)

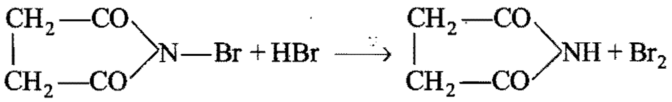


(*vi*) In 4,4-dimethyl cyclohexene there are two allylic positions *A* and *B*. In presence of NBS, it gives three allylic products.



Mechanism : Allylic bromination by NBS is believed to take place by a **free radical mechanism** since it is initiated by a peroxide or ultraviolet light.

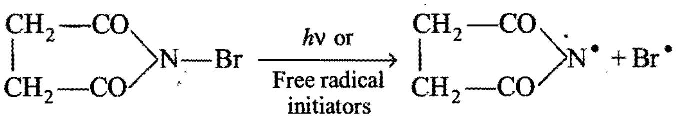
Step 1. The reaction of NBS with HBr (which is initially formed in the side reactions) to produce a low concentration of bromine.



The bromine molecule then gets dissociated into bromine free radical in presence of a peroxide or UV light.

$$Br_2 \rightleftharpoons 2Br^{\bullet} \quad \text{(Chain initiation)}$$

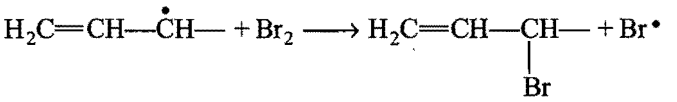
or directly



Step 2.

$$H_2C{=}CH{-}CH_2{-} + Br^{\bullet} \longrightarrow H_2C{=}CH{-}\dot{C}H{-} + HBr$$

(Chain propagation)



$$H_2C{=}CH{-}\dot{C}H{-} + Br_2 \longrightarrow H_2C{=}CH{-}\underset{\displaystyle Br}{\underset{|}{C}H}{-} + Br^{\bullet}$$

(Chain propagation)

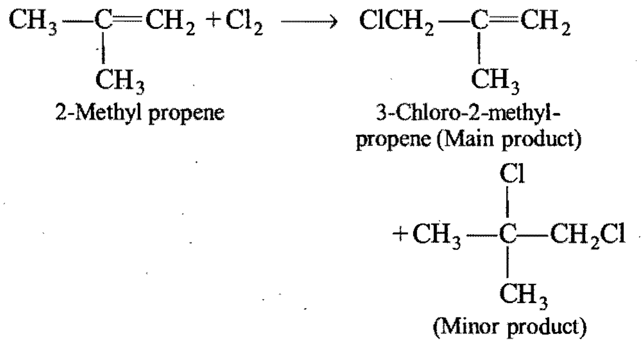
The free bromine radical can then continue the chain reaction.

It is important to note that allylic bromination is preferred over addition to the double bond by a low concentration of bromine because the addition of bromine free radical to the double bond is a reversible reaction.

$$-CH_2{-}CH{=}CH_2 + Br^{\bullet} \rightleftharpoons -CH_2{-}\dot{C}H{-}CH_2Br$$

(e) $\underset{\text{Propene}}{CH_3CH{=}CH_2} + Cl_2 \xrightarrow{400\text{–}600°C} \underset{\text{Allyl chloride}}{ClCH_2CH{=}CH_2} + HCl$

With branched chain alkenes, the substitution takes place even at room temperature.



$$\underset{\text{2-Methyl propene}}{CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2} + Cl_2 \longrightarrow \underset{\text{3-Chloro-2-methyl-propene (Main product)}}{ClCH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2} + \underset{\text{(Minor product)}}{CH_3{-}\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2Cl}$$

Substitution by halogen is a free radical reaction.

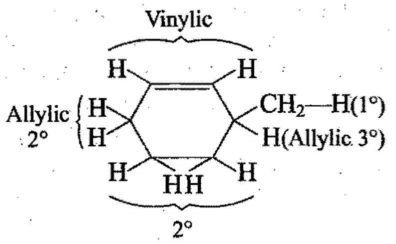
$$CH_3CH{=}CH_2 + X^{\bullet} \longrightarrow \underset{\text{Allyl free radical}}{\dot{C}H_2CH{=}CH_2} + HX$$

$$\dot{C}H_2CH{=}CH_2 + X_2 \longrightarrow \underset{\text{Allyl halide}}{XCH_2CH{=}CH_2} + X^{\bullet}$$

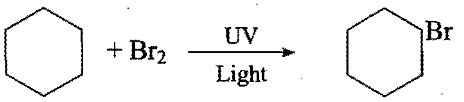
(This reaction takes place either at high temperature or low concentration of halogens.)

The ease of formation and stability of free radicals is in the order:

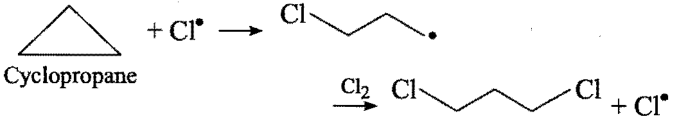
$$\text{Allyl} > 3° > 2° > 1° > \dot{C}H_3 > \text{vinyl}$$



(f) Substitution reactions of higher cycloalkanes in presence of UV light is an example of free radical reaction.

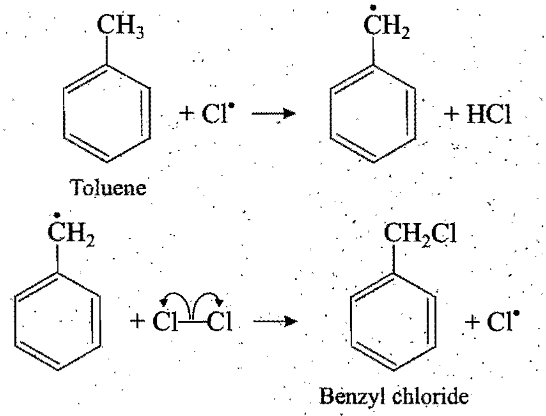


(g) Cyclopropane ring is opened by free halogen attack to form 1,3-dichloropropane.



(h) Side chain halogenation of toluene proceeds through a free radical mechanism.

$$Cl{-}Cl \xrightarrow{h\nu} 2Cl^{\bullet}$$



(ii) Nucleophilic substitution : Many substitution reactions, especially at the saturated carbon atom in aliphatic compounds such as alkyl halides, are brought about by nucleophilic reagents or nucleophiles.

$$\underset{\text{Nucleophile}}{\overset{-}{HO}} + \underset{\text{Substrate}}{R^{\delta+}—X^{\delta-}} \longrightarrow R—OH + \underset{\text{Leaving group}}{X^-}$$

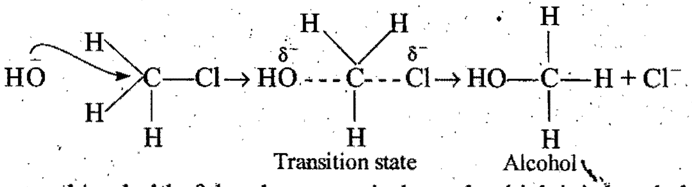
Such substitution reactions are called nucleophilic substitution reactions, *i.e.*, S_N reactions (S stands for substitution and *N* for nucleophile). The nucleophilic substitution reactions are divided into two classes:

(a) S_N2 Reactions : These are **bimolecular reactions.** When the rate of reaction depends on the concentration of both substrate and the nucleophile, the reaction is said to be S_N2, *i.e.*, 2nd order change.

$$\text{Rate} \propto [\text{Substrate}]\,[\text{Nucleophile}]$$

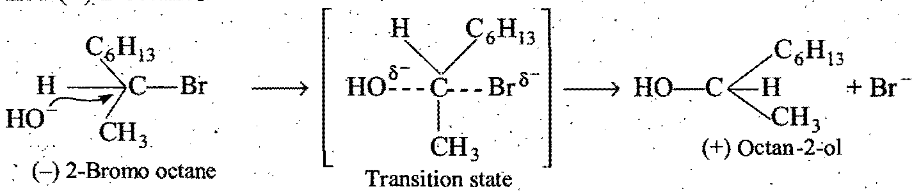
Hydrolysis of methyl chloride is an example of S_N2 reaction and high concentration of the nucleophile (OH^-) favours S_N2 reaction. The chlorine atom present in methyl chloride is more electronegative than the carbon atom. Therefore, C—Cl bond is partially polarized.

When the methyl chloride is attacked by OH^- strong nucleophile from the opposite side of the chlorine atom, an intermediate, transition state (TS) results in which both OH and Cl are partially bonded to carbon atom.

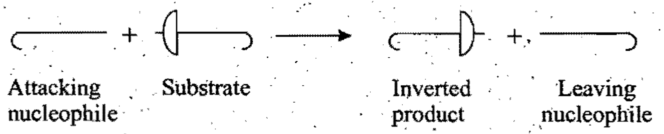


In transition state, chlorine starts taking hold of the electron pair through which it is bonded to carbon and the OH^- ion offers a pair of electrons for the formation of bond with carbon. Such a transition state is characterised by maximum potential energy and hence minimum stability. Finally, chlorine leaves the molecule as a chloride ion and OH^- ion forms a covalent bond with the carbon giving alcohol as a reaction product. According to this, hydrolysis is assumed to be a one stage process, where in two molecules simultaneously undergo covalency change and the older bond is broken and a new bond is formed simultaneously. In this reaction configuration of carbon is changed, *i.e.*, complete inversion takes place.

When (–) 2-bromo octane is allowed to react with sodium hydroxide under conditions where second order kinetics are followed, there is obtained (+) 2-octanol.



So, the alcohol obtained has a configuration opposite to that of the bromide and is said to proceed with **inversion of configuration.** Hence, an S_N2 reaction proceeds with complete stereo-chemical inversion called umbrella inversion which can be diagrammatically represented as,



Walden inversion is also based on umbrella inversion of S_N2 reaction.

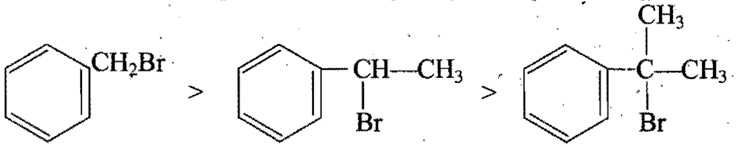
S_N2 mechanism is followed in the case of primary and secondary alkyl halides, *i.e.*, S_N2 reaction is favoured by small groups on the carbon atom attached to halogens; so the order of reactivity is:

$$CH_3-X > R-CH_2-X > R_2CH-X > R_3C-X$$

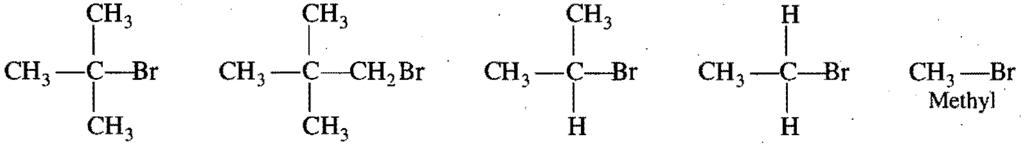
Primary is more reactive than secondary and tertiary alkyl halides, and nature of carbocation in substrate is:

S_N2 order:

Methyl > ethyl > isopropyl > tertiary butyl > allyl > benzyl halides



(Benzyl and allyl carbocations are stabilized due to resonance.)



	$(CH_3)_3C-Br$ 3°	$(CH_3)_3C-CH_2Br$ Neopentyl	$(CH_3)_2CH-Br$ 2°	CH_3-CH_2-Br 1°	CH_3-Br Methyl
Relative reactivity	< 1	1	500	40,000	2,00,000

$$\xrightarrow{\hspace{10em}}$$

Increasing S_N2 reactivity

For the reaction:

$$CH_3-Br + \bar{Nu}: \longrightarrow CH_3-Nu + Br^-$$

Nu ≈	H_2O	CH_3COO^-	NH_3	Cl^-	OH^-	CH_3O^-	I^-	CN^-	HS^-
Relative reactivity	1	500	700	1000	16,000	25,000	1,00,000	1,25,000	1,25,000

$$\xrightarrow{\hspace{10em}}$$

Increasing Nucleophile reactivity

Leaving group reactivity for S_N2 reaction is given below:

	$\underbrace{OH^-, NH_2^-, OR^-}$	F^-	Cl^-	Br^-	I^-	$TosO^-$
Relative reactivity	<< 1	1	200	10,000	20,000	60,000

$$\xrightarrow{\hspace{10em}}$$

Increasing reactivity

The presence of unsaturation on β-carbon in primary halides increases the rate of S_N2 reaction. Alkyl halides and benzyl halides are good substrates for S_N2 reaction.

The presence of carbonyl group at α-carbon is one of the most suitable substrate for S_N2 reaction. Electron withdrawing groups always increase stability of the transition state.

The presence of hetero (O, N, S) **atom on α-carbon** in primary halides also increases reactivity of the substrate for S_N2 reaction. Lone pair present on hetero atom stabilises the stability of transition state by delocalization.

Substrate	$H_2C=CHCH_2X$	$C_6H_5CH_2X$	CH_3-O-CH_2X	$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2X$
Relative reactivity	79	200	920	10^5

In fact, primary, secondary and tertiary alkyl halides having carbonyl group at α-carbon gives S_N2 reaction. This is an exceptional reaction which takes place at tertiary carbon because the carbonyl group accelerates S_N2 reaction very much.

Compounds RF, ROH, ROR' and RNH_2 do not undergo S_N2 reaction because F^-, OH^-, OR^-, NH_2^- are very poor leaving groups.

Solvent effects in S_N2 Reaction: The rates of many S_N2 reactions are affected by the solvent. *Protic solvents*—those that contain —OH or —NH group are generally the worst solvents for S_N2 reactions. *Polar protic solvents*, (like water, alcohols and carboxylic acids), which have strong dipoles but don't have —OH or —NH groups are the best. In contrast to protic solvents, which decrease the rates of S_N2 reactions by lowering the ground state energy of nucleophile, polar aprotic solvents increase the rates of S_N2 reactions by raising the ground state energy of nucleophile. Particularly valuable solvents are acetonitrile (CH_3CN); dimethyl formamide [$(CH_3)_2NOCH$, abbreviated DMF]; dimethyl sulphoxide [$(CH_3)_2SO$ abbreviated DMSO] and hexamethyl phosphoramide [$\{(CH_3)_2N\}_3PO$, abbreviated HMPA]. For instance a rate increase of 2,00,000 has been observed on changing from methanol to HMPA for the reaction of azide ion with 1-bromobutane.

$$\underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} + \underset{\text{Azide ion}}{N_3^-} \longrightarrow \underset{\text{1-Azidobutane}}{CH_3CH_2CH_2CH_2N_3} + \underset{\text{Bromide ion}}{Br^-}$$

Solvent	CH_3OH	H_2O	DMSO	DMF	CH_3CN
Type of Solvent (Polar)	Protic	Protic	Aprotic	Aprotic	Aprotic
Relative reactivity (Increasing)	1	7	1300	2800	5000
Dielectric constant (ε)	32.6	78.5	48.9	36.7	37.5

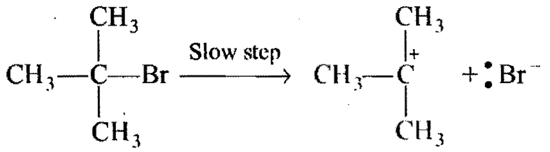
Higher concentration of nucleophile favours S_N2 reaction where low concentration favours the S_N1 mechanism. Neopentyl bromide shows S_N2 path with ethoxide ion, but S_N1 path with ethanol.

(b) S_N1 Reactions : S_N1 stands for **unimolecular reaction.** When the rate of nucleophilic substitution reaction depends only on the concentration of the substrate, the reaction is of first order change and is represented as S_N1.

$$\text{Rate} \propto [\text{Substrate}]$$

The hydrolysis of tert.-butyl bromide is an example of S_N1 reaction. The reaction consists of two steps:

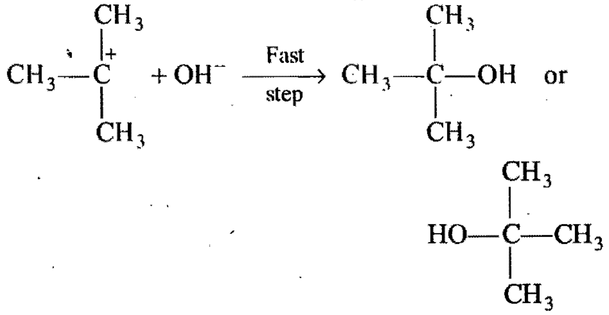
Step 1. The substrate undergoes heterolytic fission forming a carbocation. This is the slow process and rate determining step.



$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}Br \xrightarrow{\text{Slow step}} CH_3{-}\underset{CH_3}{\overset{CH_3}{C^+}} + :Br^-$$

The carbocation is planar as the central positively charged carbon atom is sp^2-hybridized.

Step 2. The nucleophile (OH^-) can attack the planar carbocation from either side to form tert.-butyl alcohol and the low concentration of OH^- favours S_N1 reaction.



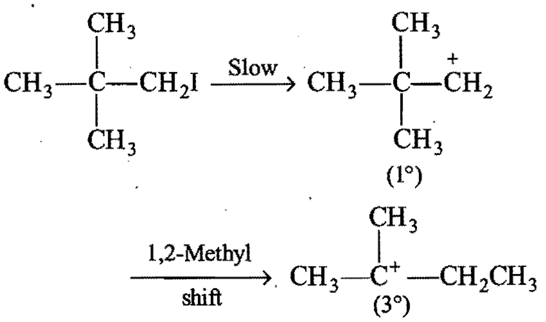
$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C^+}} + OH^- \xrightarrow[\text{step}]{\text{Fast}} CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}OH \text{ or } HO{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3$$

This is a fast process. Energy required for the first step, *i.e.*, ionisation step is supplied by the formation of many ion dipole bonds between ions produced and the solvent. Therefore, solvents have prominent role in the reaction occurring through S_N1 mechanism and the reaction is completed in two stages.

So, the older bond is broken first (step 1) and then only new bond is formed (step 2).

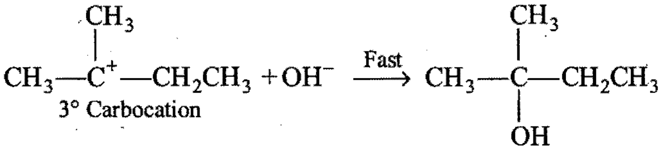
In another example, the carbocation formed (in step 1) can undergo rearrangement **(1,2-methyl shift)** to give more stable carbocation. The nucleophile then attacks to the carbocation (in step 2) to form corresponding alcohol.

Step 1.



$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2I \xrightarrow{\text{Slow}} CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\overset{+}{C}H_2 \; (1°) \xrightarrow[\text{shift}]{\text{1,2-Methyl}} CH_3{-}\overset{CH_3}{C^+}{-}CH_2CH_3 \; (3°)$$

Step 2.

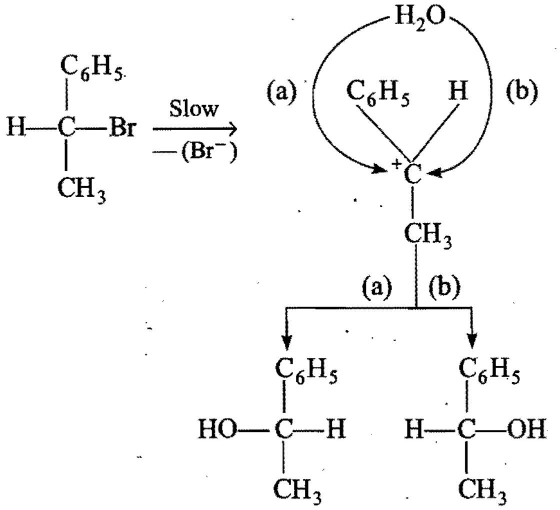


$$\underset{\text{3° Carbocation}}{CH_3{-}\overset{CH_3}{C^+}{-}CH_2CH_3} + OH^- \xrightarrow{\text{Fast}} CH_3{-}\underset{OH}{\overset{CH_3}{C}}{-}CH_2CH_3$$

As a result of S_N1 reaction, there can be **racemisation** and **inversion.** The racemisation is due to inverting nucleophilic displacement of halogen atom from the alkyl halide by the halide in solution.

For example, when (–) 2-bromo butane having chiral centre is treated with low concentration of nucleophile (OH^-), it forms (+)2-butanol. There is also loss in optical activity due to formation of *d*- and *l*-isomer (racemic) because of S_N1 reaction. The more stable the carbocation, the greater is the proportion of racemisation.

In another example of 1-bromo-1-phenylethane [$C_6H_5CH(Br)CH_3$], the S_N1 reaction involves racemisation plus inversion.



Enantiomers

(a) Inversion (b) Retention

The nucleophilic reagent attacks both (a) the back side and (b) the front side of the carbocation. Back side attack (a) predominates. The two enantiomers constitute the racemic modification.

Thus, in S_N1 reaction, racemization as well as inversion is observed, while in case of S_N2 complete inversion takes place (where chiral carbon exist).

S_N1 reaction is favoured by heavy (bulky) groups on the carbon atom attached to halogens; *i.e.*, the order of reactivity is:

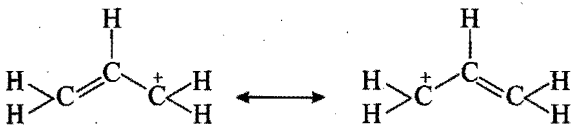
$$\underset{\text{Tertiary}}{R_3C—X} > \underset{\text{Secondary}}{R_2CH—X} > \underset{\text{Primary}}{RCH_2—X} > \underset{\text{Methyl}}{CH_3—X}$$

and nature of carbocation **(decreasing stability)** in substrate is:

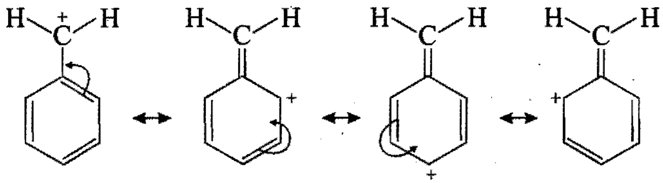
S_N1 order:

Benzyl > allyl > tertiary > secondary > primary > methyl halides

Allylic and benzylic carbocations are resonance stabilized.



(Allylic carbocation)



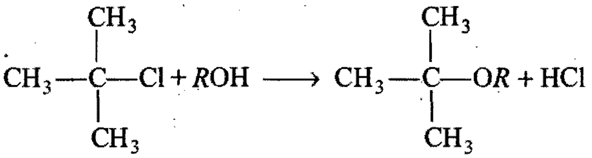
(Benzyl carbocation)

Leaving group reactivity for S_N1 reaction may be given as,

$$\xrightarrow[\text{Increasing leaving group reactivity}]{H_2O < Cl^- < Br^- < I^- \approx TosO^-}$$

The best leaving group should be those that are most stable that is conjugate bases of strong acids. An identical reactivity order is found for S_N2 and S_N1 reaction. In S_N1 reaction it is very important because leaving group is directly involved in rate determining step.

Solvent effect in S_N1 reaction: S_N1 reaction takes place much more rapidly in polar solvents than in non-polar solvents. In the reaction of 2-chloro-2-methylpropane, for example, a rate increase of 1,00,000 is observed on going from ethanol to water. The rate increase on going from hydrocarbon solvents to water are so large that they cannot be measured accurately.



$$CH_3—\underset{CH_3}{\overset{CH_3}{|C}}—Cl + ROH \longrightarrow CH_3—\underset{CH_3}{\overset{CH_3}{|C}}—OR + HCl$$

Solvent	CH_3COOH	C_2H_5OH	CH_3OH	HCOOH	HOH
Relative reactivity (increasing)	<1	1	4	5,000	1,00,000
Dielectric constant (ε)	6	7	33	58	78

Dielectric constant is a measure of the ability of a compound. Polar solvents have high dielectric constant. The positive and negative charged species are best separated in a medium with higher dielectric constant. The standard dielectric is a vacuum (ε = 1).

Distinction between S_N2 and S_N1 reactions

S. No.	Factors	S_N2 Reactions	S_N1 Reactions
1.	Number of steps	**One:** $R:L + :Nu^- \longrightarrow R:Nu + :L^-$	**Two:** (i) $R:L \xrightarrow{\text{Slow}} R^+ + :L^-$ (ii) $R^+ + :Nu^- \xrightarrow{\text{Fast}} R:Nu$
2.	Reaction rate and order	**Second order:** Rate ∝ [Substrate] [Nucleophile] or $\text{Rate} = K_2[RL][:Nu^-]$	**First order:** Rate ∝ [Substrate] or $\text{Rate} = K_1\,[RL]$
3.	Molecularity	Bimolecular	Unimolecular
4.	TS of slow step	$\overset{\delta^-}{:Nu}---C---\overset{\delta^-}{:L}$	$:Nu---\overset{\delta^+}{C}---\overset{\delta^-}{L}---Nu:$
5.	Reacting nucleophile	The nucleophile attacks the carbon of the substrate exclusively from the back side.	The nucleophile can attack the carbon of the substrate both on the back and front sides although the back side attack predominates.
6.	Stereo-chemistry	Complete inversion of configuration takes place.	Inversion and retention takes place.
7.	Reactivity order of alkyl halides	Methyl > 1° > 2° > 3° halides. (I > Br > Cl > F)	3° > 2° > 1° > methyl halide. (I > Br > Cl > F)
8.	Rearrange-ment	No rearranged product is formed (except for allylic).	Rearranged products can be formed.
9.	Nature of nucleophiles	Favoured by strong and high concentration of nucleophiles.	Favoured by mild and low concentration of nucleophiles
10.	Polarity	Favoured by solvents of low polarity.	Favoured by solvents of high polarity.
11.	Reaction rate determining factor	By steric hindrance.	By electronic factor (stability of R^+).
12.	Catalysis	Not catalysed by any catalyst (phase transfer).	Catalysed by Lewis and Bronsted acids, *e.g.*, Ag^+, $AlCl_3$, $ZnCl_2$ and strong HA.

(iii) Electrophilic substitution : Electrophilic substitution involves the attack by an electrophile. It is represented as S_E (S stands for substitution and E stands for electrophile). If the order of reaction is 1, it is written as S_{E^1} (unimolecular) and if the order is 2, it is S_{E^2} (bimolecular).

S_{E^1} Reaction Mechanism

Electrophilic substitution in aliphatic compounds (S_{E^1}) are very rare; some of the important examples are:

(a) Replacement of the metal atom in an organometallic compound by hydrogen :

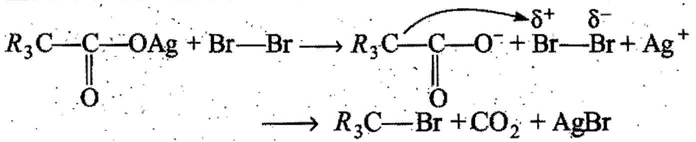
$$R—M + H^+ \longrightarrow R—H + M^+$$

e.g., $CH_3CH_2MgBr \xrightarrow{-MgBr} CH_3CH_2^- \xrightarrow{H^+} CH_3CH_3$

$$CH_3CH_2MgBr + HBr \longrightarrow CH_3CH_3 + MgBr_2$$

$$CH_3CH_2Na + C_6H_6 \longrightarrow CH_3CH_3 + C_6H_5Na$$

(b) Decarboxylation of silver salt of carboxylic acid by means of bromine :



$$R_3C—\underset{\underset{O}{\|}}{C}—OAg + Br—Br \longrightarrow R_3C—\underset{\underset{O}{\|}}{C}—O^- + \overset{\delta+}{Br}—\overset{\delta-}{Br} + Ag^+ \longrightarrow R_3C—Br + CO_2 + AgBr$$

(c) Isotopic exchange of hydrogen for deuterium or tritium :

$$R—H + D^+ \rightleftharpoons R—D + H^+$$

$$R—H + T^+ \rightleftharpoons R—T + H^+$$

S_{E^2} Reaction Mechanism

Electrophilic substitution (S_{E^2}) is very common in benzene nucleus (aromatic compounds) in which π-electrons are highly delocalized and an electrophile can attack this region of high electron density.

In all electrophilic aromatic substitution reactions, it involves:

Step 1. The formation of an electrophile, E^+, *i.e.*,

In halogenation;

$$Cl—Cl + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$$

In nitration;

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

In sulphonation;

$$2H_2SO_4 \longrightarrow SO_3 + HSO_4^- + H_3O^+$$

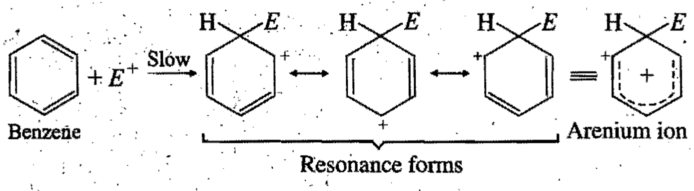
In Friedel-Crafts reaction;

$$RCl + AlCl_3 \longrightarrow R^+ + AlCl_4^-$$

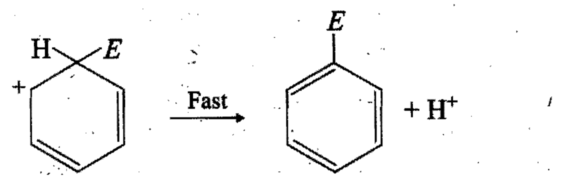
$$RCOCl + AlCl_3 \longrightarrow R\overset{+}{C}O + AlCl_4^-$$

Step 2. The electrophile attacks the aromatic ring to form an intermediate, known as carbocation (arenium ion or σ-complex or Wheland intermediate) which is stabilized by resonance.

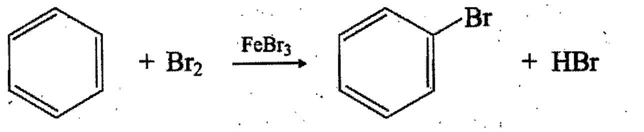
The formation of intermediate arenium ion is slow and hence rate determining step.



Step 3. Carbocation loses the proton to form substitution product.



The bromination of benzene in the presence of $FeBr_3$ is an example of electrophilic substitution.

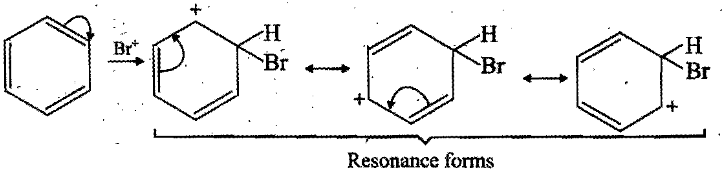


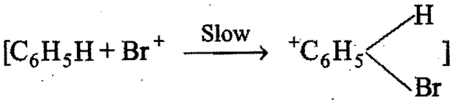
Mechanism :

Step 1. Formation of electrophile takes place.

$$Br—Br + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$$

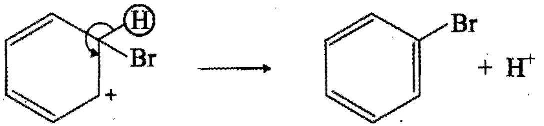
Step 2. The electrophile (Br^+) attacks the benzene ring to form a resonance stabilized carbocation.



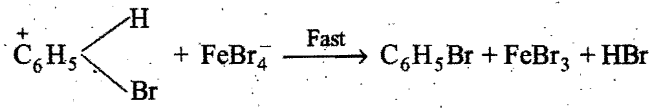


$$[C_6H_5H + Br^+ \xrightarrow{Slow} {}^+C_6H_5\begin{smallmatrix}H\\Br\end{smallmatrix}]$$

Step 3. Elimination of proton occurs and the substitution product is formed.



$$(H^+ + FeBr_4^- \longrightarrow FeBr_3 + HBr)$$



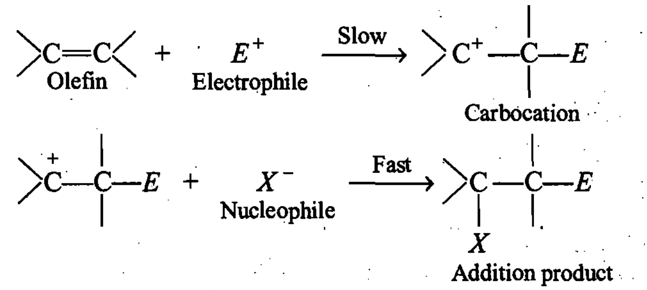
$$\overset{+}{C_6H_5}\begin{smallmatrix}H\\Br\end{smallmatrix} + FeBr_4^- \xrightarrow{Fast} C_6H_5Br + FeBr_3 + HBr$$

Similarly, nitration, sulphonation and Friedel-Crafts reaction, etc., in benzene nucleus are the other examples of electrophilic substitution (see section **16.5**).

5.9 MECHANISM OF ADDITION REACTIONS

The addition reactions are the reactions of the double or triple bonds. These reactions may be initiated by electrophiles, nucleophiles or free radicals. The molecules having $>C=C<$ or $—C \equiv C—$ are readily attacked by electrophilic reagents while molecules having $>C=O$ or $—C \equiv N$ are readily attacked by nucleophilic reagents.

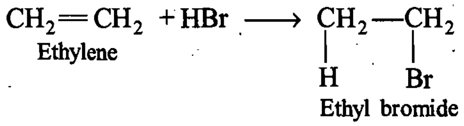
(i) Electrophilic addition reactions : In electrophilic addition reactions, an electrophile approaches the double or triple bond and in the first step forms a covalent bond with one of the carbon atoms resulting in the formation of carbocation which then takes up a nucleophile to result in addition product.



$$>C{=}C< + E^+ \xrightarrow{\text{Slow}} >\overset{+}{C}-\overset{|}{\underset{|}{C}}-E$$

$$>\overset{+}{C}-\overset{|}{\underset{|}{C}}-E + X^- \xrightarrow{\text{Fast}} >\underset{X}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-E$$

The addition of HBr on ethylene is an example of electrophilic addition. Ethylene is a symmetrical olefin.



$$CH_2{=}CH_2 + HBr \longrightarrow \underset{H}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}}$$

Mechanism :

Step 1. Hydrogen bromide gives a proton and bromide ion.

$$HBr \longrightarrow \underset{\text{Electrophile}}{H^+} + \underset{\text{Nucleophile}}{:Br^-}$$

Step 2. The electrophile attacks the double bond to form a carbocation.

$$H_2C{=}CH_2 + H^+ \longrightarrow H_2\overset{+}{C}-CH_3 \text{ or } CH_3-\overset{+}{C}H_2$$

Carbocation

Step 3. The nucleophile (Br^- ion) now attacks the carbocation to form the addition product.

$$\left.\begin{array}{l} CH_3-\overset{+}{C}H_2 + :Br^- \longrightarrow CH_3-CH_2Br \\ \overset{+}{C}H_2-CH_3 + :Br^- \longrightarrow BrCH_2-CH_3 \end{array}\right\} \text{Identical}$$

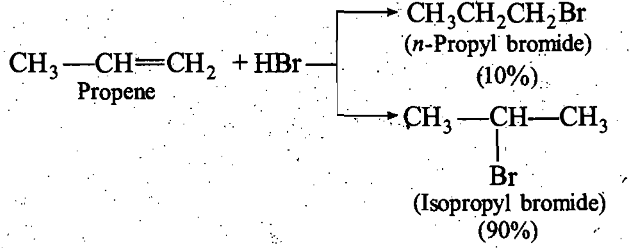
Note : Other reagents like HCl, HI, $H_2SO_4 (H^+ + HSO_4^-)$, H_3O^+, HOCl, Br_2, Cl_2, etc., add to ethylene similarly. The reactivity of halogen acids is HI > HBr > HCl while in the case of halogens, the order is $Cl_2 > Br_2 > I_2$.

This clearly indicates that the reaction proceeds in two steps: (a) formation of carbocation (more stable) and (b) attack of nucleophile on the carbocation.

Stability of carbocation:

3° > benzylic > allylic ~ 2° > 1° > methyl

In case both alkene and the adding reagent are unsymmetrical, two products are expected.



$$CH_3-CH{=}CH_2 + HBr \begin{cases} \longrightarrow CH_3CH_2CH_2Br \\ \longrightarrow CH_3-\underset{Br}{\underset{|}{CH}}-CH_3 \end{cases}$$

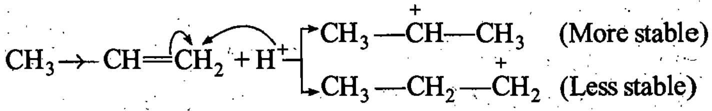
Experimentally, it is observed that isopropyl bromide is the major product. This can be explained on the basis of following mechanism:

Consider the addition of HBr to propene which is unsymmetrical in nature.

Step 1. Hydrogen bromide gives a proton (H^+) and a bromide ion (Br^-).

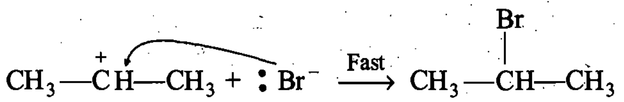
$$HBr \longrightarrow \underset{\text{Attacking electrophile}}{H^+} + :Br^-$$

Step 2. The proton (H^+) attacks the π-bond to give a stable carbocation.



$$CH_3 \rightarrow CH{=}CH_2 + H^+ \begin{cases} CH_3-\overset{+}{C}H-CH_3 \\ CH_3-CH_2-\overset{+}{C}H_2 \end{cases}$$

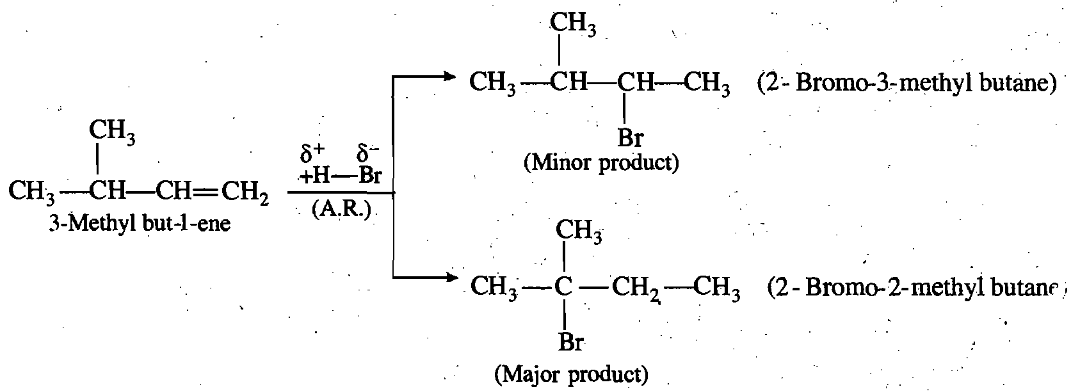
Step 3. The nucleophile bromide ion attacks the more stable carbocation to give isopropyl bromide (major product).



$$CH_3-\overset{+}{C}H-CH_3 + :Br^- \xrightarrow{\text{Fast}} CH_3-\overset{Br}{\overset{|}{C}H}-CH_3$$

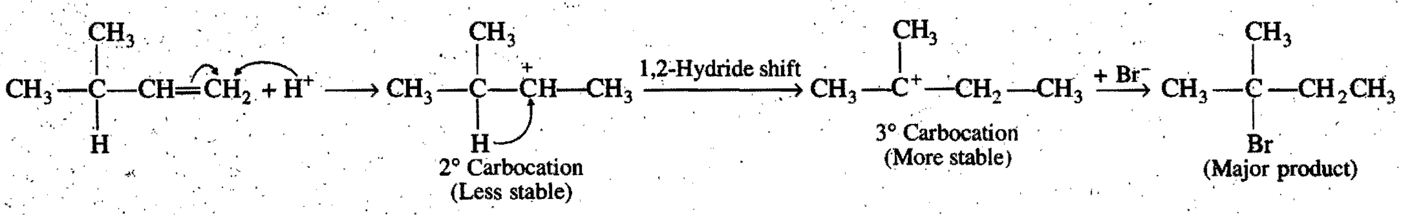
Hence, there may be 1,2-hydride shift or 1,2-methyl shift or 1,2-phenyl shift to give more stable carbocation, than the less stable one (3° > 2° > 1°).

e.g.,

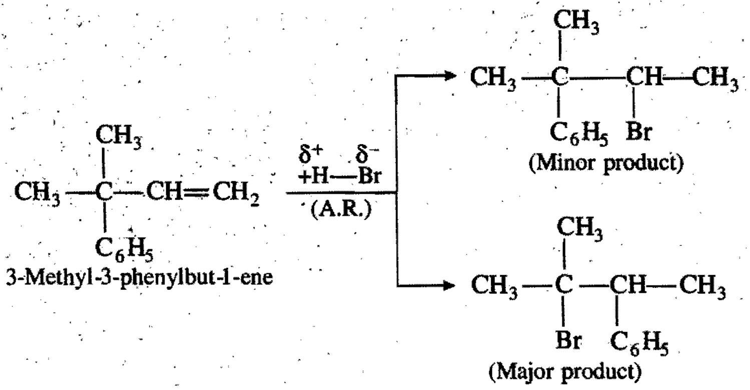


$$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH{=}CH_2 \xrightarrow[\text{(A.R.)}]{\overset{\delta+}{H}-\overset{\delta-}{Br}} \begin{cases} CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{Br}{\underset{|}{C}H}-CH_3 \\ CH_3-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_2-CH_3 \end{cases}$$

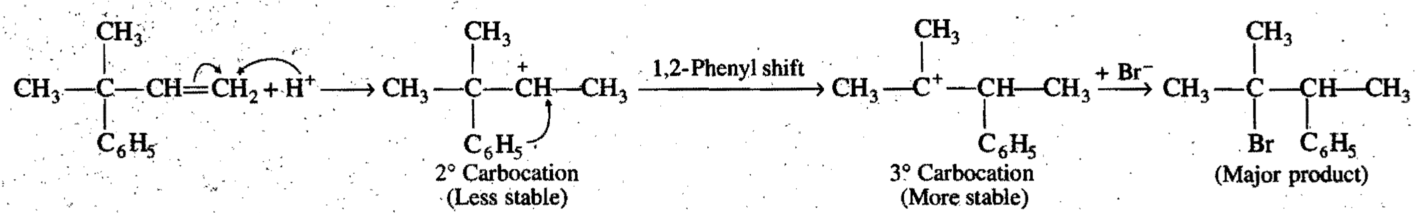
It can be explained by **1,2-hydride shift.**



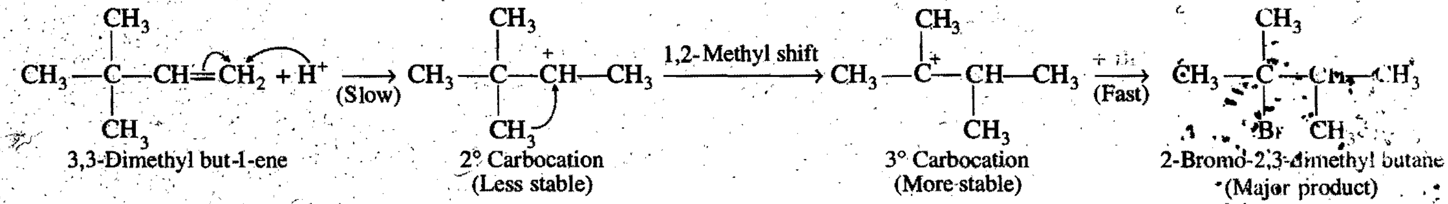
Other example is:



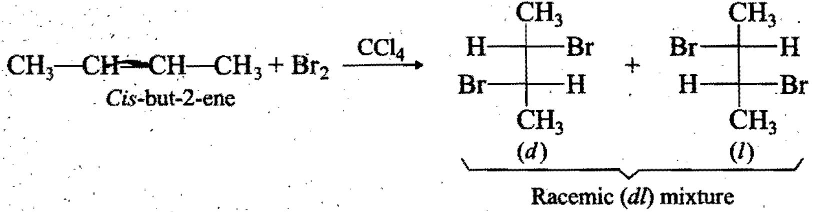
It can be explained by **1,2-phenyl shift.**



Similarly, it can be explained by **1,2-methyl shift.**



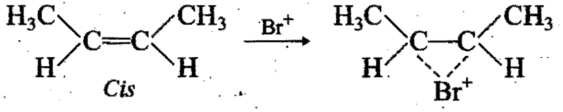
Alkene gives anti addition reaction with bromine. *Cis*-alkene gives *dl* mixture and *trans* alkene gives *meso*-form.



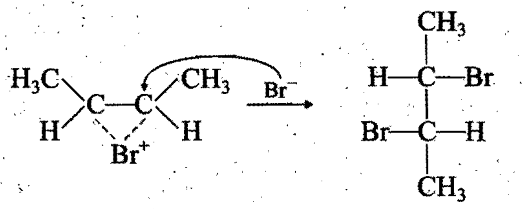
This addition proceeds through the formation of cyclic bromonium ion intermediate when Br$^+$ attacks π-electrons.

Mechanism:

Step 1.

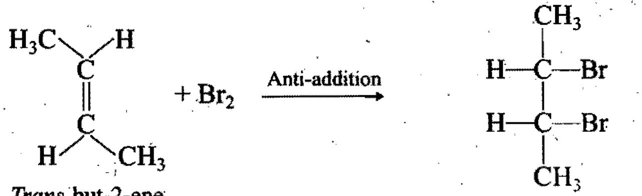


Step 2.



Racemic mixture

While *trans*-but-2-ene adds bromine in presence of CCl_4 to give the inactive *meso*-product.



Trans-but-2-ene

Meso-2,3-dibromobutane

Addition reactions in alkadienes:

Conjugated alkadienes (buta-1,3-diene) reacts with halogens, halogen acids, hydrogen and water, etc., to yield a mixture of 1,2- and 1,4-addition products. At low temperature, the **1,2-addition** is preferred, whereas at high temperature, the **1,4-addition** predominates.

Some of the important examples are:

Addition of halogens

$$\underset{\text{Buta-1,3-diene}}{H_2C{=}CH{-}CH{=}CH_2} + Br_2 \longrightarrow \underset{\substack{\text{3,4-Dibromobut-1-ene}\\ \text{(1,2-addition)}}}{CH_2Br{-}CHBrCH{=}CH_2}$$

$$\longrightarrow \underset{\substack{\text{1,4-Dibromobut-2-ene}\\ \text{(1,4-addition)}}}{BrCH_2{-}CH{=}CH{-}CH_2Br}$$

Mechanism:

Step 1. The halogen molecule (Br_2) undergoes heterolytic fission to give bromium ion (electrophile) and a bromide ion (nucleophile).

$$Br_2 \longrightarrow \underset{\substack{\text{Bromium}\\ \text{ion}}}{Br^+} + \underset{\substack{\text{Bromide}\\ \text{ion}}}{:Br^-}$$

Step 2. The bromium ion attacks the double bond to give a resonance stabilized carbocation.

$$(H_2C{=}CH{-}CH{=}CH_2 \longrightarrow H_2C{=}CH{-}\overset{+}{C}H{-}\overset{-}{C}H_2)$$

$$H_2C{=}CH{-}CH{=}CH_2 + Br^+ \longrightarrow \underset{(A)}{H_2C{=}CH{-}\overset{+}{C}H{-}CH_2Br}$$

$$\underset{(A)}{H_2C{=}CH{-}\overset{+}{C}H{-}CH_2Br} \longleftrightarrow \underset{(B)}{\overset{+}{C}H_2{-}CH{=}CH{-}CH_2Br}$$

Step 3. Bromide ion combines with (*A*) to form 3,4-dibromobut-1-ene (1,2-addition). It combines with (*B*) to form 1,4-dibromobut-2-ene (1,4-addition).

$$\underset{(A)}{H_2C{=}CH{-}\overset{+}{C}H{-}CH_2Br} + :Br^- \longrightarrow \underset{\substack{\text{3,4-Dibromobut-1-ene}\\ \text{(1,2-addition)}}}{H_2C{=}CH{-}CHBr{-}CH_2Br}$$

$$\underset{(B)}{\overset{+}{C}H_2{-}CH{=}CH{-}CH_2Br} + :Br^- \longrightarrow \underset{\substack{\text{1,4-Dibromobut-2-ene}\\ \text{(1,4-addition)}}}{BrCH_2{-}CH{=}CH{-}CH_2Br}$$

Addition of halogen acids (HBr or HCl)

$$\underset{\text{Buta-1,3-diene}}{H_2C{=}CH{-}CH{=}CH_2} + HBr \longrightarrow \underset{\substack{\text{3-Bromobut-1-ene}\\ \text{(1,2-addition)}}}{CH_3CHBr{-}CH{=}CH_2}$$

$$\longrightarrow \underset{\substack{\text{1-Bromobut-2-ene}\\ \text{(1,4-addition)}}}{CH_3{-}CH{=}CH{-}CH_2Br}$$

Mechanism :

Step 1. HBr ionises to give a proton (H^+) and a bromide ion (Br^-). $HBr \longrightarrow H^+ + :Br^-$

Step 2. Proton attacks the double bond according to Markownikoff's rule to give a resonance stabilized carbocation.

$$H^+ + H_2C{=}CH{-}CH{=}CH_2 \longrightarrow \underset{(A)}{CH_3{-}\overset{+}{C}H{-}CH{=}CH_2} \longleftrightarrow \underset{(B)}{CH_3{-}CH{=}CH{-}\overset{+}{C}H_2}$$

Step 3. Bromide ion (Br^-) combines with (*A*) to form 3-bromobut-1-ene (1,2-addition). It combines with (*B*) to form 1-bromobut-2-ene (1,4-addition).

$$\underset{(A)}{CH_3-\overset{+}{C}H-CH=CH_2} + :Br^- \longrightarrow \underset{\substack{\text{3-Bromobut-1-ene}\\\text{(1,2-addition)}}}{CH_3-CHBr-CH=CH_2}$$

$$\underset{(B)}{CH_3-CH=CH-\overset{+}{C}H_2} + :Br^- \longrightarrow \underset{\substack{\text{1-Bromobut-2-ene}\\\text{(1,4-addition)}}}{CH_3-CH=CH-CH_2Br}$$

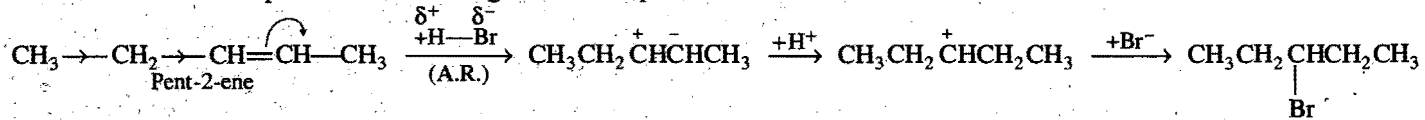
Thus, in such addition reactions, a mixture of two compounds is formed. The 1,2-addition predominates in non-ionising solvent like hexane, whereas 1,4-addition predominates in an ionising solvent like acetic acid.

After studying a large number of addition reactions (see also **Section 4.8 and 7.5**) the Russian chemist, **Markownikov**, presented a rule known as **Markownikov rule** or **Markownikoff's rule.** According to it,

"When an unsymmetrical reagent adds to an unsymmetrical alkene or alkyne, the negative part of reagent gets attached to that carbon atom of the double or triple bond which is joined to lesser number of hydrogen atoms (more substituted carbon atom)."

- Under normal conditions, always Markownikoff's rule is applied.

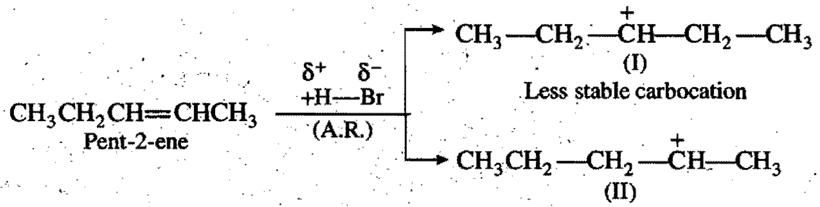
If the H-atoms linked to a double bond are equal in number, then negative part of the reagent to be added (addendum) goes to larger (higher) alkyl group. For example in pent-2-ene, the CH_3CH_2- group is more electron repelling than the CH_3- group and the addition of HBr takes place as follows to give 3-bromopentane:



$$\underset{\text{Pent-2-ene}}{CH_3\rightarrow CH_2\rightarrow CH=CH-CH_3} \xrightarrow[\text{(A.R.)}]{\overset{\delta+\ \ \delta-}{+H-Br}} CH_3CH_2\overset{+}{C}H\overset{-}{C}HCH_3 \xrightarrow{+H^+} CH_3CH_2\overset{+}{C}HCH_2CH_3 \xrightarrow{+Br^-} CH_3CH_2\underset{\substack{|\\Br}}{C}HCH_2CH_3$$

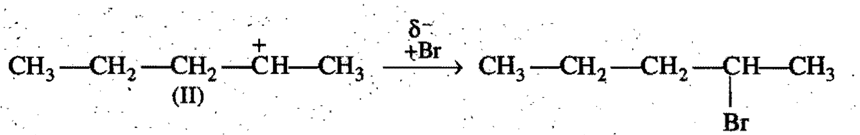
3-Bromopentane

But the addition of HBr on pent-2-ene to form 2-bromopentane can be explained on the basis of relative stabilities of the carbocation.



$$\underset{\text{Pent-2-ene}}{CH_3CH_2CH=CHCH_3} \xrightarrow[\text{(A.R.)}]{\overset{\delta+\ \ \delta-}{+H-Br}} \begin{cases} \underset{\text{(I) Less stable carbocation}}{CH_3-CH_2-\overset{+}{C}H-CH_2-CH_3} \\ \underset{\text{(II) More stable carbocation}}{CH_3CH_2-CH_2-\overset{+}{C}H-CH_3} \end{cases}$$

Since, on the basis of hyperconjugation, the carbocation (II) is more stable than the (I), hence, the addition product will be 2-bromopentane.



$$\underset{\text{(II)}}{CH_3-CH_2-CH_2-\overset{+}{C}H-CH_3} \xrightarrow{\overset{\delta-}{+Br}} CH_3-CH_2-CH_2-\underset{\substack{|\\Br}}{C}H-CH_3$$

2-Bromopentane

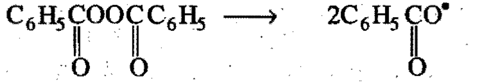
Addition in alkenes and alkynes (in solutions) are electrophilic additions, because the positive end of the adding molecule is more closer to C^- centre (carbanion) and thus, addition of electrophile, E^+, occurs in first step.

Deviation from Markownikoff's rule or Peroxide effect or Kharasch's effect or Anti-Markownikoff's rule : In presence of peroxide, propene reacts with HBr to form *n*-propyl bromide as the major product and not isopropyl bromide as expected from Markownikoff's rule.

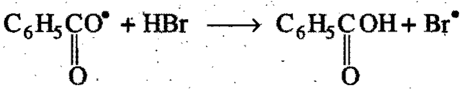
$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[+HBr]{\text{Peroxide}} \underset{n\text{-Propyl bromide}}{CH_3CH_2CH_2Br}$$

[However, this effect is not observed in the case of addition of HCl or HI]. The addition of HBr has been explained *via* free radical mechanism.

Chain initiation :



$$\underset{\text{Dibenzoyl peroxide}}{C_6H_5\underset{\substack{\|\\O}}{C}O\,O\underset{\substack{\|\\O}}{C}C_6H_5} \longrightarrow \underset{\text{Benzoyl free radical}}{2C_6H_5\underset{\substack{\|\\O}}{C}O^\bullet}$$



$$C_6H_5\underset{\substack{\|\\O}}{C}O^\bullet + HBr \longrightarrow C_6H_5\underset{\substack{\|\\O}}{C}OH + Br^\bullet$$

Chain propagation:

$$Br^\bullet + CH_3CH=CH_2 \longrightarrow \underset{\substack{\text{Secondary free radical}\\\text{as it is more stable}}}{CH_3\overset{\bullet}{C}HCH_2Br}$$

$$CH_3\dot{C}HCH_2Br + HBr \longrightarrow CH_3CH_2CH_2Br + Br^{\bullet}$$

Chain termination : $\dot{B}r + \dot{B}r \longrightarrow Br_2$

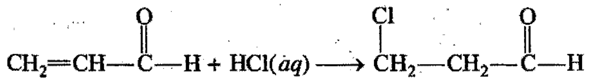
$$\dot{B}r + \dot{C}H_3 \longrightarrow CH_3Br$$

(By disproportionation)

In HBr, both the chain propagation steps are exothermic while in HCl, first step is exothermic and second step is endothermic, and in HI, first step is endothermic. On account of this, the addition of HBr is easier.

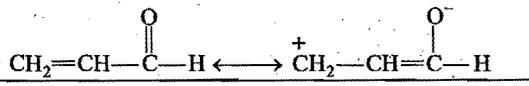
Finally, if the electron withdrawing ($-I$) groups such as $-NO_2$, $-CN$, $-CHO$, $-COR$, $-\overset{\overset{O}{\|}}{C}-Z$ ($Z = Cl, OH, OR, NH_2$), $-CX_3$, etc., are attached to the unsaturated carbon ($H_2C{=}CH{-}X$) then *anti*-Markownikoff's addition may take place.

Note: Compounds like $CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}H$ also violate Markownikoff rule.



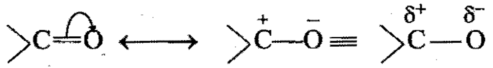
$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}H + HCl(aq) \longrightarrow \underset{}{\overset{\overset{Cl}{|}}{C}H_2}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}H$$

It is due to the following resonance:



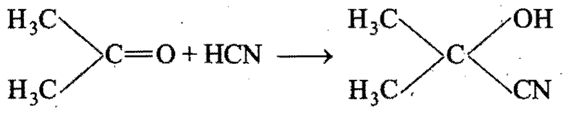
$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}H \longleftrightarrow \overset{+}{C}H_2{-}CH{=}\overset{\overset{O^-}{|}}{C}{-}H$$

(ii) Nucleophilic addition reactions : When the addition reaction occurs on account of the initial attack of nucleophile, the reaction is said to be a nucleophilic addition reaction. Due to presence of strongly electronegative oxygen atom, the π-electrons of the carbon-oxygen double bond in carbonyl group ($>C{=}O$) get shifted towards the oxygen atom and thereby such bond is highly polarised. This makes carbon atom of the carbonyl group electron deficient.



$$>C{=}\ddot{O} \longleftrightarrow >\overset{+}{C}{-}\overset{-}{O} \equiv >\overset{\delta+}{C}{-}\overset{\delta-}{O}$$

The addition of HCN to acetone ($>C{=}O$ compounds) is an example of **nucleophilic addition.**



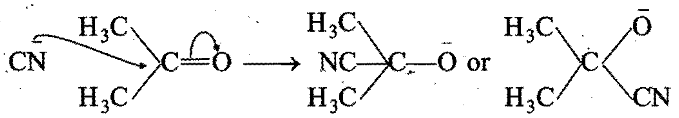
Acetone   Acetone cyanohydrin

The **mechanism** of the reaction involves the following steps:

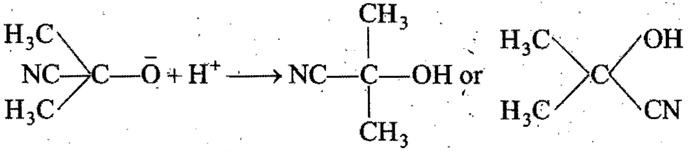
Step 1. HCN gives a proton (H^+) and nucleophile, a cyanide ion (CN^-).

$$HCN \longrightarrow H^+ + CN^-$$

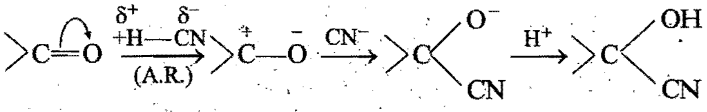
Step 2. The nucleophile (CN^-) attacks the positively charged carbon as to form an anion [H^+ does not attack the negatively charged oxygen as anion is more stable than cation].



Step 3. The proton (H^+) combines with anion to form the addition product.



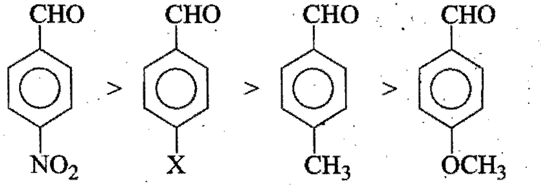
In $>C{=}O$ compounds, the addition of liquid HCN gives cyanohydrin and the addendum is CN^- ion (addition is catalysed by bases or salts of weak acids and retarded by acids or unaffected by neutral compounds) and not HCN directly.



$+I$ effect of the alkyl groups (electron releasing) decreases positive charge on carbonyl carbon atom and hence its electrophilic nature.

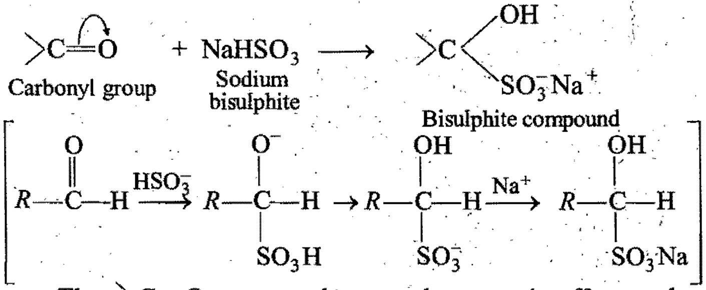
Decreasing order of $>C{=}O$ towards nuecleophilic addition (A_N) is in the order :

$$CCl_3CHO > HCHO > CH_3CHO > CH_3CH_2CHO >$$
$$CH_3COCH_3 > CH_3COC_6H_5 > C_6H_5COC_6H_5 \ldots\ldots$$



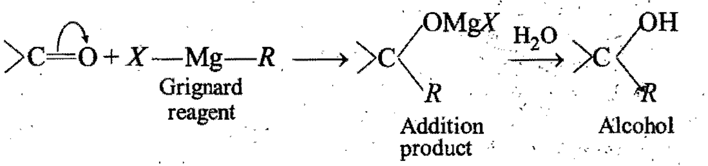
Other examples of nucleophilic addition reaction are:

(a) Addition of sodium bisulphite to $>C{=}O$ compounds:



The $>C{=}O$ group undergoes electromeric effect at the requirement of the attacking reagent. Positively charged carbon atom being less stable arrangement is attacked first by the nucleophile and the negatively charged oxygen being more stable arrangement is attacked later by electrophile.

(b) Addition of Grignard reagent to $>C{=}O$ compounds :



(c) Addition of HCN to acetylene : Acetylene as electrophilic reagent, on addition of HCN forms vinyl cyanide and since the reaction is catalysed by CN^- ion, it is described as a nucleophilic addition:

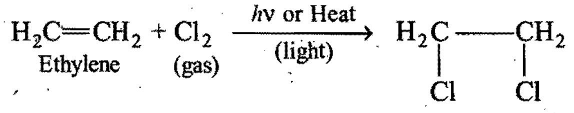
$$HC{\equiv}CH + HCN \xrightarrow{Ba(CN)_2} \underset{\text{Acrylonitrile}}{H_2C{=}CH{-}CN}$$

(d) Addition of methyl alcohol to acetylene : It forms methyl vinyl ether and the nucleophilic reagent in this reaction is alkoxide ion (—OR).

$$HC{\equiv}CH + HOCH_3 \xrightarrow{KOH} H_2C{=}CH{-}O{-}CH_3$$

(iii) Free radical addition reaction : This type of addition reaction takes place in vapour phase or in non-polar solvents (*i.e.*, Cl_2, Br_2, H_2, CO_2 and CH_4. etc.) in presence of sunlight or peroxides.

The additives are free radicals and the rate determining step suggests for addition of free radicals. For example, the photochemically catalysed addition of chlorine to ethylene may be shown as follows:



$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + \underset{\text{(gas)}}{Cl_2} \xrightarrow[\text{(light)}]{h\nu \text{ or Heat}} \underset{Cl}{\underset{|}{H_2C}}{-}\underset{Cl}{\underset{|}{CH_2}}$$

Ethylene (di)chloride

The **mechanism** of the reaction involves the following steps:

Chain initiation :

$$Cl_2(Cl{-}Cl) \longrightarrow Cl^\bullet + Cl^\bullet \qquad \ldots(i)$$

Chain propagation :

$$H_2C{=}CH_2 + Cl^\bullet \longrightarrow ClCH_2{-}\dot{C}H_2 \qquad \ldots(ii)$$

$$[\text{or } H_2C : \overset{\times}{\underset{\times}{}} CH_2 + Cl^\bullet \longrightarrow H_2\dot{C}{-}CH_2Cl]$$

$$ClCH_2{-}\dot{C}H_2 + Cl_2 \longrightarrow ClCH_2{-}CH_2Cl + \dot{C}l$$

Chain termination :

$$H_2\dot{C}{-}CH_2Cl + \dot{C}l \longrightarrow ClCH_2{-}CH_2Cl \qquad \ldots(iii)$$

Further, the addition of HBr to unsymmetrical alkenes in presence of organic peroxide, $R{-}O{-}O{-}R$ [like benzoyl peroxide, $(C_6H_5CO)_2O_2$] takes place according to **Kharasch Peroxide Effect** (anti-Markownikoff's rule) and follows the free radical addition reaction.

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + HBr \xrightarrow[\text{(Anti-MR addition)}]{ROOR} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br}$$

Peroxide effect is effective only in the case of HBr as HCl and HF do not form free radicals easily due to larger bond energy and HI with minimum bond energy is very reactive and instead forms I_2 molecule.

$$HI \longrightarrow H^\bullet + I^\bullet, \quad 2I^\bullet \longrightarrow I_2$$

(See also **section 7.6**)

5.10 MECHANISM OF ELIMINATION REACTIONS

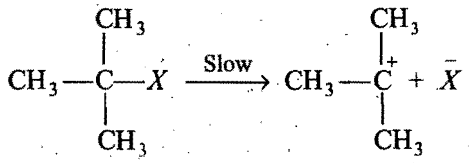
An elimination reaction, generally, involves loss of atoms or groups from adjacent carbon atoms resulting in the formation of a π-bond between these carbon atoms, so they are reverse of addition reactions. The elimination reactions are divided into two classes:

(i) E_1 reactions, E_1 stands for unimolecular elimination.

(ii) E_2 reactions, E_2 stands for bimolecular elimination.

(i) E_1 reactions : These occur in two steps.

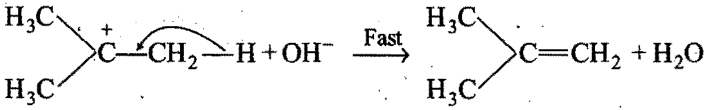
Step 1. The alkyl halide ionises to give the carbocation.



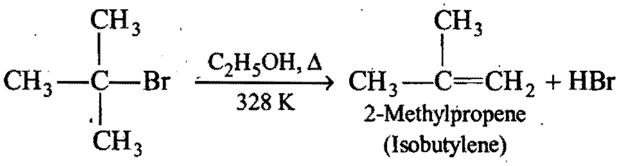
$$CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}X \xrightarrow{\text{Slow}} CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{\overset{+}{C}}}}} + \bar{X}$$

Tert. butyl halide Carbocation

Step 2. Carbocation loses a proton from the β-carbon atom by the base (nucleophile) to form alkene.



Many secondary and tertiary alkyl halides undergo E_1 elimination reactions when heated in an ionizing solvent.



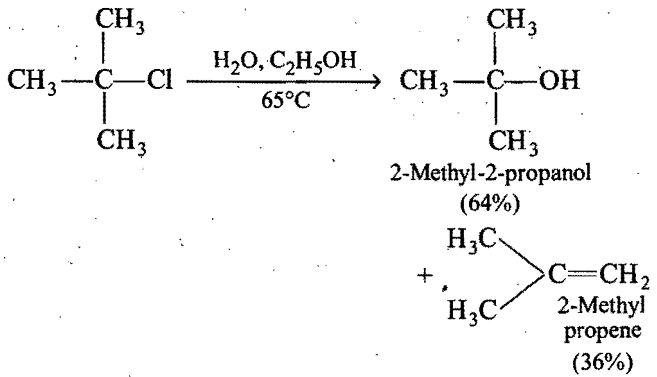
$$CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}Br \xrightarrow[328\text{ K}]{C_2H_5OH,\ \Delta} CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 + HBr$$

2-Methylpropene (Isobutylene)

Tert. butyl bromide

E_1 eliminations begin with the same unimolecular dissociation as we saw in the S_N1 reaction, but the dissociation follows the loss of H^+ from the intermediate carbocation rather than by substitution. In fact, the E_1 and S_N1 reactions normally occur in competition, whenever an alkyl halide is treated in a protic solvent with a non-basic nucleophile. The carbocations are common intermediates for both elimination and substitution reactions. Thus, the best E_1 substrates are also the best S_N1 substrates and mixtures of substitution and elimination products are usually obtained.

For example,



$$CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}Cl \xrightarrow[65°C]{H_2O,\ C_2H_5OH} CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}OH$$

2-Methyl-2-propanol (64%)

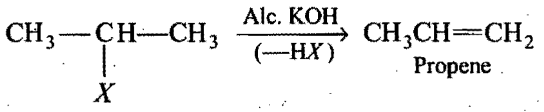
2-Methyl propene (36%)

It has been found that the mixture containing substitution and elimination products is the same whether the starting compound is chloride, bromide or iodide.

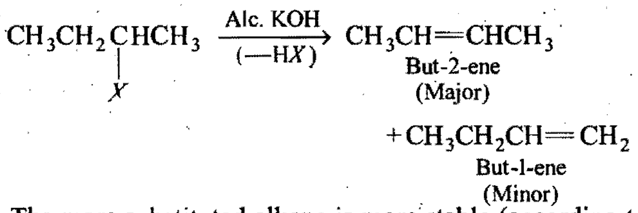
Reactivity of alkyl halide towards E_2 or E_1 elimination is the same 3° > 2° > 1°.

Dehydrohalogenation is removal of HX from alkyl halides with alcoholic KOH or KNH_2 or KO-ter-Bu (potassium tertiary butoxide) and an example of α-β elimination, *e.g.*,

$$\mathrm{CH_3{-}CH_2}X \xrightarrow[(-\mathrm{H}X)]{\text{Alc. KOH}} \underset{\text{Ethene}}{\mathrm{H_2C{=}CH_2}}$$

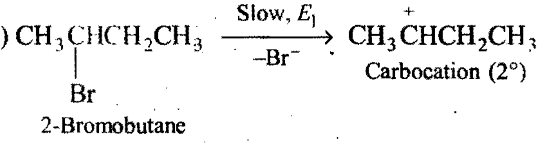


$$\mathrm{CH_3{-}\underset{\underset{X}{|}}{C}H{-}CH_3} \xrightarrow[(-\mathrm{H}X)]{\text{Alc. KOH}} \underset{\text{Propene}}{\mathrm{CH_3CH{=}CH_2}}$$



$$\mathrm{CH_3CH_2\underset{\underset{X}{|}}{C}HCH_3} \xrightarrow[(-\mathrm{H}X)]{\text{Alc. KOH}} \underset{\underset{\text{(Major)}}{\text{But-2-ene}}}{\mathrm{CH_3CH{=}CHCH_3}} + \underset{\underset{\text{(Minor)}}{\text{But-1-ene}}}{\mathrm{CH_3CH_2CH{=}CH_2}}$$

The more substituted alkene is more stable (according to Saytzeff's rule), hence, the formation of 2-butene is preferred to 1-butene.

(a) 

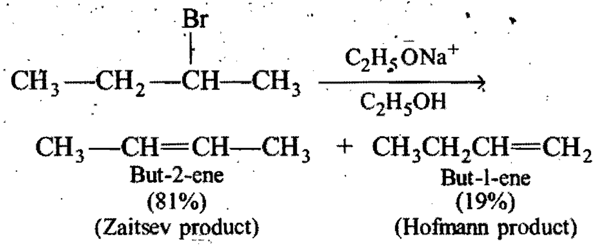
$$\underset{\text{2-Bromobutane}}{\mathrm{CH_3\underset{\underset{Br}{|}}{C}HCH_2CH_3}} \xrightarrow[-\mathrm{Br^-}]{\text{Slow, } E_1} \underset{\text{Carbocation (2°)}}{\mathrm{CH_3\overset{+}{C}HCH_2CH_3}}$$

(b) $$\underset{\text{2° Carbocation}}{\mathrm{CH_3\overset{+}{C}HCH_2CH_3}} \xrightarrow[-\mathrm{H\ (from\ C_3)}]{\text{Fast}} \underset{\underset{\text{(More substituted)}}{\text{But-2-ene}}}{\mathrm{CH_3CH{=}CHCH_3}}$$

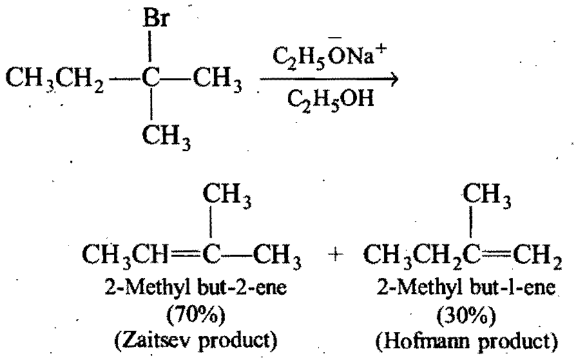
Zaitsev's rule: Elimination reactions are more complex than substitution reactions for several reasons. There is, for example, the problem of regiochemistry. What products result from loss of H*X* from an unsymmetrical halide? In fact, elimination reactions almost always give mixtures of alkene products and the best we can usually do is to predict which will be the major product.

Russian chemist, Alexander Zaitsev, proposed that base induced elimination reactions generally give the more highly substituted (more stable) alkene product—that is the alkene with more alkyl substituents on the double bond carbons.

Examples :

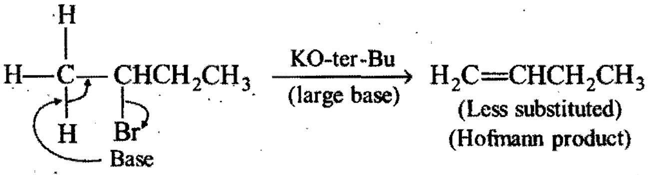
(*i*) 

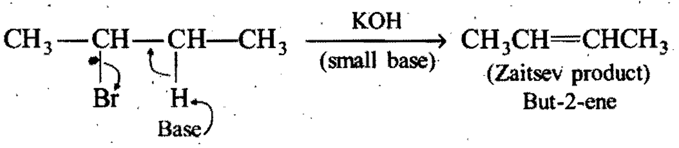
$$\mathrm{CH_3{-}CH_2{-}\overset{\overset{Br}{|}}{C}H{-}CH_3} \xrightarrow[\mathrm{C_2H_5OH}]{\mathrm{C_2H_5\bar{O}Na^+}} \underset{\underset{\underset{\text{(Zaitsev product)}}{(81\%)}}{\text{But-2-ene}}}{\mathrm{CH_3{-}CH{=}CH{-}CH_3}} + \underset{\underset{\underset{\text{(Hofmann product)}}{(19\%)}}{\text{But-1-ene}}}{\mathrm{CH_3CH_2CH{=}CH_2}}$$

(*ii*) 

$$\mathrm{CH_3CH_2{-}\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CH_3} \xrightarrow[\mathrm{C_2H_5OH}]{\mathrm{C_2H_5\bar{O}Na^+}} \underset{\underset{\underset{\text{(Zaitsev product)}}{(70\%)}}{\text{2-Methyl but-2-ene}}}{\mathrm{CH_3CH{=}\overset{\overset{CH_3}{|}}{C}{-}CH_3}} + \underset{\underset{\underset{\text{(Hofmann product)}}{(30\%)}}{\text{2-Methyl but-1-ene}}}{\mathrm{CH_3CH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2}}$$

If bases are large, due to steric hindrance, less substituted alkenes are preferred (Hofmann product).

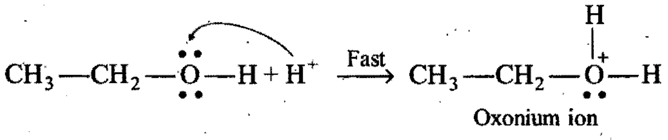




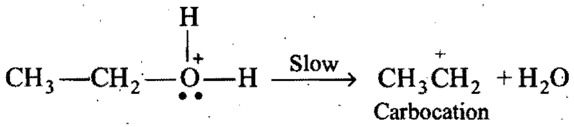
Reactivity of the substrate depends largely on the nature of leaving group (halogen atom). Thus, reactivity order is as follows:

$$\underset{\text{Fastest}}{\mathrm{I^-}} > \mathrm{Br^-} > \mathrm{Cl^-} > \underset{\text{Slowest}}{\mathrm{F^-}}$$

Dehydration of alcohol is another example of elimination reaction. When acids like conc. H_2SO_4 or H_3PO_4 are used as dehydrating agents, the mechanism is E_1. The proton given by acid is taken up by alcohol.

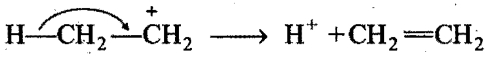


The protonated alcohol loses a water molecule and forms a carbocation.



$$\mathrm{CH_3{-}CH_2{-}\overset{\overset{H}{|_+}}{\ddot{O}}{-}H} \xrightarrow{\text{Slow}} \underset{\text{Carbocation}}{\mathrm{CH_3\overset{+}{C}H_2}} + \mathrm{H_2O}$$

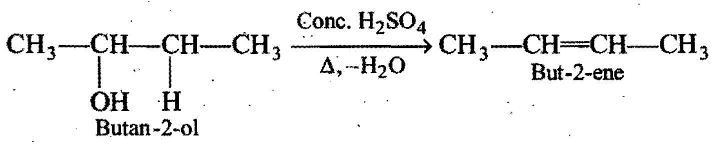
The carbocation loses a proton to form alkene.



Dehydration is removal of H_2O from alcohols, *e.g.*,

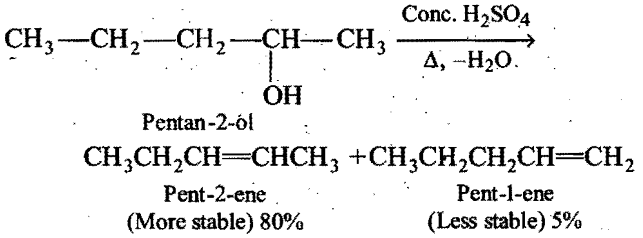
$$\mathrm{CH_3CH_2OH} \xrightarrow[(-\mathrm{H_2O})]{\text{Conc. }\mathrm{H_2SO_4}\text{, 170°C}} \mathrm{H_2C{=}CH_2}$$

$$\mathrm{CH_3CH_2CH_2OH} \xrightarrow[(-\mathrm{H_2O})]{\text{Conc. }\mathrm{H_2SO_4}\text{, 170°C}} \mathrm{CH_3CH{=}CH_2}$$



$$\underset{\text{Butan-2-ol}}{\mathrm{CH_3{-}\underset{\underset{OH}{|}}{C}H{-}\underset{\underset{H}{|}}{C}H{-}CH_3}} \xrightarrow[\Delta, -\mathrm{H_2O}]{\text{Conc. }\mathrm{H_2SO_4}} \underset{\text{But-2-ene}}{\mathrm{CH_3{-}CH{=}CH{-}CH_3}}$$

When more than one alkenes can be formed, a typical E_1 reaction yields predominantly, the more **substituted,** more stable alkene **(Saytzeff's rule)**

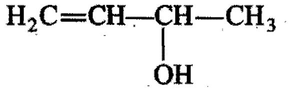


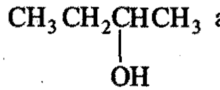
$$\underset{\text{Pentan-2-ol}}{\mathrm{CH_3{-}CH_2{-}CH_2{-}\underset{\underset{OH}{|}}{C}H{-}CH_3}} \xrightarrow[\Delta, -\mathrm{H_2O}]{\text{Conc. }\mathrm{H_2SO_4}} \underset{\underset{\text{(More stable) 80\%}}{\text{Pent-2-ene}}}{\mathrm{CH_3CH_2CH{=}CHCH_3}} + \underset{\underset{\text{(Less stable) 5\%}}{\text{Pent-1-ene}}}{\mathrm{CH_3CH_2CH_2CH{=}CH_2}}$$

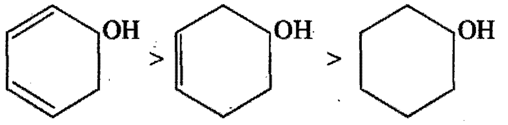
Dehydration of alcohols is in the order:

Tertiary > Secondary > Primary
(3°) (2°) (1°)

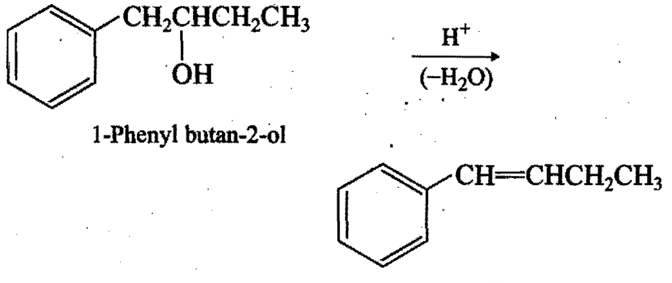
2° and 3° alcohol by E_1 process and 1° alcohol by E_2 process. Therefore, E_1 reaction is favoured in compounds in which the leaving group is at a secondary or tertiary position. Alcohols leading to conjugated alkenes are more easily dehydrated than the alcohols leading to non-conjugated alkenes.


$H_2C{=}CH{-}\underset{OH}{\underset{|}{C}H}{-}CH_3$ is more easily dehydrated than


$CH_3CH_2\underset{OH}{\underset{|}{C}H}CH_3$ and so,



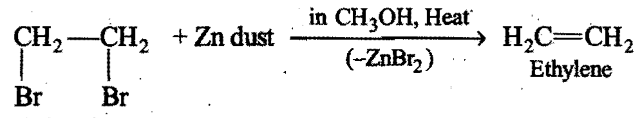
In any elimination reaction, in which the double bond can be in conjugation with a benzene ring, the conjugated product is formed in preference to the non-conjugated product (the conjugated alkene is of lower energy).


1-Phenyl butan-2-ol

1-Phenyl but-1-ene

Similarly, other examples of elimination reactions are:

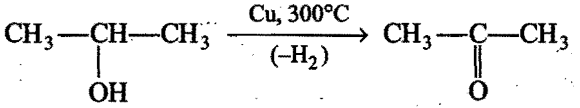
Dehalogenation : It is removal of halogens, *e.g.*,


$$\underset{Br}{\underset{|}{C}H_2}{-}\underset{Br}{\underset{|}{C}H_2} + \text{Zn dust} \xrightarrow[(-ZnBr_2)]{\text{in } CH_3OH\text{, Heat}} H_2C{=}CH_2$$

Ethylene bromide

Ethylene

Dehydrogenation : It is removal of hydrogen, *e.g.*,


$$CH_3{-}\underset{OH}{\underset{|}{C}H}{-}CH_3 \xrightarrow[(-H_2)]{Cu,\ 300°C} CH_3{-}\underset{O}{\underset{\|}{C}}{-}CH_3$$

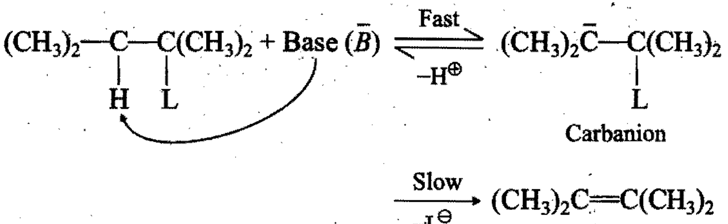
Isopropyl alcohol

Acetone

E_1-Cb (Unimolecular conjugate base elimination) reaction: If the β-hydrogen is strongly acidic and the halide ion is a poor leaving group, E_1-Cb mechanism operates, so this is another mechanism of β-elimination reaction. It involves :

Step 1. Consists of the removal of a proton by a base to form a carbanion.

Step 2. The carbanion loses a leaving group to give an alkene.


$$(CH_3)_2\underset{H}{\underset{|}{C}}{-}\underset{L}{\underset{|}{C}}(CH_3)_2 + \text{Base}(\bar{B}) \underset{-H^{\oplus}}{\overset{\text{Fast}}{\rightleftharpoons}} (CH_3)_2\bar{C}{-}\underset{L}{\underset{|}{C}}(CH_3)_2$$

Carbanion

$$\xrightarrow[-L^{\ominus}]{\text{Slow}} (CH_3)_2C{=}C(CH_3)_2$$

Alkene

Conversion of carbanion to alkene is slow step and hence the rate determining step. Since the reaction proceeds through the conjugate base (Cb) of the starting material, this is called **E_1-Cb** (elimination unimolecular conjugate base) **reaction.** Examples are:

(*i*) $CF_3{-}CHCl_2 \xrightarrow{C_2H_5O^-} CF_2{=}CCl_2$

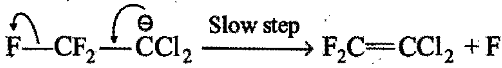
Dichlorotrifluoro ethane — 1,1-Dichloro-2,2-difluoro ethene

Mechanism :

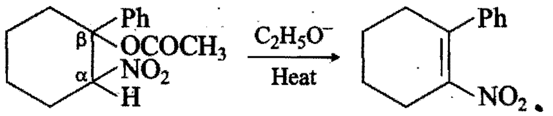
Step 1. $CF_3{-}CHCl_2 \xrightarrow[\text{Fast step}]{C_2H_5O^-} CF_3{-}\overset{\ominus}{C}Cl_2$

Carbanion

Here, carbanion is strongly stabilized by *d*-orbital resonance of Cl and strong $-I$ effect of the CF_3 group.


Step 2. $F{-}CF_2{-}\overset{\ominus}{C}Cl_2 \xrightarrow{\text{Slow step}} F_2C{=}CCl_2 + F^-$

(*ii*) $C_6H_5{-}CH_2{-}CH_2{-}F \xrightarrow{C_2H_5O^-} C_6H_5CH{=}CH_2$

(*iii*)


(ii) E_2 reactions : It is bimolecular since substrate and base are involved in the rate determining step.

$$\text{Rate} \propto [R{-}X][\text{Base}]$$

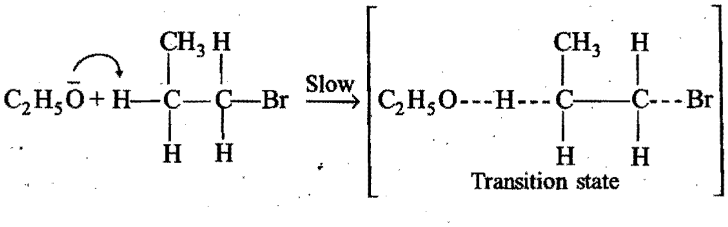
Substrate forms a transition state with a nucleophile from which abstraction of a proton from the β-carbon and expulsion of the electronegative atoms as an ion from the α-carbon atom occurs simultaneously. The dehydrohalogenation of the alkyl halides with alcoholic alkali is an example of this type. It occurs in one step. The rate of alkene formation is proportional to the concentrations of ethyl bromide as well as that of sodium ethoxide.

$$\text{Rate} = k[CH_3CH_2Br][C_2H_5O^-]$$

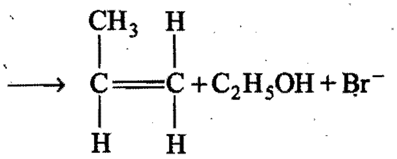
$$CH_3CH_2Br + C_2H_5O^- \longrightarrow H_2C{=}CH_2 + C_2H_5OH + Br^-$$

$$CH_3CH_2CH_2Br + C_2H_5O^- \rightarrow CH_3CH{=}CH_2 + Br^- + C_2H_5OH$$

1-Bromopropane — Propene


$$C_2H_5\bar{O} + H{-}\underset{H}{\overset{CH_3}{C}}{-}\underset{H}{\overset{H}{C}}{-}Br \xrightarrow{\text{Slow}} \left[C_2H_5O{\cdots}H{\cdots}\underset{H}{\overset{CH_3}{C}}{-}\underset{H}{\overset{H}{C}}{\cdots}Br\right]$$

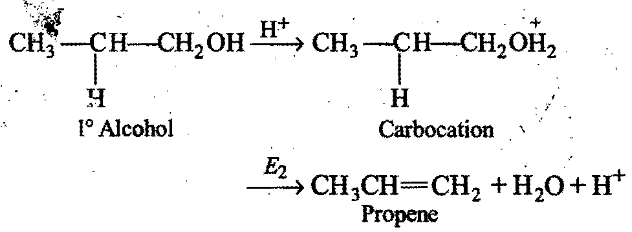
Transition state



$$\longrightarrow \underset{H}{\overset{CH_3}{C}}=\underset{H}{\overset{H}{C}} + C_2H_5OH + Br^-$$

mple is dehydration of primary alcohols.

Mechanism:

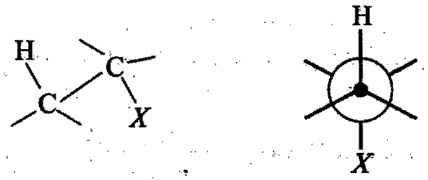


$$\underset{H}{CH_3-\underset{|}{C}H-CH_2OH} \xrightarrow{H^+} CH_3-\underset{H}{\underset{|}{C}H}-CH_2\overset{+}{O}H_2 \xrightarrow{E_2} CH_3CH=CH_2 + H_2O + H^+$$

1° Alcohol Carbocation Propene

So, dehydration of 2° and 3° alcohols takes place by E_1 process and 1° alcohol by E_2 process.

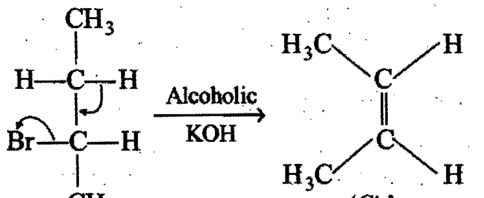
E_2 reaction always occurs with a **periplanar** geometry, meaning that all four reacting atoms—the hydrogen, the two carbons and the leaving group-lie in the same plane. Two such geometries are possible; **Syn-periplanar** in which the 'H' and '*X*' are on the same side of the molecule, and **anti-periplanar** in which 'H' and '*X*' are on opposite sides of the molecule. Of the two choices, **anti-periplanar** geometry is energetically preferred because it allows the substituents on the two carbons to adopt staggered relationship, whereas syn-geometry requires that substituents on carbon be eclipsed.



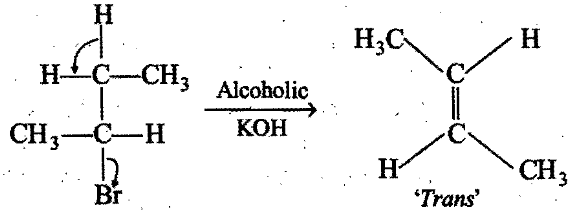
Anti-periplanar geometry
(staggered, lower energy)

Syn-periplanar geometry
(eclipsed, higher energy)

E_2 elimination is stereospecific.



'Cis'



2-Bromobutane 'Trans' 2-Butene

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

14. Which of the following is not a nucleophile?
(a) H_2 (b) CH_3OH (c) H_2O (d) NH_3
[**Ans.** (a)]

15. The peroxide effect occurs by:
(a) ionic mechanism
(b) heterolytic fission of double bond
(c) homolytic fission of double bond
(d) free radical mechanism
[**Ans.** (d)]

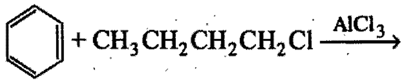
16. The nitration of benzene is:
(a) S_N1 reaction (b) S_N2 reaction
(c) S_E1 reaction (d) S_E2 reaction
[**Ans.** (d)]
[**Hint**: The first or slow step involves the attack by an electrophile (NO_2^+) with the formation of a transitory intermediate carbonium or arenium ion. In the second or fast step, hydrogen breaks as hydrogen proton to complete the substitution.]

17. Classify the following as electrophiles and nucleophiles:
(a) CN^-, (b) H_2O, (c) Br^+, (d) NO_2^-, (e) $\overset{+}{N}O_2$,
(f) CH_3OH, (g) $H_2C{=}CH_2$, (h) $RCOCl$, (i) $H_2N{-}OH$,
(j) $:CCl_2$, (k) H_3O^+, (l) NH_3, (m) BF_3, (n) $AlCl_3$,
(o) OH^-, (p) R_3N

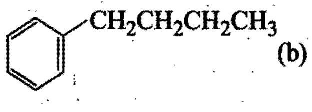
[**Ans.** Electrophiles—(c),(e),(h),(i),(j),(k),(m),(n)
Nucleophiles—(a),(b),(d),(f),(g),(l),(o),(p)]

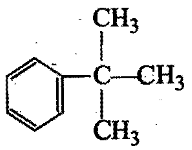
18. Which of the following most readily undergoes E_2 elimination with a strong base?
(a) 2-Bromopentane
(b) 2-Bromo-2-methyl butane
(c) 1-Bromo-2,2-dimethyl propane
(d) 2-Bromo-3-methyl butane
[**Ans.** (b)]

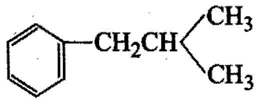
19. In the reaction:



the product formed will be:

(a)


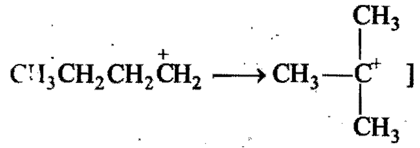
(b)


(c)


(d) all of these

[**Ans.** (b)]

[**Hint:** 3° carbocation is most stable, therefore, 1° carbocation will change into 3° carbocation.

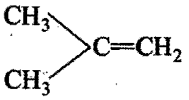


$$\mathrm{CH_3CH_2CH_2\overset{+}{C}H_2 \longrightarrow CH_3-\begin{array}{c}CH_3\\|\\C^+\\|\\CH_3\end{array}}\ ]$$

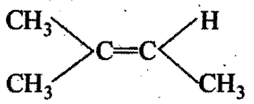
20. Which of the following alkene is most stable?

(a) $CH_3CH{=}CH_2$

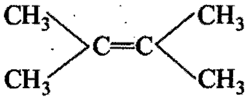
(b)



(c)



(d)



[**Ans.** (d)]

[**Hint:** In this alkene, 12-hyperconjugative forms can be written, which is maximum.]

SOME SOLVED PROBLEMS

Problem 1. *Arrange the following groups in order of increasing +I effect:*

$$CH_3^-;\quad (CH_3)_2CH^-;\quad (CH_3)_3C^-$$

Solution : Atoms or groups which release electrons towards a carbon atom are said to have a +*I* effect. Methyl group releases electrons towards carbon, *i.e.*, it has +*I* effect. +*I* effect increases as the number of methyl groups increases. Thus, the order is:

$$\underset{\text{Lowest}}{CH_3^-} < (CH_3)_2CH^- < \underset{\text{Highest}}{(CH_3)_3C^-}$$

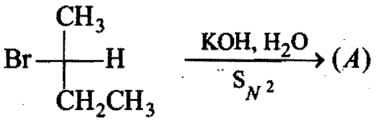
Problem 2. *Select the most stable carbocation from the following:*

$$\overset{+}{C}H_3,\ (CH_3)_2CH^+,\ CH_3\overset{+}{C}H_2,\ (CH_3)_3C^+$$

Solution : Electron releasing groups having +*I* effect stabilize the carbocations by partial neutralisation of the positive charge on carbon. A tertiary carbocation is more stable than a secondary and primary carbocation because of +*I* effect which is maximum in tertiary carbocation. Thus, $(CH_3)_3C^+$ is most stable.

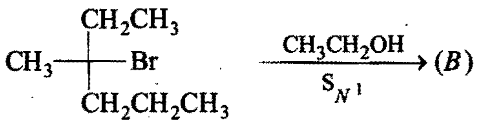
Problem 3. *What is the nature of the products in each of the following:*

(i)



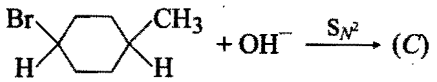
$$\begin{array}{c}CH_3\\ \mathrm{Br}-\!\!\!+\!\!\!-\mathrm{H}\\ CH_2CH_3\end{array} \xrightarrow[S_N2]{KOH,\ H_2O} (A)$$

(ii)

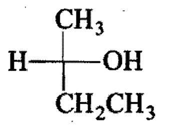


$$\begin{array}{c}CH_2CH_3\\ CH_3-\!\!\!+\!\!\!-\mathrm{Br}\\ CH_2CH_2CH_3\end{array} \xrightarrow[S_N1]{CH_3CH_2OH} (B)$$

(iii)



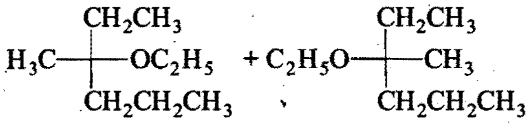
Solution : (i) (*A*) is



$$\begin{array}{c}CH_3\\ \mathrm{H}-\!\!\!+\!\!\!-\mathrm{OH}\\ CH_2CH_3\end{array}$$

(Stereospecific inversion of configuration due to S_N2 reaction)

(ii) (*B*) is



$$\mathrm{H_3C}-\!\!\!\begin{array}{c}CH_2CH_3\\ +\\ CH_2CH_2CH_3\end{array}\!\!\!-OC_2H_5 \ +\ C_2H_5O-\!\!\!\begin{array}{c}CH_2CH_3\\ +\\ CH_2CH_2CH_3\end{array}\!\!\!-CH_3$$

(Retention) (Inversion)

A mixture is formed due to S_N1 reaction (non-stereospecific reaction or racemisation)

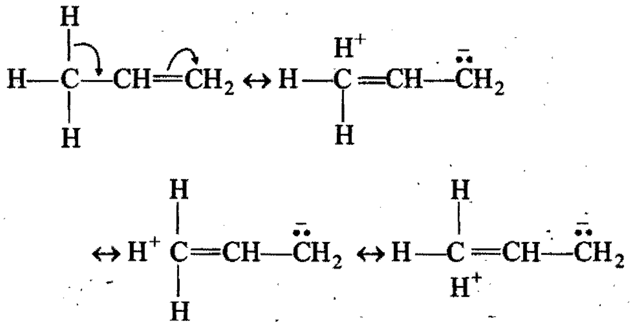
(iii)

(*trans*)

(When reaction takes place by S_N2 mechanism, there is inversion)

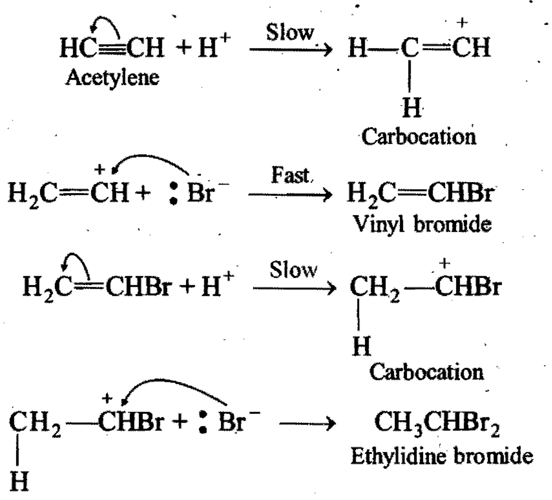
Problem 4. *Explain why alkyl group acts as electron donars when attached to a π-system.*

Solution : Due to hyperconjugation, alkyl group acts as electron donars when attached to a π-system as shown below:



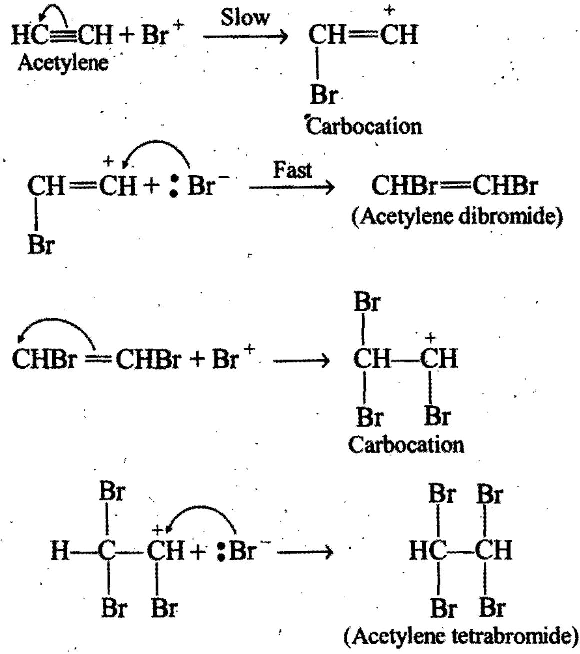
Problem 5. *Explain the reaction mechanism of the addition of* HBr *on acetylene by equations only.*

Solution : HBr ⟶ H^+ + $:Br^-$



Problem 6. *Explain the reaction mechanism of the addition of bromine on acetylene by equations only.*

Solution : $Br \colon Br \longrightarrow Br^+ + \colon Br^-$



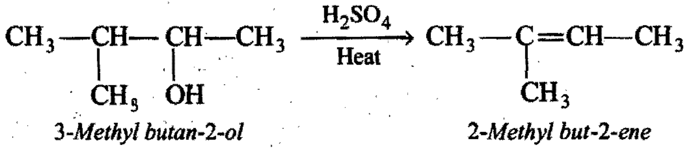
$$\underset{\text{Acetylene}}{HC\equiv CH} + Br^+ \xrightarrow{\text{Slow}} \underset{\text{Carbocation}}{\underset{\underset{Br}{|}}{CH}=\overset{+}{C}H}$$

$$\underset{\underset{Br}{|}}{CH}=\overset{+}{C}H + \colon Br^- \xrightarrow{\text{Fast}} \underset{\text{(Acetylene dibromide)}}{CHBr{=}CHBr}$$

$$CHBr{=}CHBr + Br^+ \longrightarrow \underset{\text{Carbocation}}{\underset{Br}{\overset{Br}{\overset{|}{\underset{|}{C}H}}}-\underset{\underset{Br}{|}}{\overset{+}{C}H}}$$

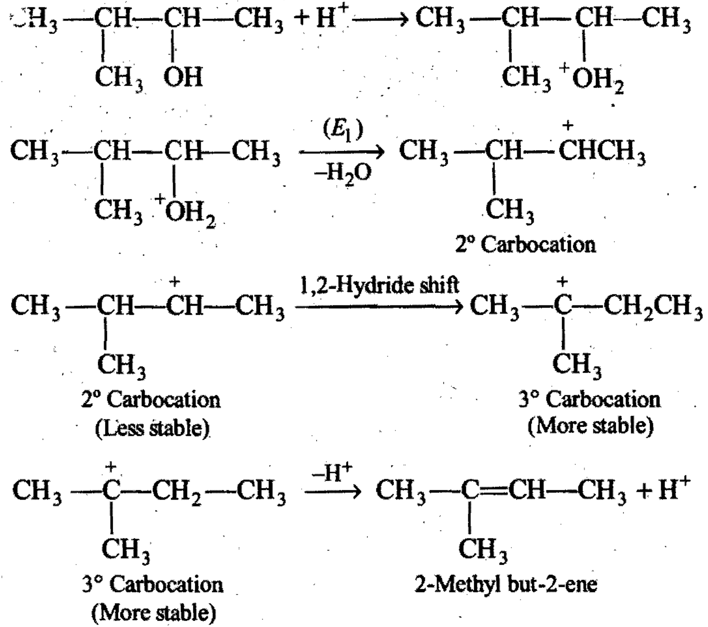
$$H-\underset{Br}{\overset{Br}{\overset{|}{\underset{|}{C}}}}-\underset{\underset{Br}{|}}{\overset{+}{C}H} + \colon Br^- \longrightarrow \underset{\text{(Acetylene tetrabromide)}}{\underset{Br}{\overset{Br}{\overset{|}{\underset{|}{HC}}}}-\underset{Br}{\overset{Br}{\overset{|}{\underset{|}{CH}}}}}$$

Problem 7. *Explain the reaction mechanism of the following reaction by equations only:*



$$\underset{\text{3-Methyl butan-2-ol}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow[\text{Heat}]{H_2SO_4} \underset{\text{2-Methyl but-2-ene}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3}$$

Solution : $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3 + H^+ \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{^+OH_2}{|}}{CH}-CH_3$$

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{^+OH_2}{|}}{CH}-CH_3 \xrightarrow[-H_2O]{(E_1)} \underset{2^\circ\ \text{Carbocation}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{+}{C}HCH_3}$$

$$\underset{\substack{2^\circ\ \text{Carbocation}\\ \text{(Less stable)}}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{+}{C}H-CH_3} \xrightarrow{\text{1,2-Hydride shift}} \underset{\substack{3^\circ\ \text{Carbocation}\\ \text{(More stable)}}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-CH_2CH_3}$$

$$\underset{\substack{3^\circ\ \text{Carbocation}\\ \text{(More stable)}}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-CH_2-CH_3} \xrightarrow{-H^+} \underset{\text{2-Methyl but-2-ene}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3} + H^+$$

Problem 8. *Classify the following reactions as S_N1, S_N2, E_1 and E_2:*

(*i*) *A first order reaction between an alkyl halide and alkali, to give alcohol, the order in alkali being zero.*

(*ii*) *The formation of an olefin from an alkyl halide and alkali, the reaction being first order in each of the reactants.*

Solution : (i) $R-X \xrightarrow{\text{Slow}} R^+ + X^-$

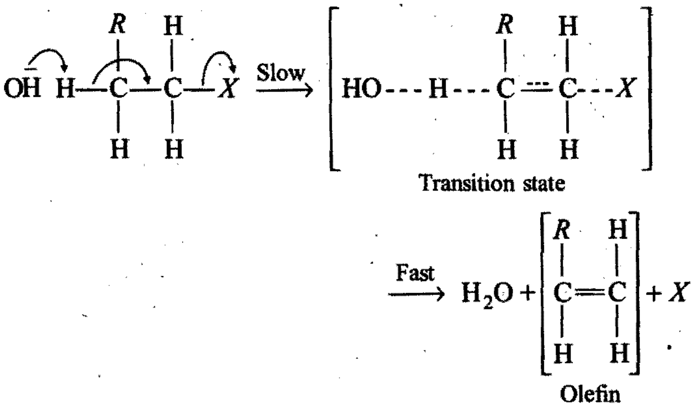
$$R^+ + OH^- \xrightarrow{\text{Fast}} ROH$$

The reaction proceeds *via* S_N1 mechanism, *i.e.*,

$$\text{Rate} \propto [\text{Alkyl halide}]$$

(ii) Rate of reaction $\propto$ [Alkyl halide][Alkali]

Thus, the reaction is bimolecular. It proceeds *via* E_2.



$$\overset{-}{O}H\ H-\underset{H}{\overset{R}{\overset{|}{\underset{|}{C}}}}-\underset{H}{\overset{H}{\overset{|}{\underset{|}{C}}}}-X \xrightarrow{\text{Slow}} \underset{\text{Transition state}}{\left[HO\text{---}H\text{---}\underset{H}{\overset{R}{\overset{|}{\underset{|}{C}}}}\overset{\text{---}}{=}\underset{H}{\overset{H}{\overset{|}{\underset{|}{C}}}}\text{---}X\right]}$$

$$\xrightarrow{\text{Fast}} H_2O + \underset{\text{Olefin}}{\left[\underset{H}{\overset{R}{\overset{|}{\underset{|}{C}}}}=\underset{H}{\overset{H}{\overset{|}{\underset{|}{C}}}}\right]} + X$$

Problem 9. *Calculate the pK values of the following organic acids and bases from their given K constants:*

(*a*) $CH_3COOH, K_a = 1.8 \times 10^{-5}$

(*b*) $CH_3OH, K_a = 3.1 \times 10^{-16}$

(*c*) $CH_3NH_2, K_b = 4.5 \times 10^{-4}$

Solution :

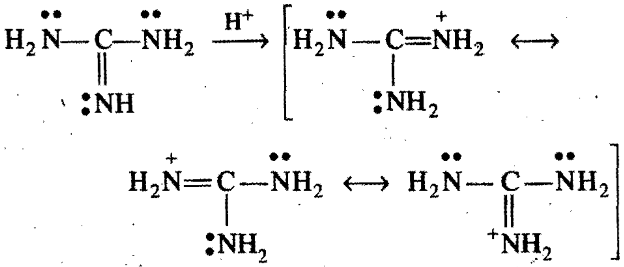
(a) $pK_a = -\log(1.8 \times 10^{-5}) = 5 - 0.255 = 4.745$

(b) $pK_a = -\log(3.1 \times 10^{-16}) = 16 - 0.491 = 15.509$

(c) $pK_b = -\log(4.5 \times 10^{-4}) = 4 - 0.653 = 3.347$

Problem 10. *Explain that, unlike other amines (RNH_2), guanidine,* $(H_2N-\underset{\underset{NH}{\|}}{C}-NH_2)$, *is a strong base.*

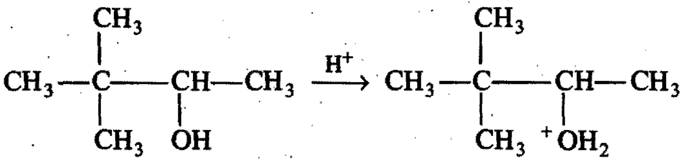
Solution : The cation formed by the addition of H^+ has three equivalent contributing structures. This greatly stabilizes the conjugate acid making it very weak and so a strong base.



$$H_2\ddot{N}-\underset{\underset{\colon NH}{\|}}{C}-\ddot{N}H_2 \xrightarrow{H^+} \left[H_2\ddot{N}-\underset{\underset{\colon NH_2}{|}}{C}=\overset{+}{N}H_2 \longleftrightarrow H_2\overset{+}{N}=\underset{\underset{\colon NH_2}{|}}{C}-\ddot{N}H_2 \longleftrightarrow H_2\ddot{N}-\underset{\underset{^+NH_2}{\|}}{C}-\ddot{N}H_2\right]$$

Problem 11. 3,3-*Dimethyl butan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetra- methylethylene as a major product. Suggest a suitable mechanism.*

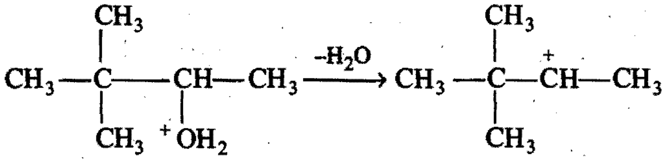
Solution : (i) Step is the protonation of hydroxyl group.



$$CH_3-C(CH_3)_2-CH(OH)-CH_3 \xrightarrow{H^+} CH_3-C(CH_3)_2-CH(\overset{+}{O}H_2)-CH_3$$

3,3-Dimethyl butan-2-ol

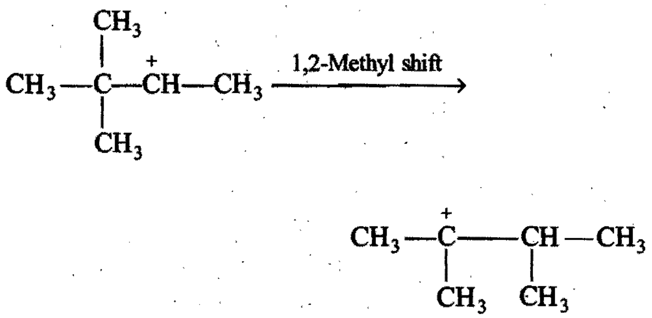
(ii) Step is the removal of H_2O to form 2° (sec.) carbocation.



$$CH_3-C(CH_3)_2-CH(\overset{+}{O}H_2)-CH_3 \xrightarrow{-H_2O} CH_3-C(CH_3)_2-\overset{+}{C}H-CH_3$$

2° Carbocation

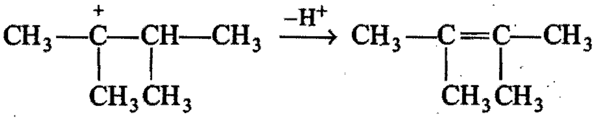
(iii) Step is the conversion of 2° carbocation to more stable 3° carbocation by 1,2-methyl shift.



$$CH_3-C(CH_3)_2-\overset{+}{C}H-CH_3 \xrightarrow{\text{1,2-Methyl shift}} CH_3-\overset{+}{C}(CH_3)-CH(CH_3)-CH_3$$

3° Carbocation

(iv) Step is the removal of H^+ to form a double bond.



$$CH_3-\overset{+}{C}(CH_3)-CH(CH_3)-CH_3 \xrightarrow{-H^+} CH_3-C(CH_3)=C(CH_3)-CH_3$$

2,3-Dimethyl but-2-ene
(Tetramethyl ethylene)

Problem 12. *Explain a possible mechanism for the S_N1 reaction of Me_3C-Br and $MeOH$.*

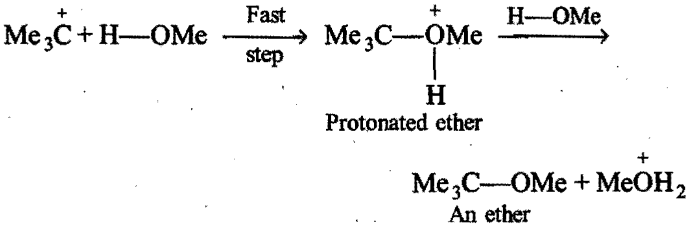
Solution :

$$Me_3C-Br + H-OMe \longrightarrow \underset{\text{An ether}}{Me_3C-OMe} + HBr$$

Step 1. The substrate undergo heterolytic fission forming a carbocation. This is the slow rate determining step.

$$Me_3C-Br \xrightarrow{\text{Slow step}} Me_3C^+ + Br^-$$

Step 2. The fast step is the attack of nucleophile, MeOH on the carbocation to form protonated ether, and is followed by the rapid loss of its proton to a second molecule of nucleophile to form an ether.



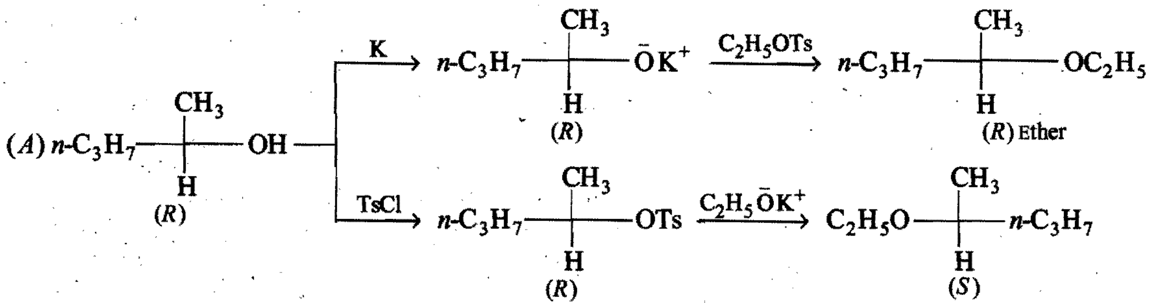
$$Me_3\overset{+}{C} + H-OMe \xrightarrow[\text{step}]{\text{Fast}} \underset{\text{Protonated ether}}{Me_3C-\overset{+}{O}(H)Me} \xrightarrow{H-OMe} \underset{\text{An ether}}{Me_3C-OMe} + Me\overset{+}{O}H_2$$

In general,

$$\left[R-L \xrightarrow{\text{Slow}} :L^- + R^+ \xrightarrow[\text{Fast}]{:NuH} R-NuH^+ \xrightarrow[\text{Fast}]{-H^+} R-Nu\right]$$

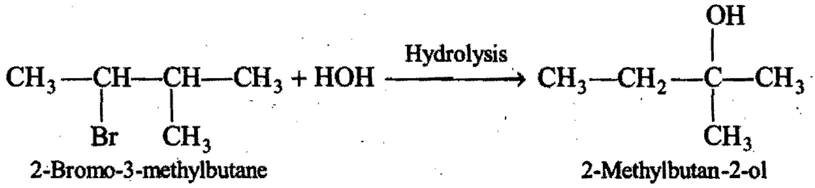
Problem 13. *Suggest the possible pathways of converting (R)-n-$C_3H_7CH(OH)CH_3$ (A) into its ethyl ether n-$C_3H_7CH(OC_2H_5)CH_3$ using Fischer projections and give their R, S designations.*

Solution : There are two pathways. In path 1, (*A*) reacts first with K and then with ethyl tosylate (C_2H_5OTs) to form (*R*) ethyl ether. [Tosyl(Ts) is *p*-$MeC_6H_4SO_2^-$]. In path 2, (*A*) reacts first with tosyl chloride (TsCl) and then with $C_2H_5\bar{O}K^+$ to form (*S*) enantiomer.



In path 1, the chiral centre is in the nucleophile and none of its bonds are broken, resulting in retention of the configuration in the ether. Path 2 differs in that ethoxide attacks the chiral carbon back side in an S_N2 reaction with inversion of configuration.

Problem 14. *Explain the S_N1 reaction mechanism of the following by equations only.*

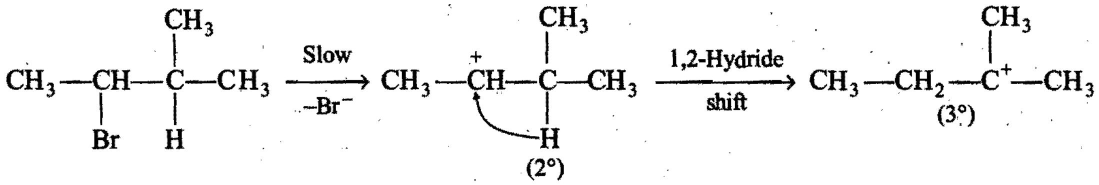


$$CH_3-\underset{\overset{|}{Br}}{CH}-\underset{\overset{|}{CH_3}}{CH}-CH_3 + HOH \xrightarrow{\text{Hydrolysis}} CH_3-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

2-Bromo-3-methylbutane 2-Methylbutan-2-ol

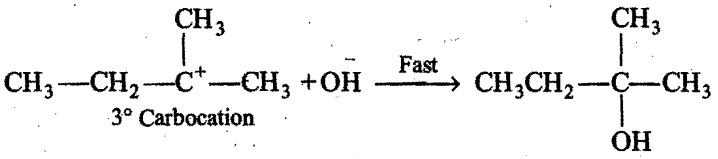
Solution :

Step 1.



$$CH_3-\underset{\overset{|}{Br}}{CH}-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_3 \xrightarrow[-Br^-]{\text{Slow}} \underset{(2^\circ)}{CH_3-\overset{+}{CH}-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_3} \xrightarrow[\text{shift}]{\text{1,2-Hydride}} CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{(3^\circ)}{C^+}}-CH_3$$

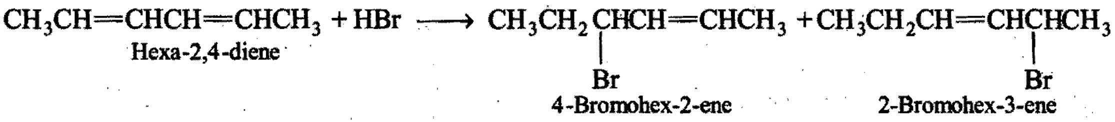
Step 2.



$$\underset{3^\circ\text{ Carbocation}}{CH_3-CH_2-\overset{\overset{CH_3}{|}}{C^+}-CH_3} + \overset{-}{O}H \xrightarrow{\text{Fast}} CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

Problem 15. *Explain a suitable mechanism for the following addition of* HBr *to hexa-2,4-diene.*

Solution :

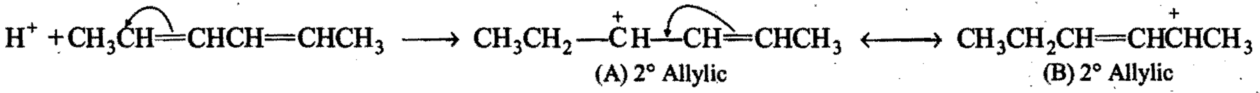


$$\underset{\text{Hexa-2,4-diene}}{CH_3CH{=}CHCH{=}CHCH_3} + HBr \longrightarrow \underset{\text{4-Bromohex-2-ene}}{CH_3CH_2\underset{\overset{|}{Br}}{CH}CH{=}CHCH_3} + \underset{\text{2-Bromohex-3-ene}}{CH_3CH_2CH{=}CH\underset{\overset{|}{Br}}{CH}CH_3}$$

Step 1. HBr ionises to give a proton (H^+) and a bromide ion (Br^-).

$$HBr \longrightarrow H^+ + \mathbf{:}Br^-$$

Step 2. Proton attacks the double bond according to Markownikoff's rule to give a resonance stabilized carbocation.



$$H^+ + CH_3CH{=}CHCH{=}CHCH_3 \longrightarrow \underset{\text{(A) }2^\circ\text{ Allylic}}{CH_3CH_2-\overset{+}{C}H-CH{=}CHCH_3} \longleftrightarrow \underset{\text{(B) }2^\circ\text{ Allylic}}{CH_3CH_2CH{=}CH\overset{+}{C}HCH_3}$$

[2° allylic carbocation is more stable than 2° alkyl ($CH_3\overset{+}{C}HCH_2CH{=}CHCH_3$)]

Step 3. Bromide ion (Br^-) combines with (A) to give 4-bromo-2-hexene. It combines with (B) to give 2-bromo-3-hexene.

$$\underset{\text{(A)}}{CH_3CH_2\overset{+}{C}H-CH{=}CHCH_3} + \mathbf{:}Br^- \longrightarrow \underset{\text{4-Bromohex-2-ene}}{CH_3CH_2CHBr-CH{=}CHCH_3}$$

$$\underset{\text{(B)}}{CH_3CH_2CH{=}CH\overset{+}{C}HCH_3} + \mathbf{:}Br^- \longrightarrow \underset{\text{2-Bromohex-3-ene}}{CH_3CH_2CH{=}CHCHBr-CH_3}$$

Problem 16. *Complete the following and identify the type for the intermediate species:*

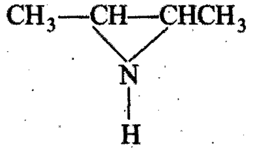
(*a*) $CH_3-N{\equiv}N \xrightarrow{\text{Heat}}$ ------ + N_2

(*b*) $C_6H_5-N_3 \xrightarrow{\text{Light}}$ ------ + N_2

(*c*) $CH_3-N{=}C{=}O \xrightarrow{\text{Light}}$ ------ + CO

(*d*) $CH_3CON_3 \xrightarrow{\text{Light}}$ ------ + N_2

(*e*) $CH_3CH{=}CHCH_3$ + --- $\longrightarrow$



(*f*) $(CH_3)_3CH$ + ------ $\longrightarrow (CH_3)_3CNHCOCH_3$

Solution : (a) $\overset{+}{C}H_3$, a carbocation;

(b) $C_6H_5-\ddot{N}\mathbf{:}$, a phenyl nitrene;

(c) $CH_3-\ddot{N}\mathbf{:}$, a methyl nitrene;

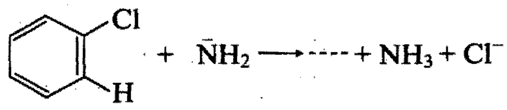
(d) $CH_3CO\ddot{N}\mathbf{:}$, acetyl nitrene;

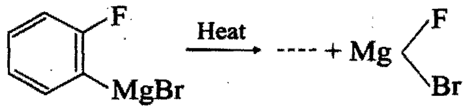
(e) $H-\ddot{N}\mathbf{:}$, nitrene;

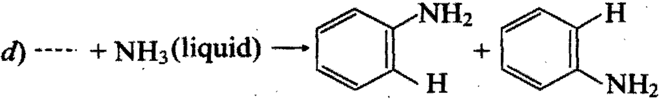
(f) $CH_3CO\ddot{N}\mathbf{:}$, acetyl nitrene.

Problem 17. *Complete the following and identify the type for the intermediate species:*

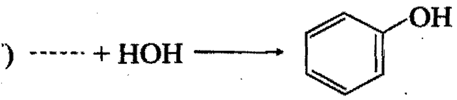
(*a*) $N_3H \xrightarrow{h\nu}$ ------ + N_2

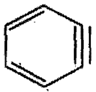
(*b*) 

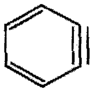
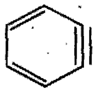
(*c*) 

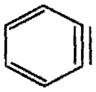
(*d*) 

(*e*) $CH_3CH_2CH_3$ + ------ $\longrightarrow$ $CH_3CH_2CH_2CH_3$ + $(CH_3)_3CH$

(*f*) 

Solution : (a) $H\ddot{N}:$, a nitrene; (b)  , benzyne;

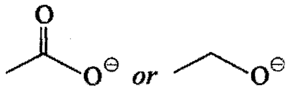
(c)  , benzyne; (d)  , benzyne;

(e) $:CH_2$, carbene; (f)  , benzyne.

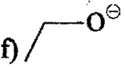
Problem 18. *Choose the member of each of the following pairs of compounds that is likely to be the stronger base:*

(*a*) NH_3 *or* $\overset{\ominus}{N}H_2$ (*b*) H_2O *or* $\overset{\ominus}{O}H$

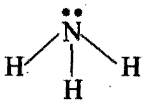
(*c*) NH_3 *or* $\overset{\oplus}{N}H_4$ (*d*) H_2O *or* $H_3\overset{\oplus}{O}$

(*e*) $\overset{\ominus}{O}H$ *or* $\overset{\ominus}{S}H$ (*f*) 

(*g*) $C_6H_5\overset{\ominus}{O}$ *or* C_5H_5N (*h*) $I^{\ominus}$ *or* $F^{\ominus}$

Solution : (a) $\overset{\ominus}{N}H_2$; (b) $\overset{\ominus}{O}H$; (c) NH_3; (d) H_2O; (e) $\overset{\ominus}{O}H$; (f)  ; (g) $C_6H_5\overset{\ominus}{O}$; (h) $I^{\ominus}$.

Problem 19. *Write equations showing ambiphilic nature of the following molecules:*

(*a*) $H-\ddot{F}:$ (*b*) 

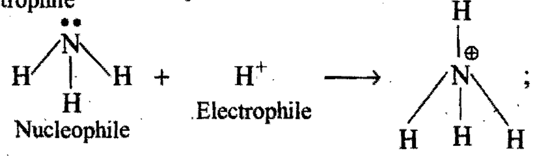
Solution :

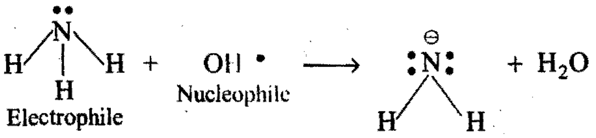
(a) (i) $H-\ddot{F}: + H^+ \longrightarrow H-\overset{\oplus}{\ddot{F}}-H$;

Nucleophile Electrophile

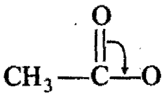
(ii) $H-\ddot{F}: + OH^- \longrightarrow H-\ddot{O}-H + :\ddot{F}:^-$

Electrophile Nucleophile

(b) (i) 

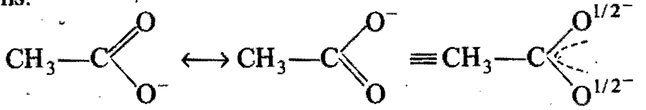
(ii) 

Problem 20. *Which one of the following is a better nucleophile and why?*

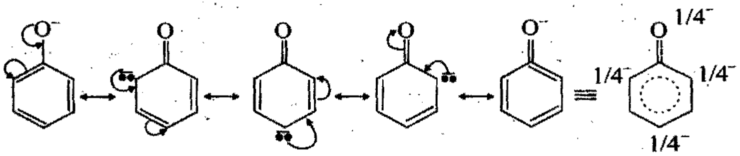
(*a*)  (*b*) $C_6H_5O^-$ (*c*) $CH_3CH_2O^-$

Solution : (c) $CH_3CH_2O^-$ is a good nucleophile because the –ve charge is concentrated on one oxygen only.

(a) CH_3COO^- is a resonance hybrid of the following structures and the –ve charge is divided on the two carbon atoms.



(b) $C_6H_5O^-$ is not a good nucleophile because the –ve charge is distributed at four positions.



IMPORTANT POINTS TO REMEMBER (SUMMARY)

Inductive effect

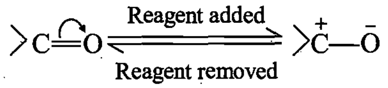
When an electron withdrawing or electron releasing group is attached to carbon chain, a permanent charge (polarity) is induced all along the basic chain. It is due to electron displacement because of the difference in electronegativities. This is called **inductive effect (*I*-effect).**

- *I*-effect is a permanent effect and decreases rapidly as the distance from the source (*X*) increases. Any atom or group which attracts electrons more strongly than hydrogen is said to have **–*I* effect (electron attracting** or **withdrawing).** $C_3^{\delta\delta\delta+} \rightarrow C_2^{\delta\delta+} \rightarrow C_1^{\delta+} \rightarrow X^{\delta-}$. The atoms or groups which attract electrons less strongly than hydrogen are said to have **+*I* effect (electron releasing or donating).** $C_3^{\delta\delta\delta-} \leftarrow C_2^{\delta\delta} \leftarrow C_1^{\delta-} \leftarrow Y^{\delta+}$. Relative inductive effects have been measured with reference to hydrogen.
- **Due to –*I* effect,** the electron density decreases, hence basic nature is decreased and naturally **acidic nature is increased.** For example, chloroacetic acid is stronger than acetic acid due to –*I* effect and aniline is weaker base than NH_3 due to electron withdrawing nature of phenyl group (–*I* effect).

- ☐ **Due to +*I* effect,** the electron density increases, hence basic nature is also increased and so **acidic nature is decreased.** For example, methyl alcohol is more basic than water (H—O—H) due to +*I* effect and tert. alcohol is more basic than secondary and than primary (due to +*I* effect of methyl group).

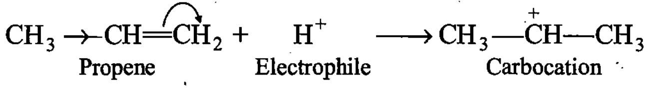
Electromeric effect

The effect involving the complete transfer of a shared pair of electrons to one of atoms joined by a multiple bond at the requirement of attacking reagent is known as electromeric effect. It is a temporary effect and comes into play instantaneously at the demand of the attacking reagent and as soon as the reagent is removed, the original condition is restored.



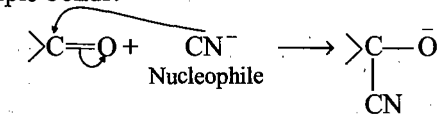
$$>C=O \underset{\text{Reagent removed}}{\overset{\text{Reagent added}}{\rightleftharpoons}} >\overset{+}{C}-\overset{-}{O}$$

- ☐ **+*E* effect:** When the transfer of electrons is towards the attacking reagent, *i.e.*,



$$\underset{\text{Propene}}{CH_3 \rightarrow CH=CH_2} + \underset{\text{Electrophile}}{H^+} \longrightarrow \underset{\text{Carbocation}}{CH_3-\overset{+}{C}H-CH_3}$$

- ☐ **–*E* effect:** When the transfer of electrons is away from the attacking reagent, *i.e.*, transfer of π-electrons takes place to more electronegative atom (O, N, S) joined by multiple bonds.

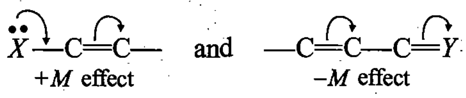


$$>C=O + \underset{\text{Nucleophile}}{CN^-} \longrightarrow >\underset{\underset{CN}{|}}{C}-\overset{-}{O}$$

Mesomeric effect

In a conjugated system (having alternate single and double bonds), the permanent polarity produced in a molecule as a result of interaction between two π-bonds or a π-bond and lone pair of electrons is referred as **mesomeric effect** or **conjugate effect.** Examples are benzene, buta-1,3-diene and acrolein etc.

- ☐ The π-electrons get delocalised as a result of mesomeric effect giving a number of resonance structures.
- ☐ Due to mesomeric effect terminal carbon is almost as positive as the first carbon. This is quite different from inductive effect due to which charge decreases as one moves away from the source.
- ☐ Like inductive effect, **mesomeric effect** may be +*M* or –*M*. It is **+*M*** when the direction of electron displacement is away from the atom or group and **–*M*** when π-electron displacement is towards atom or group (but away from conjugate system).

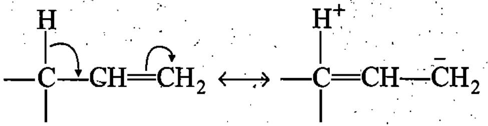


$$\underset{+M\text{ effect}}{\ddot{X}-C=C-} \quad \text{and} \quad \underset{-M\text{ effect}}{-C=C-C=Y}$$

- ☐ +*M* effect activates benzene nucleus for S_E reaction at *o*- and *p*-positions while –*M* effect deactivates benzene nucleus for S_E reaction and electrophile attacks at the *m*-position.

Hyperconjugation

Electron release by an alkyl group attached to unsaturated system (H—C—C=C) is called **hyperconjugation** (involving delocalization of σ and π-bond orbitals, *i.e.*, **σ-π conjugation**) or kind of delocalization involving sigma bond orbital is called **hyperconjugation** (Baker-Nathan effect or No bond resonance).



$$-\overset{\overset{H}{|}}{\underset{|}{C}}-CH=CH_2 \longleftrightarrow -\overset{\overset{H^+}{|}}{\underset{|}{C}}=CH-\overset{-}{C}H_2$$

- ☐ There should be atleast one H-atom at α-carbon with respect to sp^2-hybrid carbon (C=C) and greater the number of C—H bonds at α-carbon to the unsaturated system, greater will be the electron release and thus greater the hyperconjugation effect.
- ☐ On the basis of heat of hydrogenation, the stability order of different alkenes is:

Tetrasubstituted > Trisubstituted > Disubstituted > Monosubstituted > $H_2C=CH_2$

- ☐ Due to hyperconjugation, C=C bond length of substituted alkenes is always more than the ethylene. Hyperconjugation also decreases C—H bond length and C—C bond length.
- ☐ Stability order of different alkyl carbocations is in the following order:

Tertiary > Secondary > Primary > Methyl

This order can be explained by the number of resonating structures of these carbocations.

- ☐ Stability of alkyl free radicals is also in the same order:

$$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3,$$

i.e., more the number of hyperconjugative structures, the greater is its stability.

- ☐ Alkyl group of alkyl benzene is *o*- and *p*-directing and activates aromatic S_E reactions. This property of alkyl group can be explained by hyperconjugation.
- ☐ **Fission (Cleavage or Breaking) of a covalent bond:** The reaction intermediates (carbocations, carbanions, free radicals, carbenes, nitrenes and benzyne) are formed due to cleavage of covalent bonds in an organic reaction by:

Homolytic fission or Homolysis: This involves the breaking of a covalent bond in such a way that each atom separates with one electron of the shared pair. Such atoms are electrically neutral, extremely reactive and possess a small permanent magnetic moment due to the presence of unpaired electron. These atoms or fragments are called **free radicals.**

Heterolytic fission or Heterolysis: This involves the breaking of a covalent bond in such a way that both the electrons of the shared pair are attracted by the more electronegative atoms.

$A : B \longrightarrow A^{-}: + B^{+}$ (A is more electronegative than B)

$A : B \longrightarrow A^{+} + :B^{-}$ (B is more electronegative than A)

So, heterolytic fission results in the formation of cation and anion.

- ☐ An organic ion containing positively charged carbon centre is called **carbocation** (or **carbonium ion**) and an organic ion with a pair of available electrons and containing negatively charged carbon centre is called a **carbanion**.

Reaction Intermediates

- ☐ Highly reactive and short lived fragments called reaction intermediates result from homolytic and heterolytic bond fission. Examples are,
- ☐ **Free radicals:** Carbon free radicals have no charge but the central carbon atom carries odd (unpaired) electrons. These are produced by homolytic fission of a covalent bond. For example,

$$\dot{H},\ \dot{C}H_3,\ CH_3\dot{C}H_2,\ (CH_3)_2\dot{C}H,\ (CH_3)_3\dot{C},\ \dot{C}l, \text{etc.}$$

- ☐ The formation of free radical is initiated by heat, light or catalyst. Their stability is in the order:

$$\underset{\text{Tertiary}}{R_3\dot{C}} > \underset{\text{Secondary}}{R_2\dot{C}H} > \underset{\text{Primary}}{R\dot{C}H_2} > \dot{C}H_3$$

Benzyl and allyl free radicals are resonance stabilized and hence are more stable. The relative stabilities of free radicals are:

3° > benzyl > allyl > 2° > 1° > methyl, vinyl

(decreasing order)

- ☐ **Carbocations (Carbonium ions):** Organic ions carrying a positive charge on carbon atoms are known as **carbocations.** For example,

$$\overset{+}{C}H_3,\ CH_3\overset{+}{C}H_2,\ (CH_3)_2\overset{+}{C}H,\ (CH_3)_3\overset{+}{C},$$
$$C_6H_5\overset{+}{C}H_2,\ (C_6H_5)_2\overset{+}{C}H, \text{ etc.}$$

Carbocations are very reactive and have six electrons (sextet), therefore, it is electron deficient species. Carbocation is a **planar structure** and the +vely charged carbon is sp^2-hybridized (trigonal planar).

- ☐ The stability of carbocations is influenced by both resonance and inductive effects. This dispersal of the charge stabilizes the carbocations. Their stability is in the order:

$$R_3\overset{+}{C} > R_2\overset{+}{C}H > R\overset{+}{C}H_2 > \overset{+}{C}H_3$$

Benzyl and allyl carbocations are much more stable due to resonance. The relative stability of carbocations are:

$$(C_6H_5)_3\overset{+}{C} > (C_6H_5)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C} > C_6H_5\overset{+}{C}H_2$$
$$> H_2C{=}CH\overset{+}{C}H_2 > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

The presence of electron attracting groups (—NO_2, —CN and Br) which have $-I$ effect reduces the stability of carbocations.

- ☐ **Carbanions:** Organic ions containing a negatively charged carbon are known as carbanions. For example,

$$H_3\bar{C}:,\ CH_3\bar{C}H_2,\ (CH_3)_2\bar{C}H,\ (CH_3)_3\bar{C},\ C_6H_5\bar{C}H_2,$$
$$H_2C{=}CH{-}\bar{C}H_2, \text{ etc.}$$

Carbanions are highly reactive and contain eight electrons in the valence shell, *i.e.*, complete octet. It has a **pyramidal structure** because the carbon bearing –ve charge is sp^3-hybridised.

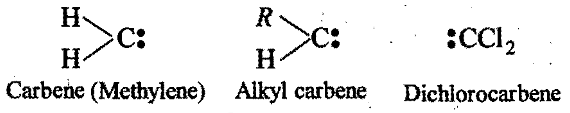
- ☐ The stability of carbanions is influenced by resonance, inductive effect and *s*-character of orbitals. The groups having $+I$ effect decrease the stability while groups having $-I$ effect increase the stability of carbanions.

$$H_3\bar{C} > R\bar{C}H_2 > R_2\bar{C}H > R_3\bar{C}$$

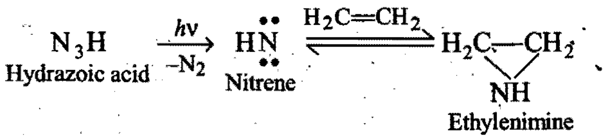
Benzyl and allyl carbanions are stabilized due to resonance. The relative stability of carbanions are:

$$(C_6H_5)_3\bar{C} > (C_6H_5)_2\bar{C}H > C_6H_5\bar{C}H_2 > H_2C{=}CH{-}\bar{C}H_2$$
$$> \bar{C}H_3 > CH_3\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$$

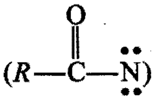
- ☐ **Carbenes:** They are short lived, reactive, sp^2-hybridized, neutral species and transitory reaction intermediates in which the carbon atom has six electrons in the outer shell, out of which two constitute a lone pair and two are shared. So, they are divalent carbon species containing two unpaired electrons and possess no charge. For example,



- ☐ The carbon atom is sp^2-hybridized in **singlet carbene** and has a **bent** structure. It is less stable and highly reactive. **Triplet carbene** is a diradical, sp-hybridized and is believed to be a **linear** molecule. It is more stable.
- ☐ **Nitrenes (Imidogenes):** These are nitrogen similar to carbenes and neutral univalent nitrogen intermediates $(\text{—}\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}})$. The electron deficient species in which N has a sextet of electrons are called **nitrenes.** They are highly reactive and act as strong **electrophiles.** The parent species is $:N{-}H$, and is formed when hydrazoic acid (N_3H) is irradiated with UV light. In the presence of C_2H_4, nitrene is trapped to form ethylenimine.



- ☐ Nitrenes can exist in the **singlet** and **triplet** states. The triplet state is the ground state and most nitrenes exist in this state. Nitrenes are highly reactive unstable compounds and give addition and insertion reactions.

- Acyl nitrene ( $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\ddot{\underset{\cdot\cdot}{N}}$) has been proposed as a possible intermediate in the Hofmann, Curtius and Lossen rearrangements.
- **Benzyne:** It is a neutral, highly reactive reaction intermediate in which the aromatic character has not been markely disturbed. It contains carbon-carbon triple bond in benzene ring involving the formation of a new weaker C—C bond by sideways overlapping of sp^2-hybridized orbitals of two adjacent carbon atoms.
- Formation of aniline from chlorobenzene proceeds through the formation of benzyne intermediate. This reaction is also known as **cine-substitution.** Benzyne reacts with nucleophilic reagents and form addition product.

Attacking reagents

These are of three types:

- **Electrophiles (Electrophilic reagents):** These are electron loving species and carry either positive charge or neutral molecules with electron deficient centre. These are **Lewis acids** and can accept a pair of electrons in a reaction. Examples are:
- Positively charged ions: $H^+, Cl^+, Br^+, I^+, NO_2^+, R^+, CH_3CO^+, R_3C^+, SO_3^+H$, etc.

  Neutral molecules: SO_3, BF_3, $AlCl_3$, $ZnCl_2$, $FeCl_3$, $BeCl_2$, RCOCl, $(R\mathrm{CO})_2O$, RMgX, $:CCl_2$, $:\ddot{N}COOC_2H_5$, etc.

  Further, **cation carriers,** *e.g.*, Br—Br, H—Br, Cl—OH, O_2N—OH, etc., and oxidising agents such as Fe^{3+}, O_3, R—O—O—R, etc., also act as electrophilic reagents.
- **Nucleophiles (Nucleophilic reagents):** These are electron rich (donating) species and carry either negative charge or neutral molecules with free electron pair to donate (N in NH_3, and O in H_2O). These are **Lewis bases** (electron-pair donor). Examples are:

  Negatively charged ions: $Cl^-, Br^-, NO_2^-, R^-, OH^-, CN^-, H^-, NH_2^-, R NH^-, R_2N^-, R_3C^-, [CH(COOC_2H_5)_2]^-, [CH_3COCHCOOC_2H_5]^-, OR^-, CH_3COO^-, N_3^-, S^-$, etc.

  Neutral molecules: $:NH_3$, $R\ddot{N}H_2$, $R_2\ddot{N}H$, $R_3\ddot{N}$, $H{-}\ddot{\underset{\cdot\cdot}{O}}{-}H$, $R{-}\ddot{\underset{\cdot\cdot}{O}}{-}H$, $R{-}\ddot{\underset{\cdot\cdot}{S}}H$, $R{-}\ddot{\underset{\cdot\cdot}{S}}{-}R$, $R{-}\ddot{\underset{\cdot\cdot}{O}}{-}R$, $R_3P:$, $(C_6H_5)_3P:$, $H{-}\ddot{\underset{\cdot\cdot}{S}}{-}H$, etc.

  In addition, **anion carriers,** *e.g.*, $\overset{\curvearrowleft}{H{-}H}$, $\overset{\curvearrowleft}{R{-}MgX}$, $\overset{\curvearrowleft}{H{-}H_3AlLi}$, $\overset{\curvearrowleft}{H{-}C_6H_5}$, C=C, etc., and reducing agents such as Fe^{2+}, $[Fe(CN)_6]^{4-}$, etc., also act as nucleophilic reagents.
- **Ambiphile (Ambident):** They behave both like electrophiles (electron attracting) and nucleophiles (electron repelling) site and hence, have dual (amphoteric) nature, *e.g.*, $H{-}\underset{\underset{\text{nucleophile}}{\uparrow}}{\ddot{\underset{\cdot\cdot}{O}}}{-}H \leftarrow$ electrophile, $R{-}\ddot{O}H$, $CH_3{-}C{\equiv}N:$ and $H_2C{=}\ddot{O}:$ etc.
- Nucleophiles attack electrophiles during the course of the reaction. The nucleophiles which can attack through two or more atoms are called **ambident nucleophiles.** For example, CN^- can attack through N or C to give cyanide (RCN) or isocyanide (RNC).

Types of organic reactions

- **Substitution reactions:** An atom or group of atoms in a molecule is replaced by another atoms or groups of the same bonding capacity. Halogenation, nitration, sulphonation, replacement of halogen atoms or —OH groups, etc. are some important examples of substitution reactions.
- **Addition reactions:** The attacking reagent adds to unsaturated (π-bonded) compounds having double or triple bonds without elimination to form saturated (σ-bond) molecule. Addition of H_2, X_2, HX, HOH and HCN, etc. to double or triple bond compounds are some important examples of addition reactions.
- **Elimination reactions:** The reverse of addition reactions are termed as elimination reactions. In most elimination reactions, the two atoms or groups from two adjacent carbon atoms (α, β) in the substrate molecule are removed and multiple (double or triple) bond is formed. Important examples are dehydrogenation, dehalogenation, dehydrohalogenation and dehydration reactions, etc.
- **Rearrangement reactions:** These reactions involve transfer of an atom or group from one position to another within the molecule forming a new compound which is actually the structural isomer of the original one. Examples are:

  the change of ammonium cyanate into urea and acetoxime into N-methyl acetamide, etc.

Mechanism of substitution reactions

- **Free radical mechanism:** The reactions involving the attack of free radicals on the substrate molecule is referred to free radical mechanism and the reaction involves three steps: **initiation, propagation and termination.**
- Halogenation, nitration and sulphonation of alkanes proceed by free radical substitution. Other examples of **free radical substitution** are:
- Wurtz reaction (formation of higher alkanes from lower alkyl halides).
- Arylation of aromatic compounds (Gomberg reaction) to form diphenyl by the reaction of benzene diazonium halide with benzene.
- Allylic bromination by NBS (N-Bromosuccinimide) brominates the ethylenic compounds in the allylic ($CH_2{=}CH{-}CH_2{-}$) position and is a free radical reaction.

- Substitution reactions of higher cycloalkanes in presence of UV light is an example of free radical reaction.
- High temperature reaction of chlorine with propene is a free radical substitution.
- Cyclopropane ring is opened by free halogen attack to form 1,3-dichloropropane.
- Side chain halogenation of toluene to form benzyl chloride is also a free radical substitution reaction.
- **Nucleophilic substitution:** When a substitution reaction is brought about by a nucleophile, the reaction is called S_N **reaction.**

$$\underset{\text{Substrate}}{R—X} + Nu^- \longrightarrow \underset{\text{Product}}{R—Nu} + \underset{\text{Leaving group}}{X^-}$$

S_N reactions are of two types:

- **S_N1 reactions (Unimolecular):** The rate of substitution depends on the concentration of the substrate, and the reaction is of **first order** change.

$$\text{Rate} \propto [\text{Substrate}]$$

- It is a two step process in the first step alkyl halide ionises to give a planar carbocation (electrophile). This is a slow process and rate determining step. In the second step, the nucleophile attacks the carbocation from either side to form the product. This is a fast process.
- The hydrolysis of tert. butyl halide is an example of **S_N1 reaction.**
- In another example, the carbocation formed (in step 1) can undergo rearrangement (1,2-methyl shift) to give more stable carbocation before attack of the nucleophile (in step 2).
- As a result of S_N1 reaction, there can be **racemisation** and **inversion.**
- S_N1 reaction is favoured by heavy (bulky) groups on the carbon atom attached to halogens, *i.e.*,

$$R_3C—X > R_2CH—X > R—CH_2—X > CH_3X$$

- Increasing carbocation stability results in increasing S_N1 rate of RX:

$$\underset{\text{Methylium}}{\overset{+}{C}H_3} < \underset{1°}{CH_3\overset{+}{C}H_2} < \underset{2°}{(CH_3)_2\overset{+}{C}H} < \underset{3°}{(CH_3)_3\overset{+}{C}}$$

$$< \underset{\text{Allylium}}{H_2C{=}CH—\overset{+}{C}H_2} < \underset{\text{Benzilium}}{C_6H_5\overset{+}{C}H_2}$$

- **S_N2 reaction (Bimolecular):** The rate of substitution depends on the concentration of both substrate and the nucleophile, hence it is a bimolecular and **second order** reaction.

$$\text{Rate} \propto [\text{Substrate}][\text{Nucleophile}]$$

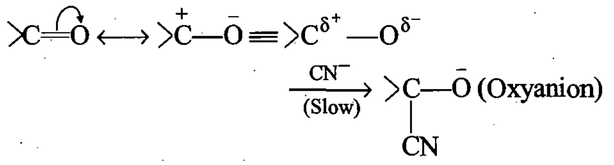
- The hydrolysis of methyl halide is an example of S_N2 **reaction.** The strong nucleophile OH^- attacks from the opposite side of the chlorine atom to give an intermediate (transition state) which is unstable (carbon is pentavalent) and breaks to yield the product and leaving (X^-) group.
- Since, the slow step involves two moles, hence it is bimolecular and called S_N2 reaction. The alcohol (product) obtained has a configuration opposite to that of the bromide and is said to proceed with **inversion of configuration.**
- S_N2 reaction is favoured by small groups on the carbon atom attached to halogen, *i.e.*, the order of reactivity is:

$$CH_3—X > R—CH_2—X > R_2CH—X > R_3C—X$$

- Increasing carbocation stability is in the order:

Benzyl < allyl < tertiary butyl (3°) < isopropyl (2°) < ethyl < methyl

- Higher concentration of nucleophile favours S_N2 reaction, whereas low concentration favours the S_N1 mechanism. Neopentyl bromide shows S_N2 path with ethoxide ion, but S_N1 path with ethanol.
- **Electrophilic substitution (S_E):** It involves the attack by an electrophile. It can be S_E1 (unimolecular) or S_E2 (bimolecular). The electrophile (E^+) attacks to a point of high electron density. The reactions like halogenation, nitration, sulphonation, alkylation and acylation of benzene and its derivatives (aromatic compounds) are electrophilic substitution (S_E) reactions.
- S_E2 is very common in benzene nucleus (aromatic compounds). In **step 1** the formation of electrophile (E^+) takes place that attacks the benzene ring to form an intermediate carbocation (in **step 2**) which is stabilized by resonance and finally carbocation (σ-complex) loses the proton to the base (Nu^-) to form substitution product (**step 3**).
- An additional reagent (called Lewis acid) like Fe or conc. H_2SO_4 is always required that can help in the formation of an electrophile.
- **Addition reactions:** These are the reactions of the compounds containing double or triple bonds. The π-bond in addition reactions is involved with the attacking reagent (electrophile or nucleophile) and σ-bond remains intact.
- **Electrophilic addition reactions:** In **step 1,** an electrophile (E^+) is added in a slow step (rate determining step) to the double or triple bond to form carbocation. In **step 2,** the nucleophile (Nu^-) is added to the carbocation (in a fast step) to form addition product.
- Addition of HX to alkenes is an example of electrophilic addition. The mechanism of such addition reactions is consistent with the occurrence of rearrangement (1,2-hydride or 1,2-methyl or 1,2-phenyl shift) resulting the formation of more stable carbocation (3° > 2° > 1°).
- Addition of halogens is usually predominantly *trans, i.e.,* the addition is stereoselective. *Cis*-but-2-ene on addition of Br_2 gives racemic mixture while *trans*-but-2-ene adds Br_2 to give the inactive meso-product.
- **Nucleophilic addition reaction:** This addition reaction takes place in $>C{=}O$ compounds.

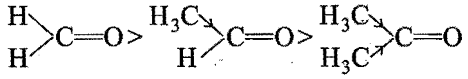


$$>C{=}O \longleftrightarrow >\overset{+}{C}—\overset{-}{O} \equiv >C^{\delta+}—O^{\delta-}$$

$$\xrightarrow[\text{(Slow)}]{CN^-} >\underset{\underset{CN}{|}}{C}—\overset{-}{O}\ \text{(Oxyanion)}$$

The nucleophilic reagent attacks the +vely charged carbon to form more stable oxyanion. Hence, it is known as nucleophilic addition.

- The reactivity of >C=O compounds is in the order:

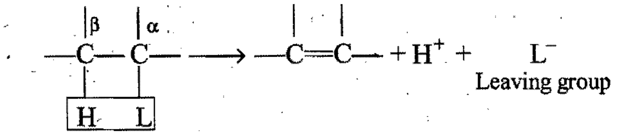


- Important examples of nucleophilic addition reactions are the addition of HCN, $NaHSO_3$, R—MgX and CH_3OH etc., on >C=O compounds.
- **Free radical addition reaction:** Addition of HBr to unsymmetrical alkenes in presence of organic peroxide, R_2O_2 [like benzoyl peroxide $(C_6H_5CO)_2O_2$] takes place according to **Kharasch Peroxide Effect** (anti-Markownikoff's rule) and follows the free radical addition reaction.

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + HBr \xrightarrow[\text{(Anti-MR addition)}]{ROOR} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br}$$

(Mechanism : See **sec. 7.6)**.

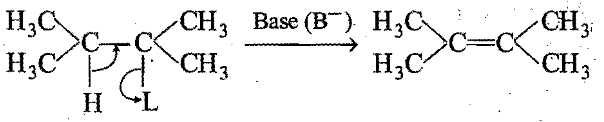
- HF, HCl and HI do not give anti-MR addition even when peroxides are present. It is because HCl and HF do not produce free radicals easily due to large bond energy and HI with minimum bond energy gives free iodine.
- **Elimination reactions:** The removal of two atoms or groups, one is generally hydrogen (H^+) and the other is a leaving group (L^-) resulting in the formation of unsaturated compound (π-bond), are known as elimination reactions.



- E_1 **(Elimination) Reactions:** In **step 1,** the C—L bond is broken heterolytically to form a carbocation (as in S_N1 reaction) in which (L^-) is lost (rate determining step), hence called E_1 **(unimolecular elimination) reaction.** In **step 2,** the carbocation loses a proton from the β-carbon atom by a base (nucleophile) to form an alkene.
- Dehydrohalogenation, dehydration, dehalogenation and dehydrogenation are some important examples of elimination reaction.
- E_1 reaction is favoured in compounds in which the leaving group is at secondary (2°) or tertiary (3°) position.
- E_1**-Cb** (Elimination unimolecular conjugate base) **reaction** involves:

  Step 1. Removal of a proton by a conjugate base to produce carbanion.

  Step 2. The carbanion loses a leaving group to form an alkene and is a slow step (rate determining).
- E_2 **(Elimination) Reaction:** In this reaction, two σ-bonds are broken and a π-bond is formed simultaneously.



$+ \text{H-base} + L^{\ominus}$

- It is bimolecular since substrate and base are involved in the rate determining step and the product obtained takes place through the formation of transition state.
- E_2 elimination is lowest energy path in comparison to E_1 and E_1-Cb reactions. Hence, E_2 reaction is most common and better the leaving group, higher is the E_2 reaction.

Substrate:	$PhCH_2CH_2Cl$	$PhCH_2CH_2Br$	$PhCH_2CH_2I$
Rate:	0.007×10^3	4.2×10^3	27×10^3

- In E_2 reaction, both the leaving groups should be antiplanar, *i.e.*, E_2 mechanism is stereospecific.
- In acyclic compounds, E_2 elimination is given by the most stable conformation in which both leaving groups are anti-periplanar.

QUESTIONS

VERY SHORT ANSWER TYPE

1. Fill in the blanks:

(a) Fission of a covalent bond may be of two types, ... and ....

(b) Homolytic fission of a covalent bond produces ....

(c) Heterolytic fission occurs when carbon is linked with an atom of different ....

(d) Among the given cations ...... is the most stable. (Sec-butyl carbocation, tert-butyl carbocation, *n*-butyl carbocation)

(e) The positively charged carbon of carbocation contains ...... valence electrons.

(f) Carbon of the carbanion consists ...... valence electrons.

(g) Electron rich reagents are called ....

(h) NO_2^+ is a/an ...... reagent.

(i) The negatively charged carbon of carbanion is ...... hybridized.

(j) ...... electrons are displaced in mesomeric effect.

(k) The order of stability of alkyl carbocation is ....

(l) A molecule with alternate single and double bonds is termed as a ....

(m) Acetic acid is ...... acid than formic acid due to ...... effect of methyl group.

(n) The addition of HBr to an unsymmetrical alkene takes place according to ....

(o) A reaction proceeds in presence of peroxide through ...... mechanism.

(p) Dehydration of alcohol to form alkene is an ...... reaction.

(q) Free radical is paramagnetic while carbocation and carbanion ions are ....

(r) Geometry of $\bar{C}H_3$ is ....

(s) $C_2H_5Br + \bar{O}C_2H_5 \longrightarrow C_2H_5OC_2H_5 + Br^-$ is an example of ...... reaction.

(t) Reaction, $CH_3COCH_3 + HCN \longrightarrow$ product, is an example of ...... addition reaction.

(u) Amongst $\bar{C}H_2CHO, \bar{C}H_3$ and $\bar{C}H_2—NO_2$, the most stable carbanion is ....

(v) The kind of delocalization involving sigma bond orbitals is called ....

(w) Inductive effect is ...... while electromeric effect is ....

(x) The shape of $\overset{+}{C}H_3$ is ....

(y) In the protonation of an alkene, the electrophile is ...... and nucleophile is ....

(z) The bond dissociation energy needed to form the benzyl radical from toluene is ...... than the formation of methyl radical from methane.

2. State whether the following statements are **True** or **False**:

(a) Homolytic fission of C—C bonds gives free radicals.

(b) The decreasing order of electron affinity of F, Cl, Br is F > Cl > Br.

(c) The electronegative atom in the carbon chain produces +*I* effect.

(d) Electromeric effect is a permanent effect.

(e) Carbocation has a planar structure.

(f) Substitution of benzene occurs through nucleophilic attack.

(g) Reaction between methane and chlorine in presence of sunlight proceeds through free radical mechanism.

(h) The dipole moment of CH_3F is greater than that of CH_3Cl.

(i) The hydrolysis of $(CH_3)_3C—Cl$ by aqueous NaOH follows S_N1 mechanism.

(j) The following fission is a heterolytic fission:

$$CH_3CH_2CH_3 \longrightarrow CH_3\overset{+}{C}H_2 + \bar{C}H_3$$

(k) The free radicals, carbonium ions or carbanions are reaction intermediates.

(l) Alkyl amines are more basic than ammonia due to –*I* effect.

(m) Nucleophiles act as Lewis bases.

(n) $CH_3CH{=}CH_2 + Cl_2 \xrightarrow{500°C} CH_2Cl—CH{=}CH_2 + HCl$

The above reaction is a substitution reaction.

(o) Anti-Markownikoff's rule is followed when addition of HBr in alkene occurs in presence of peroxide.

(p) During S_N1 reaction, the leaving group leaves the molecule before the incoming group is attached to the molecule.

(q) Free radicals are always electrically charged species.

(r) Nucleophiles are also Lewis acids.

(s) "Addition of unsymmetrical reagent to unsymmetrical unsaturated compounds, the negative part of the reagent adds to the less hydrogenated carbon". This is Markownikoff's rule.

(t) Tertiary alkyl halides undergo hydrolysis by S_N2 mechanism.

(u) Primary alkyl halides undergo hydrolysis by S_N1 mechanism.

(v) S_N2 mechanism is accompanied with inversion of configuration.

(w) Dipole moment increases, as the inductive effect increases.

$$\xrightarrow{R—I \quad R—Br \quad R—Cl}$$ Inductive effect increases. Dipole moment increases.

(x) Benzoic acid is stronger acid than acetic acid because C_6H_5 group produces more +*I* effect than CH_3 group.

(y) Inductive effect is more powerful than mesomeric effect.

(z) The stability of carbocations is influenced by both resonance and inductive effect. –*I* effect reduces the stability while +*I* effect increases the stability of carbocation.

3. Match the following:

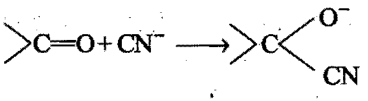
(a) Substitution reaction	(i) $A : B \longrightarrow \overset{+}{A} + :B^-$
(b) Addition reaction	(ii) $A : A \longrightarrow \overset{\bullet}{A} + \overset{\bullet}{A}$
(c) Elimination reaction	(iii) $CH_3Cl \xrightarrow{KOH} CH_3OH$
(d) Homolytic fission	(iv) BF_3
(e) Heterolytic fission	(v) $H_2C{=}CH_2 + HBr \longrightarrow CH_3CH_2Br$
(f) Electrophile	(vi) $CH_3CH_2OH \xrightarrow{H_2SO_4} H_2C{=}CH_2$
(g) Nucleophile	(vii) NH_3

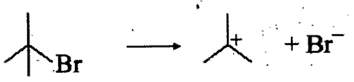
4(A). Classify the following into electrophilic and nucleophilic reagents:
(a) H^+, (b) Cl^-, (c) NH_3, (d) NO_2^+, (e) $\bar{C}N$, (f) H_2O, (g) Br^+, (h) ROH, (i) BF_3, (j) RNH_2, (k) $AlCl_3$, (l) ROR, (m) Carbocations, (n) Carbanions, (o) $\overset{+}{S}O_3H$, (p) $BeCl_2$, (q) I^-, (r) $SnCl_4$, (s) $:CCl_2$, (t) $:P(CH_3)_3$, (u) $H_2C{=}CH_2$

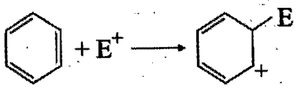
4(B). Classify the following as Lewis acids and Lewis bases: **[BCECE 2005]**
(a) CH_3NH_2 (b) CN^- (c) $AlCl_3$ (d) Fe^{3+} (e) CO_2^-

5. For the following bond cleavages, use curved arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced during the fission.

(i) $CH_3O{-}OCH_3 \longrightarrow CH_3\overset{\bullet}{O} + \overset{\bullet}{O}CH_3$

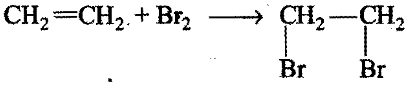
(ii)


(iii)


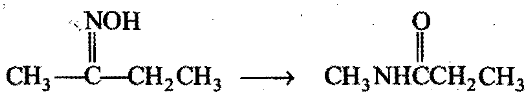
(iv)


6. Identify each of the following as carbon-intermediates:

(a) $CH_3{-}CH{=}\overset{+}{C}H$
(b) $(CH_3)_3\overset{\bullet}{C}$
(c) $(CH_3)_3\bar{C}$
(d) $C_2H_5\overset{\bullet}{C}CH_3$
(e) $CH_3{-}\bar{C}H{-}CH_3$
(f) $C_2H_5\overset{\bullet\bullet}{C}{-}H$
(g) $C_6H_5{-}\underset{\bullet\bullet}{\overset{\bullet\bullet}{N}}$
(h) $:CCl_2$

7. Classify the following reactions by type:
(a) $HCHO + HCN \longrightarrow CH_2(OH)CN$
(b) $(CH_3)_2CHOH \xrightarrow{Heat,\ Cu} (CH_3)_2C{=}O + H_2$
(c) $CH_3Cl + KOH(aq.) \longrightarrow CH_3OH + KCl$
(d)


$CH_2{=}CH_2 + Br_2 \longrightarrow \underset{Br}{CH_2}{-}\underset{Br}{CH_2}$

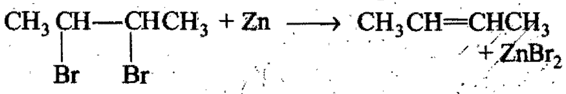
(e)


$CH_3{-}\overset{NOH}{\overset{\|}{C}}{-}CH_2CH_3 \longrightarrow CH_3NH\overset{O}{\overset{\|}{C}}CH_2CH_3$

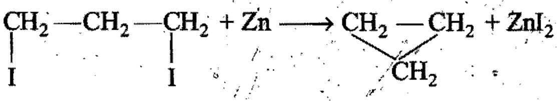
Ethyl methyl ketoxime *N*-Methyl propionamide

(f)


(g) $CHCl_3 + \overset{\bullet}{O}H^- \longrightarrow :CCl_2 + H_2O + \bar{C}l$

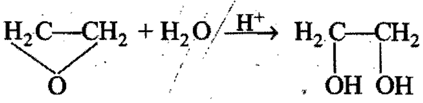
(h)


$CH_3\underset{Br}{CH}{-}\underset{Br}{CH}CH_3 + Zn \longrightarrow CH_3CH{=}CHCH_3 + ZnBr_2$

(i)


$\underset{I}{CH_2}{-}CH_2{-}\underset{I}{CH_2} + Zn \longrightarrow CH_2{-}CH_2 + ZnI_2$ (with CH_2 below, ring)

(j) $NH_4NCO \longrightarrow O{=}C(NH_2)_2$
(k) $(CH_3)_2NH_2^+ + CH_3O^- \longrightarrow (CH_3)_2NH + CH_3OH$
(l) $H_3C{-}N{=}N{-}CH_3 \xrightarrow{Heat} H_3C{-}CH_3 + N_2$
(m) $C_2H_5Br + OH^- \longrightarrow C_2H_5OH + Br^-$

(n)


8. (a) Arrange the following according to their stability:

$CH_3CH_2CH_2\overset{+}{C}H_2, (CH_3)_3\overset{+}{C}, CH_3CH_2\overset{+}{C}H_2,$

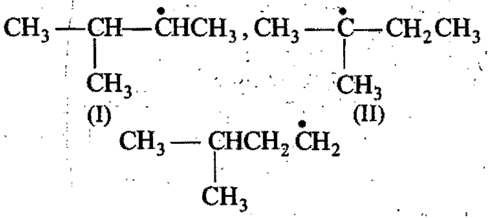
$CH_3CH_2\overset{+}{C}HCH_3, CH_3\overset{+}{C}H_2, \overset{+}{C}H_3$

(b) Arrange the following according to their stability:

$C_6H_5\bar{C}H_2, (CH_3)_3\bar{C}, \bar{C}Cl_3, \bar{C}H_3, (CH_3)_2\bar{C}H$

(c) Arrange the following according to their stability:

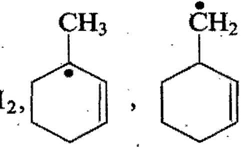
(i) $\overset{\bullet}{C}H_3, (CH_3)_3\overset{\bullet}{C}, (C_6H_5)_3\overset{\bullet}{C}, C_6H_5\overset{\bullet}{C}H_2, CH_3\overset{\bullet}{C}H_2$

(ii)


$CH_3{-}\underset{CH_3}{CH}{-}\overset{\bullet}{C}HCH_3$ (I), $CH_3{-}\underset{CH_3}{\overset{\bullet}{C}}{-}CH_2CH_3$ (II)

$CH_3{-}\underset{CH_3}{C}HCH_2\overset{\bullet}{C}H_2$ (III)

(iii) $H_2C{=}\overset{\bullet}{C}H, H_2C{=}CH\overset{\bullet}{C}H_2,$
(I) (II)



(III) (IV)

(d) Arrange the following in order of their:
(i) increasing basicity:
$H_2O, OH^-, CH_3OH, CH_3O^-$
(ii) increasing reactivity in nucleophilic substitution reaction: CH_3F, CH_3I, CH_3Br, CH_3Cl.
(iii) increasing order of expected enol content: CH_3COCH_2CHO, CH_3COCH_3, CH_3CHO, $CH_3COCH_2COCH_3$.
(iv) decreasing order of S_N2 reactivity:
RCH_2X, R_2CHX, R_3CX, MeX.
(v) decreasing order of S_N1 reactivity:
(i) 2-bromopentane (A), 1-bromopentane (B), 2-bromo-2-methylbutane (C).
(ii) 1-bromo-3-methylbutane(A), 2-bromo-2-methylbutane (B), 2-bromo-3-methylbutane (C)

(vi) decreasing order of S_N2 reactivity:
1-bromobutane (*A*), 1-bromo-2,2-dimethylpropane (*B*), 1-bromo-2-methylbutane (*C*), 1-bromo-3-methylbutane (*D*).

(vii) decreasing order of S_N2 reactivity in alkoxide nucleophiles:

$$Me_2CH\bar{O},\ Me_3C\bar{O},\ MeCH_2\bar{O},\ Me\bar{O}$$

(e) Arrange the following as stated:

(i) increasing order of acid strength:
$ClCH_2COOH$, CH_3CH_2COOH, $ClCH_2CH_2COOH$, $(CH_3)_2CHCOOH$, CH_3COOH

(ii) increasing order of acidity: $HClO$, $HClO_2$, $HClO_3$, $HClO_4$. **(IIT 2001)**

(iii) increasing strength of H-bonding (X ---H—X):
O, S, F, Cl, N

9. Answer the following:
   - (a) How many types of fission are possible of a covalent bond?
   - (b) How many types of ions are formed by heterolytic fission and what are their names?
   - (c) What are the names and nature of the parts formed by homolytic fission?
   - (d) How many electrons are present in the valence shell of the carbon atom of the carbonium ion?
   - (e) How many electrons are present in the valence shell of the carbon atom of the carbanion ion?
   - (f) Name the attacking reagents and give their nature.
   - (g) Write the names of the parts obtained when C—Cl bond of ethyl chloride undergoes heterolytic fission.
   - (h) What is the major factor that influences the relative stabilities of carbocations, carbanions and free radicals.

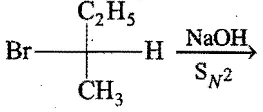
❖

Define the following with suitable examples:
- (a) Substitution reactions
- (b) Addition reactions
- (c) Elimination reactions
- (d) Markownikoff's rule
- (e) Homolytic fission
- (f) Heterolytic fission
- (g) Anti-Markownikoff's rule

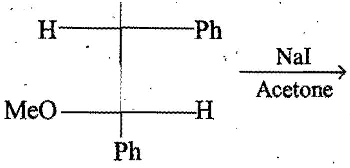
Write short notes on:
- (i) Inductive effect
- (ii) Mesomeric effect
- (iii) Carbocation
- (iv) Carbanion
- (v) Free radicals
- (vi) Electrophiles
- (vii) Nucleophiles
- (viii) S_N1 and S_N2 reactions
- (ix) Carbenes
- (x) Nitrenes
- (xi) Benzyne
- (xii) Hyperconjugation

Discuss the mechanism of the following reactions:
- (a) Dehydration of alcohols to form alkenes.
- (b) Peroxide effect in alkenes.
- (c) Addition of HBr in alkenes.
- (d) Dehydrohalogenation of alkyl halides.
- (e) Addition of Br_2 on ethylene.
- (f) Hydrolysis of methyl chloride.
- (g) Hydrolysis of tertiary alkyl halides.
- (h) Halogenation of alkanes.
- (i) Nitration of benzene.

13. Explain:
   - (i) Why trichloroacetic acid is stronger than acetic acid?
   - (ii) Why formic acid is stronger than butyric acid?
   - (iii) Why alkyl amines are stronger bases than ammonia?
   - (iv) Why benzyl carbocation is more stable than ethyl carbocation?
   - (v) What is the effect of introduction of an alkyl group on the stability of the carbocation?
   - (vi) Why allyl cation is more stable than ethyl cation?
   - (vii) Why does tert.-butyl chloride react with sodium hydroxide solution by S_N1 mechanism while *n*-butyl chloride react by S_N2 mechanism?
   - (viii) In acylium ion, the structure $R—C\equiv\overset{+}{O}\colon$ is more stable than $R—\overset{+}{C}=O$.
   - (ix) Why toluene reacts with bromine in presence of light gives benzyl bromide while in presence of $FeBr_3$, it gives *p*-bromotoluene?
   - (x) Why aryl halides are less reactive than alkyl halides towards nucleophilic reagents?
   - (xi) Draw the stereochemical structures of the products in the following reaction:

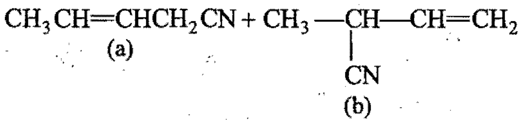


   - (xii) Predict the structure of the product in the following reaction:



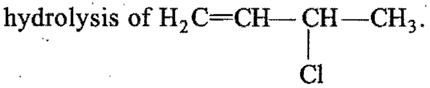
   - (xiii) Which CX_2 (X = F, Cl, Br, I) is the most stable singlet as compared to the corresponding triplet?
   - (xiv) The formation of following products (a) and (b) in the given reaction:

$$CH_3CH{=}CHCH_2Cl + \bar{C}N \longrightarrow$$



$$\underset{(a)}{CH_3CH{=}CHCH_2CN} + \underset{(b)}{CH_3—\underset{\displaystyle CN}{\underset{|}{C}H}—CH{=}CH_2}$$

   - (xv) The formation of $HOCH_2CH{=}CHCH_3$ from the hydrolysis of $H_2C{=}CH—\underset{\displaystyle Cl}{\underset{|}{C}H}—CH_3$.



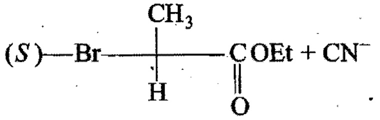
Complete the following and identify the type for the intermediate species:
- (a) $CH_3CH(OH)CH_3 + H^+ \xrightarrow{Heat}$ ...... + HOH
- (b) $CH_3—C\equiv C—H + Na^+NH_2^- \longrightarrow$ .....+ $Na^+ + NH_3$
- (c) $CH_3CH_2—N{=}N—CH_2CH_3 \xrightarrow{Heat}$ ...... + N_2
- (d) $CH_3—CH{=}CH—CH_3 + HI \longrightarrow$ ...... + I^-
- (e) $CH_3CHI_2 + Zn \longrightarrow$ ...... + ZnI_2
- (f) $CH_3CH_2Cl + AlCl_3 \longrightarrow$ ...... + $AlCl_4$

15. Complete the following and identify the type of displacement reactions:
   - (a) (R)—$CH_3CH(Br)CH_2CH_3 + MeO^- \longrightarrow$ ...

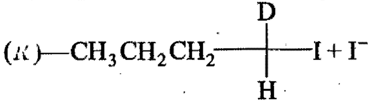
(b) (S)—$CH_3CH(Br)CH_2CH_3 + MeO^- \longrightarrow \ldots$

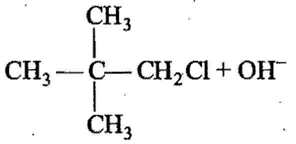
(c) $(CH_3)_3C$—$Br + MeOH \longrightarrow \ldots$

(d) $[Me_3C$—$SMe_2]^+Cl^- + 2MeOH \longrightarrow \ldots$
A sulphonium salt

(e) 
(S)—Br—$C(CH_3)(H)$—$\underset{\Vert}{C}OEt + CN^- \longrightarrow \ldots$

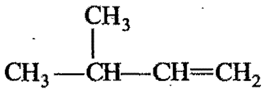
(f) CH_3CH_2—O—$CH_2Cl + C_2H_5OH \longrightarrow \ldots$

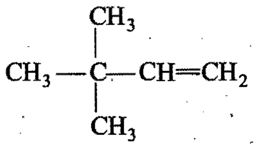
(g) 
(R)—$CH_3CH_2CH_2$—$C(D)(H)$—$I + I^- \longrightarrow \ldots$

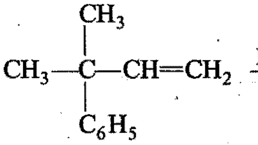
(h) 
CH_3—$C(CH_3)_2$—$CH_2Cl + OH^- \longrightarrow \ldots$

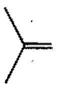
(i) Me_3C—$Br + HCOOH \longrightarrow \ldots$

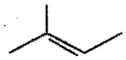
16. Complete the following addition reactions through the intermediate formation of stable carbocation (A):

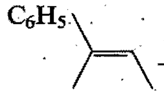
(i) 
CH_3—$CH(CH_3)$—$CH{=}CH_2 \xrightarrow{HCl} (A) \xrightarrow{Cl^-} (B)$

(ii) 
CH_3—$C(CH_3)_2$—$CH{=}CH_2 \xrightarrow{HCl} (A) \xrightarrow{Cl^-} (B)$

(iii) 
CH_3—$C(CH_3)(C_6H_5)$—$CH{=}CH_2 \xrightarrow{HBr} (A) \xrightarrow{Br^-} (B)$

(iv)  $\xrightarrow{HCl} (A) \xrightarrow{Cl^-} (B)$

(v)  $\xrightarrow{HBr} (A) \xrightarrow{Br^-} (B)$

(vi)  $\xrightarrow{HCl} (A) \xrightarrow{Cl^-} (B)$

(vii) $H_2C{=}CH$—$CH{=}CH_2 \xrightarrow{HBr} (A) \xrightarrow{Br^-} (B)$.

17. What are the various alkanes obtained due to insertion when 2-methyl butane reacts with singlet methylene $(\mathbf{:}CH_2)$?

18. Suggest a possible mechanism for the formation of R—Li from R—X by equation only.

ANSWERS

1. (a) homolytic, heterolytic; (b) free radicals; (c) electronegativity; (d) tert.-butyl carbonium ion; (e) six; (f) eight; (g) nucleophiles; (h) electrophilic; (i) sp^3; (j) π; (k) Tert. > Sec. > Prim.; (l) conjugated molecule; (m) weaker, $+I$ (inductive effect); (n) Markownikoff's rule; (o) free radical; (p) elimination; (q) diamagnetic; (r) pyramidal; (s) S_N2; (t) nucleophilic; (u) $\bar{C}H_2$—NO_2; (v) hyperconjugation; (w) permanent, temporary; (x) planar; (y) proton alkene; (z) less.

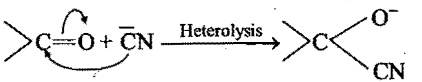
2. (a) True; (b) False; (c) False—produces $-I$ effect; (d) False—is a temporary effect; (e) True; (f) False—electrophilic attack; (g) True; (h) False; (i) True; (j) True; (k) True; (l) False—due to $+I$ effect; (m) True; (n) True; (o) True; (p) True; (q) False—electrically neutral; (r) False—Lewis bases; (s) True; (t) False—undergo S_N1 mechanism; (u) False—undergo hydrolysis by S_N2 mechanism; (v) True; (w) True; (x) False—C_6H_5 group produces $-I$ effect while CH_3 group produces $+I$ effect; (y) False—mesomeric effect is more powerful than inductive effect; (z) True.

3. (a—iii); (b—v); (c—vi); (d—ii); (e—i); (f—iv); (g—vii).

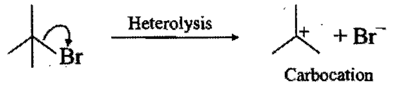
4(A) Electrophilic reagents: (a), (d), (g), (i), (k), (m), (o), (p), (r), (s).
Nucleophilic reagents: (b), (c), (e), (f), (h), (j), (l), (n), (q), (t), (u).

4(B) Lewis acids : (c), (d)
Lewis bases : (a), (b), (e)

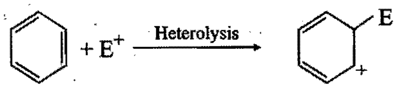
5. (i) CH_3O—$OCH_3 \xrightarrow{\text{Homolysis}} CH_3\dot{O} + \dot{O}CH_3$
Free radicals
(Homolysis, free radical intermediate)

(ii) 

Carbanion
(Heterolysis, carbanion intermediate)

(iii) 

Carbocation
(Heterolysis, carbocation intermediate)

(iv) 

Carbocation
(Heterolysis, Carbocation intermediate)

6. (a) Carbocation, (b) Free radical, (c) Carbanion, (d) Free radical, (e) Carbanion, (f) Singlet carbene, (g) Nitrene, (h) Carbene.

7. (a) Addition, (b) Elimination, (c) Substitution, (d) Addition, (e) Rearrangement, (f) Allylic bromination, (g) α-elimination, (h) β-elimination, (i) γ-elimination, (f) Rearrangement, (k) Displacement (substitution), (l) Decomposition, (m) Displacement (substitution), (n) Addition.

8. (a) $(CH_3)_3\overset{+}{C} > CH_3CH_2\overset{+}{C}HCH_3 > CH_3CH_2CH_2\overset{+}{C}H_2$
$> CH_3CH_2\overset{+}{C}H_2 > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$

(b) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > \bar{C}H_3 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

(c) (i) $(C_6H_5)_3\dot{C} > C_6H_5\dot{C}H_2 > (CH_3)_3\dot{C} > CH_3\dot{C}H_2 > \dot{C}H_3$
(ii) II > I > III
(iii) IV > III > II > I

(d) (i) $H_2O < CH_3OH < OH^- < CH_3O^-$
(ii) $CH_3F < CH_3Cl < CH_3Br < CH_3I$
(iii) $CH_3CHO < CH_3COCH_3 < CH_3COCH_2CHO$
$< CH_3COCH_2COCH_3$
(iv) $MeX > RCH_2X > R_2CHX > R_3CX$
(v) (i) C (3°) > A (2°) > B (1°)
(ii) B (3°) > C (2°) > A (1°)
(vi) $A(n\text{-}) > D(\text{iso-}) > C(\text{sec.-}) > B(\text{tert.-})$
(vii) $Me\bar{O} > MeCH_2\bar{O} > Me_2CH\bar{O} > Me_3C\bar{O}$

(e) (i) $(CH_3)_2CHCOOH < CH_3CH_2COOH$
$< CH_3COOH < ClCH_2CH_2COOH < ClCH_2COOH$
(ii) $HClO < HClO_2 < HClO_3 < HClO_4$

(iii) $S < Cl < N < O < F$

9. (a) Two; homolytic and heterolytic.

(b) Two; carbonium and carbanion.

(c) Parts are free radicals. These are electrically neutral.

(d) Six electrons.

(e) Eight electrons.

(f) Electrophilic reagents—Positively charged ions or neutral molecules which have affinity for electrons.
Nucleophilic reagents—Negatively charged ions or neutral molecules which have the tendency to lose an electron pair.

(g) $CH_3CH_2—Cl \longrightarrow CH_3\overset{+}{C}H_2 + \overset{-}{Cl}$
Ethyl chloride — Ethyl carbocation — Chloride ion

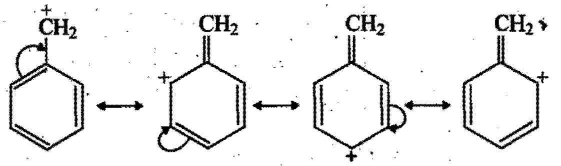
(h) Any diminution of + or – charge or of electron deficiency on the carbon stabilizes the intermediate.

13. (i) Due to $-I$ effect of chlorine.

(ii) Alkyl group has a $+I$ effect. Hence, butyric acid gives H^+ with difficulty and therefore, weaker than formic acid.

(iii) Alkyl groups increase electron density on nitrogen due to $+I$ effect and thus, the electron pair donating capacity of nitrogen increases.

(iv) Benzyl carbocation is more stable due to the presence of resonance.



(v) Alkyl group is electron releasing group ($+I$ effect). It partially neutralises the positive charge on carbon and thus, increases the stability of carbocation.

(vi) Allyl carbocation is more stable due to the presence of resonance.

$$H_2C{=}CH—\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2—CH{=}CH_2$$

(vii) Tert. butyl chloride reacts by S_N1 mechanism because it forms stable carbocation. *n*-Butyl chloride reacts by S_N2 mechanism as the reaction is non-ionic. Transition state is formed in which both OH and Cl are partially bonded to the halide carbon.

(viii) In $R—C{\equiv}\overset{+}{O}:$, the octet of every atom is complete while in $R—\overset{+}{C}{=}O$, the carbon has only 6 electrons.

(ix) Side chain bromination of toluene to give benzyl bromide is favoured under photo-chemical irradiation and involves a free radical mechanism.

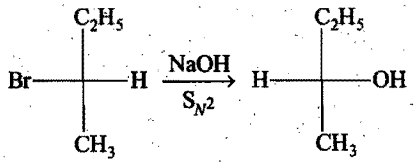
While in presence of $FeBr_3$, electrophilic substitution in the benzene ring occurs and it forms *p*-bromo toluene.

(x) Aryl halides are less reactive and more stable than alkyl halides due to

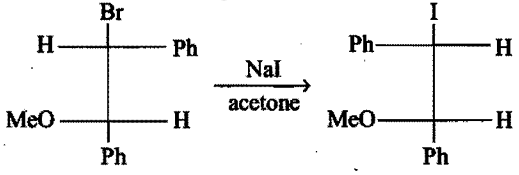
(a) Resonance: In aryl halides, the delocalization of electron pair occurs (see section **16.10**) and gives a partial double bond character to C— *X* bond making it stronger than C— *X* bond in alkyl halides.

(b) Difference in hybridization of carbon: In alkyl halides, the C—*X* bond is sp^3-hybridized while in aryl halides it is sp^2-hybridized. Therefore, the C—*X* bond length in aryl halides is shorter than alkyl halides.

(xi) In S_N2 reactions, the substitution occurs with stereochemical inversion. Hence, the reaction is:

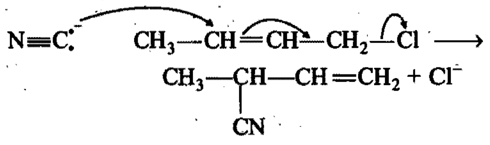


(xii) Br is replaced by I following S_N2 mechanism. There will be Walden inversion at the place of replacement.



(xiii) $:CF_2$. Since, F and C are in the same period of the periodic table, their *p* AO's are about the same size permitting more efficient overlap. Furthermore, of the *X*—C bonds, the F—C bond length is the shortest.

(xiv) Formation of product (a) is obtained from the expected S_N2 reaction at C^1. However, CN^- can also bond to C^3 with the nucleophile π $\bar{e}$'s, displacing Cl^- as the allylic rearrangement occurs.



$$N{\equiv}C: \quad CH_3—CH{=}CH—CH_2—Cl \longrightarrow CH_3—\underset{\displaystyle CN}{\underset{|}{C}H}—CH{=}CH_2 + Cl^-$$

(b)

This is called S_N2-prime mechanism.

(xv) $(H_2C{=}CH—\overset{+}{C}{}^3H—CH_3 \longleftrightarrow H_2\overset{+}{C}{}^1—CH{=}CHCH_3)$
The intermediate R^+ can react with H_2O at either C^1 or C^3 each of which has δ^+ charge. Reaction at C^3 (2°) has more δ^+ and forms $HOCH_2CH{=}CHCH_3$.

14. (a) $(CH_3)_2\overset{+}{C}H$, a carbocation; (b) $CH_3—C{\equiv}\overset{-}{C}:$, a carbanion;

(c) $CH_3\dot{C}H_2$, a free radical;

(d) $CH_3—\overset{+}{C}H—CH_2—CH_3$, a carbocation;

(e) $CH_3\ddot{C}H$, a carbene (singlet);

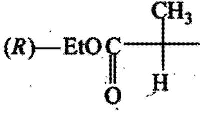
(f) $CH_3—\overset{+}{C}H_2$, a carbocation.

15. (a) (*S*)—$CH_3CH(OMe)CH_2CH_3$ (S_N2 invert configuration)

(b) (*R*)—$CH_3CH(OMe)CH_2CH_3$ (S_N2 invert configuration)

(c) $(CH_3)_3C—OMe$, an ether (S_N1 reaction)

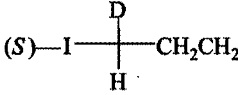
(d) $Me_3COMe + Me_2S + MeOH$ (S_N1 reaction, methanolysis)

(e) 

$$(R)—EtO\underset{\underset{\displaystyle O}{\|}}{C}—\overset{\displaystyle CH_3}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—CN$$

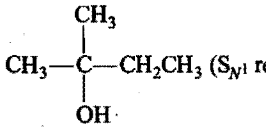
(S_N2 invert configuration)

(f) $CH_3CH_2—O—CH_2OC_2H_5$ (S_N1 reaction, ethanolysis)

(g) 

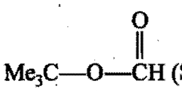
$$(S)—I—\overset{\displaystyle D}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—CH_2CH_2CH_3$$

(S_N2 invert configuration)

(h) 

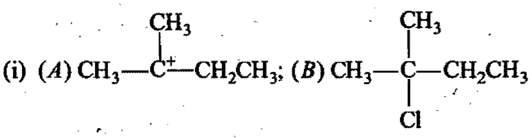
$$CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}—CH_2CH_3$$

(S_N1 reaction, methyl shift)

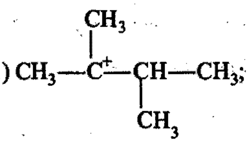
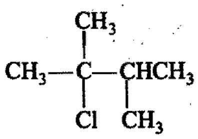
(i) 

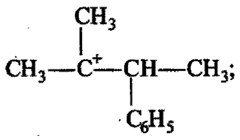
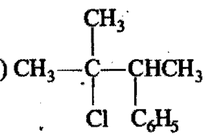
$$Me_3C—O—\overset{\displaystyle O}{\overset{\|}{C}}H$$

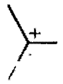
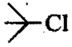
(S_N1 reaction, a formate ester)

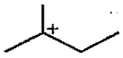
16. (i) 

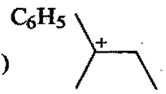
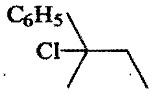
$$(A)\ CH_3—\overset{\displaystyle CH_3}{\overset{|}{C^+}}—CH_2CH_3;\ (B)\ CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}—CH_2CH_3$$

(ii) (*A*)

$CH_3-\overset{CH_3}{\overset{|}{C^+}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$;
(*B*)

$CH_3-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-\underset{CH_3}{\underset{|}{CHCH_3}}$

(iii) (*A*)

$CH_3-\overset{CH_3}{\overset{|}{C^+}}-\underset{C_6H_5}{\underset{|}{CH}}-CH_3$;
(*B*)

$CH_3-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-\underset{C_6H_5}{\underset{|}{CHCH_3}}$

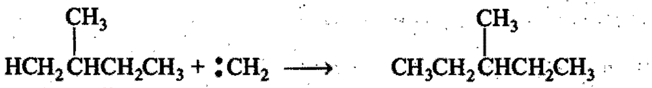
(iv) (*A*)

;
(*B*)


(v) (*A*)

;
(*B*)


(vi) (*A*)

;
(*B*)


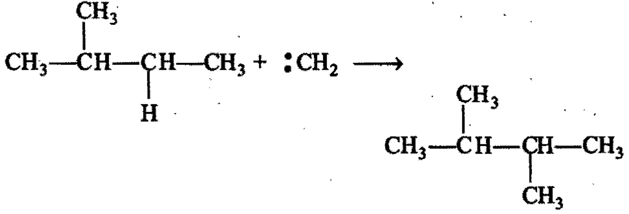
(vii) (*A*) $CH_3HC{=}CH\overset{+}{C}H_2$; (*B*) $CH_3HC{=}CHCH_2Br$
(Major)

17. Singlet methylene can be inserted into all C—H bonds of 2-methyl butane with equal ease.

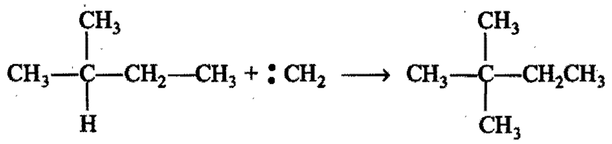

$HCH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3 + :CH_2 \longrightarrow CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

2-Methylbutane

3-Methylpentane
(Insertion on primary carbon)


$CH_3-\overset{CH_3}{\overset{|}{C}}H-\underset{H}{\underset{|}{C}}H-CH_3 + :CH_2 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}H-\underset{CH_3}{\underset{|}{C}}H-CH_3$

2,3-Dimethylbutane
(Insertion on secondary carbon)


$CH_3-\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-CH_2-CH_3 + :CH_2 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2CH_3$

2,2-Dimethylbutane
(Insertion on tertiary carbon)

18. $R-Li \xrightarrow{\text{Homolysis}} R^{\bullet} + Li^{\bullet}$

(i) $R-X: + Li^{\bullet} \longrightarrow [R-X:]^{\bullet} + Li^+$
A radical anion

(ii) $[R-X:]^{\bar{\bullet}} \longrightarrow R^{\bullet} + X:^-$

(iii) $R^{\bullet} + Li^{\bullet} \longrightarrow R:Li$

Complete equation is $RX + 2Li \longrightarrow R-Li + Li^+X^-$

OBJECTIVE QUESTIONS

SET I : This set contains questions with single correct answer.

1. Inductive effect refers to:

(a) electron displacement along a carbon chain ☐
(b) complete transfer of one of the shared pair of electrons to one of the atoms joined by a double bond ☐
(c) complete transfer of electrons hitherto unshared ☐
(d) none of the above ☐

2. $+I$ effect is shown by: **[MGIMS (Wardha) 2008]**

(a) $—NO_2$ ☐ (b) —Cl ☐
(c) —Br ☐ (d) $—CH_3$ ☐

3. Polarisation of electrons in acrolein may be written as:

(a) $H_2\overset{\delta^+}{C}{=}CH{—}CH{=}\overset{\delta^-}{O}$ ☐
(b) $H_2\overset{\delta^+}{C}{=}CH{—}\overset{\delta^-}{C}H{=}O$ ☐
(c) $H_2\overset{\delta^-}{C}{=}\overset{\delta^+}{C}H{—}CH{=}O$ ☐
(d) $H_2\overset{\delta^-}{C}{=}CH{—}CH{=}\overset{\delta^+}{O}$ ☐

4. Choose the weakest acid among the following : **[PET (Kerala) 2010]**

(a) F_3CCOOH ☐ (b) FCH_2COOH ☐
(c) CH_3COOH ☐ (d) CH_3CH_2COOH ☐
(e) $(CH_3)_2CHCOOH$ ☐

5. Among the following which one is most basic?

(a) NH_3 ☐ (b) CH_3NH_2 ☐
(c) $CH_3CH_2NH_2$ ☐ (d) $C_6H_5NH_2$ ☐

6. Most acidic compound is:

(a) CH_3COOH ☐ (b) C_6H_5COOH ☐
(c) $O_2NC_6H_4CO_2H$ ☐ (d) C_6H_5OH ☐

7. Maximum $-I$ effect is exerted by the group:

(a) $C_6H_5—$ ☐ (b) $—OCH_3$ ☐
(c) Cl ☐ (d) NO_2 ☐

8. Zero inductive effect is exerted by:

(a) $C_6H_5—$ ☐ (b) H ☐
(c) $CH_3—$ ☐ (d) Cl ☐

9. Electromeric effect:

(a) comes into play at the demand of attacking reagent ☐
(b) involves displacement of electrons in a sigma bond ☐
(c) comes into play in the molecule when at least one atom has unshared pair of electrons ☐
(d) involves the distortion of the electron cloud ☐

10. The reaction intermediate produce by homolytic cleavage of bond is called: **[CET (J&K) 2007; PMT (Kerala) 2010]**

(a) carbocations ☐ (b) carbanions ☐
(c) free radicals ☐ (d) carbenes ☐

11. Heterolytic fission of carbon-chlorine bond produces:

(a) two free radicals ☐
(b) two carbocations ☐
(c) two carbanions ☐
(d) one cation and one anion ☐

12. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is:

(a) C—C ☐ (b) C—O ☐
(c) C—H ☐ (d) O—H ☐

13. The most stable carbocation is:

(a) methyl carbocation ☐
(b) primary carbocation ☐
(c) secondary carbocation ☐
(d) tertiary carbocation ☐

14. The most stable carbanion is:

(a) methyl carbanion ☐
(b) primary carbanion ☐
(c) secondary carbanion ☐
(d) tertiary carbanion ☐

15. Which of the following ions is most stable?

(a) $CH_3CH_2\overset{+}{C}H_2$ ☐ (b) $CH_3\overset{+}{C}HCH_2CH_3$ ☐
(c) $(CH_3)_3\overset{+}{C}$ ☐ (d) $(CH_3)_3C\overset{+}{C}H_2$ ☐

16. A free radical is:

(a) shortly lived species ☐ (b) neutral in nature ☐
(c) paramagnetic ☐ (d) all of these ☐

17. Which one is the characteristic feature of a free radical?

(a) Presence of negative or positive charge ☐
(b) Presence of unpaired electron ☐
(c) Presence of even number of electrons ☐
(d) Associated with high stability ☐

18. The number of electrons, present in the valence shell of carbon of $CH_3\overset{+}{C}H_2$ ion bearing +ve charge, is:

(a) 8 ☐ (b) 7 ☐
(c) 6 ☐ (d) 4 ☐

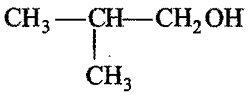
19. The number of electrons, present in the valence shell of carbon of carbanion bearing –ve charge, is:

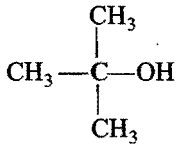
(a) 8 ☐ (b) 7 ☐
(c) 6 ☐ (d) 4 ☐

20. Dehydration of alcohol involves:

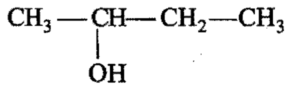
(a) free radical ☐ (b) carbocation ☐
(c) carbanion ☐ (d) carbene ☐

21. The compound which gives the most stable carbocation on dehydration is:

(a) 
$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}H}—CH_2OH$ ☐

(b) 
$CH_3—\underset{\displaystyle CH_3}{\underset{|}{\overset{\overset{\displaystyle CH_3}{|}}{C}}}—OH$ ☐

(c) $CH_3CH_2CH_2CH_2OH$ ☐

(d)  $CH_3{-}\underset{|\atop OH}{CH}{-}CH_2{-}CH_3$ ☐

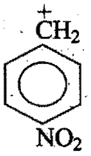
22. Which one of the following is a free radical?
(a) H^+ ☐ (b) H^- ☐
(c) H ☐ (d) H_2 ☐

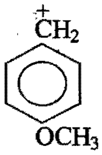
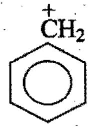
23. The shape of $[CH_3]^+$ is:
(a) triangular planar ☐ (b) square planar ☐
(c) tetrahedral ☐ (d) none of these ☐

24. Which of the following statements is wrong?
(a) A tertiary free radical is more stable than a secondary free radical ☐
(b) A secondary free radical is more stable than a primary free radical ☐
(c) A tertiary carbocation is more stable than a secondary carbocation ☐
(d) A primary carbocation is more stable than a secondary carbocation ☐

25. Most stable carbocation is:
(a) $CH_3{-}\overset{+}{C}H_2$ ☐ (b) $\overset{+}{C}H_2CHCl_2$ ☐
(c) $\overset{+}{C}H_2CH_2Cl$ ☐ (d) $CH_2{-}CH_2NO_2$ ☐

26. Most stable carbocation is:

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

27. The shape of carbanion, $[CH_3]^-$ is:
(a) linear ☐ (b) pyramidal ☐
(c) planar ☐ (d) tetrahedral ☐

28. In carbocation, the carbon atom bearing the positive charge is:
(a) sp^3-hybridized ☐ (b) sp-hybridized ☐
(c) dsp^2-hybridized ☐ (d) sp^2-hybridized ☐

29. An electrophilic reagent is:
(a) electron-rich species ☐
(b) electron-deficient species ☐
(c) a Lewis base ☐
(d) negatively charged species ☐

30. A nucleophile is:
(a) electron-rich species ☐
(b) electron-deficient species ☐
(c) a Lewis acid ☐
(d) positively charged species ☐

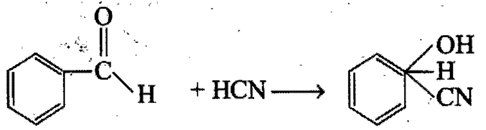
31. Which of the following is an electrophilic reagent?
(a) H_2O ☐ (b) OH^- ☐
(c) NO_2^+ ☐ (d) none ☐

32. Which of the following is not an electrophile?
(a) $AlBr_3$ ☐ (b) BF_3 ☐
(c) $SnCl_4$ ☐ (d) NH_3 ☐

33. Alkenes readily undergo:
(a) substitution reactions ☐
(b) addition reactions ☐
(c) elimination reactions ☐
(d) rearrangement reactions ☐

34. The following reaction is:
$$C_2H_5Br + KOH \longrightarrow C_2H_5OH + KBr:$$
(a) electrophilic substitution ☐
(b) elimination ☐
(c) nucleophilic substitution ☐
(d) addition ☐

35. The following reaction is an example of:



[JEE (Orissa) 2007]

(a) nucleophilic substitution ☐
(b) electrophilic substitution ☐
(c) electrophilic addition ☐
(d) nucleophilic addition ☐

36. The reaction between ethylene and bromine is an example of:
(a) electrophilic addition ☐
(b) electrophilic substitution ☐
(c) nucleophilic addition ☐
(d) nucleophilic substitution ☐

37. In the nitration of benzene with a mixture of conc. HNO_3 and conc. H_2SO_4, the active species involved is:
(a) nitrite ion ☐ (b) nitrate ion ☐
(c) nitronium ion ☐ (d) nitrogen dioxide ☐

38. Nitration of benzene is:
(a) nucleophilic substitution ☐
(b) nucleophilic addition ☐
(c) electrophilic substitution ☐
(d) free radical substitution ☐

39. Consider the following structures

$$\underset{\text{I}}{H_2C{=}\overset{+}{C}H}\ ,\quad \underset{\text{II}}{CH_3{-}\overset{+}{C}H_2}\ ,$$
$$\underset{\text{III}}{H_2C{=}CH{-}\overset{+}{C}H_2}\ ,\quad \underset{\text{IV}}{C_6H_5{-}\overset{+}{C}H{-}C_6H_5}$$

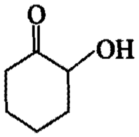
The correct sequence of these carbocations in the decreasing order of their stability is :
(a) I, II, III, IV ☐ (b) IV, III, II, I ☐
(c) IV, II, III, I ☐ (d) I, III, II, IV ☐

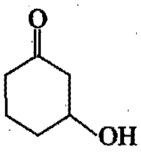
40. Addition of HI on the double bond of propene yields isopropyl iodide and not *n*-propyl iodide as the major product. This is because the addition proceeds through:
(a) a more stable carbonium ion ☐
(b) a more stable carbanion ion ☐
(c) a more stable free radical ☐
(d) none of the above is a correct statement ☐

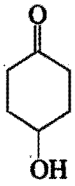
41. Which of the following alkyl halides is hydrolysed by S_N1 mechanism?
(a) CH_3Cl ☐ (b) CH_3CH_2Cl ☐
(c) $CH_3CH_2CH_2Cl$ ☐ (d) $(CH_3)_3CCl$ ☐

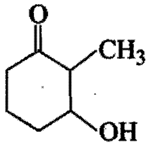
42. Which of the following statements does not apply to free radical chain reaction?
(a) It may be initiated by ultraviolet rays ☐
(b) One mole of product is obtained for each mole of free radical produced in the initiation step ☐
(c) It is not affected by changes in polarity of solvents ☐
(d) It is inhibited by the presence of certain reagents ☐

43. Which is dehydrated to a maximum extent using conc. H_2SO_4?

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

44. Which one of the following statements is wrong about S_N2 reaction?
(a) The rate of reaction is independent of the concentration of nucleophile ☐
(b) Nucleophile attacks the carbon from the side opposite to where the leaving group is attached ☐
(c) Only in one step the bond formation and bond breaking takes place ☐
(d) The rate of reaction ∝ [substrate] [nucleophile] ☐

45. Markownikoff's rule is applicable to which of the following reactions?
(a) $C_2H_4 + HBr$ ☐ (b) $C_3H_6 + Cl_2$ ☐
(c) $C_3H_6 + HBr$ ☐ (d) $C_3H_6 + Br_2$ ☐

46. The addition of HBr to propylene takes place opposite to Markownikoff's rule in presence of:
(a) sunlight ☐ (b) hydrogen peroxide ☐
(c) platinum catalyst ☐ (d) none of these ☐

47. Anti-Markownikoff's addition is not observed in:
(a) propene ☐ (b) 1-butene ☐
(c) 2-pentene ☐ (d) 2-butene ☐

48. Ammonia is iso-structural with:
(a) carbanion ☐ (b) free radical ☐
(c) carbocation ☐ (d) carbene ☐

49. Which of the following statements is correct?
(a) Allyl carbocation ($H_2C=CH-\overset{+}{C}H_2$) is more stable than propyl carbocation ☐
(b) Propyl carbocation is more stable than allyl carbocation ☐
(c) Both are equally stable ☐
(d) None of the above ☐

50. Which of the following statements is correct about a carbocation?
(a) It reacts with nucleophile ☐
(b) It can undergo rearrangement ☐
(c) It can eliminate an H^+ to form an olefin ☐
(d) All are correct ☐

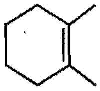
51. S_N1 mechanism for the hydrolysis of an alkyl halide involves the formation of intermediate:
(a) free radical ☐ (b) carbocation ☐
(c) carbanion ☐ (d) none of these ☐

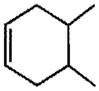
52. Stability of $\overset{+}{C}H_2-CH=CH_2$ can be explained by:
(a) inductive effect ☐ (b) electromeric effect ☐
(c) resonance ☐ (d) polar effect ☐

53. Nucleophilic part of the reagent attacks the substrate $CH_3CH_2COCH_3$ on the:
(a) carbon atom of carbonyl group ☐
(b) oxygen atom of carbonyl group ☐
(c) methyl group ☐
(d) CH_2 group ☐

54. Elimination reaction generally occurs with the formation of:
(a) one sigma bond ☐
(b) one pi bond ☐
(c) one sigma and one pi bond ☐
(d) none of the above ☐

55. Which of the following orders is correct for the ease of electrophile addition on these alkenes?


I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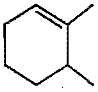

III

(a) III > II > I ☐ (b) I > II > III ☐
(c) I > III > II ☐ (d) III > I > II ☐

56. Hyperconjugation is most useful for stabilizing which of the following carbocations ? **[PET (Kerala) 2010]**
(a) *neo*-Pentyl ☐ (b) *tert.*-Butyl ☐
(c) *iso*-Propyl ☐ (d) Ethyl ☐
(e) Methyl ☐

57. Which of the following explanations accounts for *o*-nitro phenol to be more volatile than *p*-nitro phenol?
(a) Intermolecular hydrogen bonding ☐
(b) Resonance ☐
(c) Intramolecular hydrogen bonding ☐
(d) Inductive effect ☐

58. The peroxide effect in anti-Markownikoff's addition involves:
(a) ionic mechanism ☐
(b) free radical mechanism ☐
(c) heterolytic fission of double bond ☐
(d) homolytic fission of double bond ☐

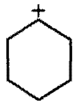
59. What is the decreasing order of strength of the bases, OH^- (I), NH_2^- (II), $H-C\equiv C^-$ (III), $CH_3CH_2^-$ (IV)?
(a) IV > II > III > I ☐
(b) III > IV > II > I ☐

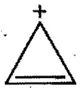
(c) I > II > III > IV ☐
(d) II > III > I > IV ☐

60. Arrange the following compounds in order of increasing dipole moment,
Toluene (I), *m*-dichlorobenzene (II), *o*-dichlorobenzene (III), *p*-dichlorobenzene (IV):
(a) I < IV < II < III ☐
(b) IV < I < II < III ☐
(c) IV < I < III < II ☐
(d) IV < II < I < III ☐

61. Which is the decreasing order of acidity in the following compounds?
CH_3CH_2OH(I) CF_3CH_2OH(II)
$CCl_3—CH_2OH$(III) $(NO_2)_3C—CH_2OH$(IV)
(a) I > II > III > IV ☐ (b) II > I > III > IV ☐
(c) IV > II > I > III ☐ (d) IV > II > III > I ☐

62. The stability of the following carbocation decreases in the order :


I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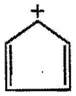
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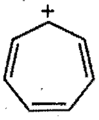
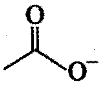
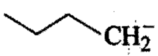

IV

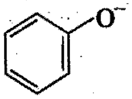
(a) IV > III > II > I ☐ (b) IV > II > III > I ☐
(c) IV > II > I > III ☐ (d) IV > I > II > III ☐

63. Order of base strength of the compounds :


(I)


(II)

NH_2^-
(III)


(IV)

[AMU (Engg.) 2010]
(a) IV > II > I > III ☐ (b) III > II > IV > I ☐
(c) II > III > IV > I ☐ (d) II > III > I > IV ☐

64. Carbocation is a reaction intermediate in which of the following reactions?
(a) E_1 reactions ☐
(b) Electrophilic addition reactions of alkenes and alkynes ☐
(c) $S_{N}1$ reactions ☐
(d) All of the above ☐

65. Methyl chloride reacts with the solution of NaOH by the mechanism:
(a) S_N1 ☐ (b) S_N2 ☐
(c) S_E1 ☐ (d) S_E2 ☐

66. S_N1 reaction is favoured by:
(a) bulky groups on the carbon atom attached to halogen atom ☐
(b) small groups on the carbon atom attached to halogen atom ☐
(c) non-polar solvents ☐
(d) none of the above ☐

67. Halogenation of an alkane takes place through the intermediate:
(a) carbocation ☐ (b) carbanion ☐
(c) carbon free radical ☐ (d) carbene ☐

68. Heterolytic fission of a covalent bond can form:
(a) free radical ☐
(b) both carbocation and carbanion ☐
(c) only carbocation ☐
(d) only carbanion ☐

69. Reimer-Tiemann reaction of phenol with chloroform and aqueous alkali takes place through the intermediate formation of:
(a) carbocations ☐ (b) carbanions ☐
(c) carbon radicals ☐ (d) carbenes ☐

70. The reaction intermediate carbenes are produced from:
(a) diazo methane ☐ (b) ketene ☐
(c) $CHCl_3/C_2H_5ONa$ ☐ (d) all of these ☐

71. Markownikoff's addition product lies in the formation of intermediate stable:
(a) carbocation ☐ (b) carbanion ☐
(c) carbon radical ☐ (d) unsaturation ☐

72. Peroxide effect of addition of HBr to alkenes occurs through a stable:
(a) carbocation ☐ (b) carbanion ☐
(c) carbon radical ☐ (d) carbene ☐

73. In addition reactions of alkenes, the Markownikoff's rule follow:
(a) ionic mechanism ☐
(b) radical mechanism ☐
(c) substitution mechanism ☐
(d) rearrangement mechanism ☐

74. Addition of HBr to propene in presence of peroxide (anti-Markownikoff's addition) occurs when:
(a) Br^+ first adds to propene ☐
(b) Br^- first adds to propene ☐
(c) H^+ first adds to propene ☐
(d) Br first adds to propene ☐

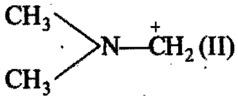
75. Removal of hydride ion from CH_4 molecule will give:
(a) methyl radical ☐ (b) methyl group ☐
(c) methyl carbanion ☐ (d) methyl carbocation ☐

76. In a Friedel-Crafts reaction, the electrophile is:
(a) Cl^- or X^- ☐ (b) CH_3^+ or CH_3CO^+ ☐
(c) CH_3Cl ☐ (d) CH_3COCl ☐

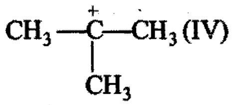
77. Arrange the following carbanions in decreasing order of stability:
$HC{\equiv}\bar{C}$(I), $H_3C—C{\equiv}\bar{C}$(II),
$H_2C{=}\bar{C}H$(III), $H_3C—\bar{C}H_2$(IV)
(a) IV > III > I > II ☐ (b) II > I > III > IV ☐
(c) IV > III > II > I ☐ (d) I > II > III > IV ☐

78. Arrange the following carbocations in decreasing order of stability:

$CH_3CH_2\overset{+}{C}H_2$ (I),


$(CH_3)_2N—\overset{+}{C}H_2$ (II)

$CH_3—\overset{+}{C}H—CH_3$ (III),

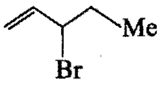

$CH_3—\overset{+}{C}(CH_3)—CH_3$ (IV)

(a) I > II > III > IV ☐ (b) IV > III > I > II ☐
(c) II > IV > III > I ☐ (d) IV > III > II > I ☐

79. Which behaves both as a nucleophile and electrophile?
(a) CH_3NH_2 ☐ (b) CH_3OH ☐
(c) CH_3CN ☐ (d) CH_3Cl ☐

80. Consider the following bromides :


(I)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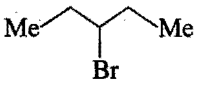
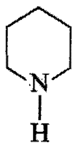

(III)

The correct order of S_N1 reactivity is : **[AIEEE 2010]**
(a) I > II > III ☐ (b) II > III > I ☐
(c) II > I > III ☐ (d) III > II > I ☐

81. In the following compounds, the order of basicity is :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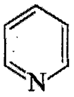
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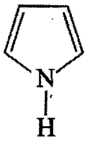
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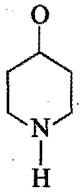

IV

(a) I > IV > II > III ☐ (b) II > I > IV > III ☐
(c) III > I > IV > II ☐ (d) IV > I > III > II ☐

82. Which one is the correct order of decreasing stability of carbanions?
(a) $P > S > T > C_6H_5CH_2$ ☐
(b) $C_6H_5CH_2 > P > S > T$ ☐
(c) $T > S > P > C_6H_5CH_2$ ☐
(d) $C_6H_5CH_2 > T > S > P$ ☐

83. The stability order in the following carbocations, $CH_3CH_2^+$ (I), $(CH_3)_2\overset{+}{C}H$ (II), $(CH_3)_3C^+$ (III) and $\overset{+}{C}H_3$ (IV) is: **[CBSE (Med.) 2005; JIPMER 2007]**
(a) I > IV > III > II ☐ (b) I > II > III > IV ☐
(c) III > IV > I > II ☐ (d) III > II > I > IV ☐

84. Which one of the following carbocations is most stable?
(a) $C_6H_5—\overset{+}{C}H—C_6H_5$ ☐ (b) $CH_3—\overset{+}{C}H—CH_3$ ☐
(c) $H_2C=CH—\overset{+}{C}H_2$ ☐
(d) $H_2C=CH—\overset{+}{C}H—CH_3$ ☐

85. Which is the weakest base of the following whose pK_b values are?
(a) 4.75 ☐ (b) 3.23 ☐
(c) 3.12 ☐ (d) 3.07 ☐

86. Which is the decreasing order of acidity in, HCOOH (I), CH_3COOH (II), CH_3CH_2COOH (III) and C_6H_5COOH (IV)?
(a) I > II > III > IV ☐ (b) IV > III > II >I ☐
(c) IV > I > II > III ☐ (d) I > IV > II > III ☐

87. Which one of the following is the weakest base?
(a) $(C_2H_5)_3N$ ☐ (b) $(C_2H_5)_2NH$ ☐
(c) $C_2H_5NH_2$ ☐ (d) NH_3 ☐

88. Which is the strongest acid of the following whose pK_a values are?
(a) 15.88 ☐ (b) 9.95 ☐
(c) 7.70 ☐ (d) 3.77 ☐

89. Which one of the following compounds is most acidic?
(a) Phenol ☐ (b) Trichloroacetaldehyde ☐
(c) Trichloroacetic acid ☐ (d) Benzoic acid ☐

90. Arrange basicity of the following compounds in decreasing order:
$CH_3CH_2NH_2$ (I), $H_2C=CH—NH_2$ (II),
$HC\equiv C—NH_2$ (III), $C_6H_5NH_2$ (IV)
(a) I > II > III > IV ☐ (b) IV > III > II > I ☐
(c) III > II > I > IV ☐ (d) I > III > II > IV ☐

91. Which of the following compounds does not contain acidic hydrogen?
(a) Phenol ☐ (b) Methyl amine ☐
(c) Acetic acid ☐ (d) Methyl alcohol ☐

92. Which of the following compounds is not a Lewis acid?
(a) BF_3 ☐ (b) $SnCl_4$ ☐
(c) $R—OR$ ☐ (d) $R—MgX$ ☐

93. Which of the following contains three pairs of electron?
(a) Carbocation ☐ (b) Carbanion ☐
(c) Free radical ☐ (d) None of these ☐

94. In the following compounds phenol (I), *p*-cresol (II), *m*-nitrophenol (III) and *p*-nitrophenol (IV), the order of acidity is:
(a) III > IV > I > II ☐ (b) I > IV > III > II ☐
(c) II > I > III > IV ☐ (d) IV > III > I > II ☐

95. In the following compounds piperidine (I), pyridine (II), morpholine (III) and pyrrole (IV), the order of basicity is:
(a) IV > I > III > II ☐ (b) III > I > IV > II ☐
(c) II > I > III > IV ☐ (d) I > III > II > IV ☐

96. The kind of delocalization involving sigma bond orbitals is called:
(a) hybridization ☐ (b) conjugation ☐
(c) hyperconjugation ☐ (d) conformation ☐

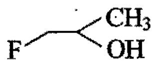
97. Hyperconjugation phenomenon is possible in:
(a) $H_2C=CH_2$ ☐
(b) $CH_3CH_2—CH=CH_2$ ☐
(c) $C_6H_5CH=CH_2$ ☐
(d) $(CH_3)_3C—CH=CH_2$ ☐

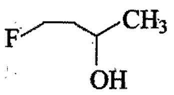
98. In the following compounds, anisole (I), benzene (II) and nitrobenzene (III), the ease of reaction with electrophiles is:
(a) II > III > I ☐ (b) III > II > I ☐
(c) II > I > III ☐ (d) I > II > III ☐

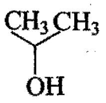
99. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is:
(a) MeCOCl ☐ (b) MeCHO ☐
(c) MeCOOMe ☐ (d) MeCOOCOMe ☐

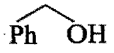
100. Among the following compounds, the strongest acid is:
(a) $HC\equiv CH$ ☐ (b) C_6H_6 ☐
(c) C_2H_6 ☐ (d) CH_3OH ☐

101. The order of reactivity of following alcohols, towards conc. HCl is:


(i)

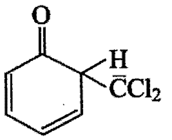

(ii)

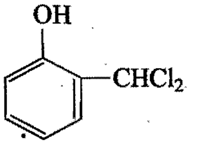

(iii)

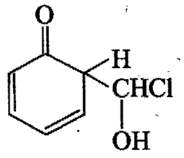

(iv)

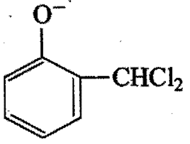
(a) I > II > III > IV ☐ (b) I > III > II > IV ☐
(c) IV > III > II > I ☐ (d) IV > III > I > II ☐

102. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates?

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

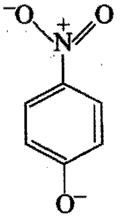
103. In the reaction of phenol with $CHCl_3$ and aqueous NaOH at 70°, the electrophile attacking the ring is:

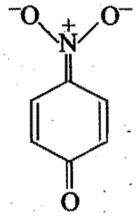
(a) $CHCl_3$ ☐ (b) $CHCl_2$ ☐
(c) $:CCl_2$ ☐ (d) $COCl_2$ ☐

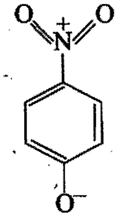
104. A solution of (+)-2-chloro-2-phenyl ethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of:

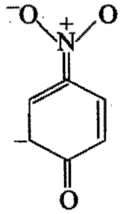
(a) carbanion ☐ (b) carbene ☐
(c) free radical ☐ (d) carbocation ☐

105. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is:

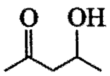
(a)  ☐

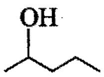
(b)  ☐

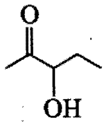
(c)  ☐

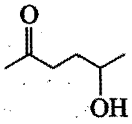
(d)  ☐

106. Which one of the given will most readily be dehydrated in acidic condition? **[IIT (S) 2000]**

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

107. Which of the following has the highest nucleophilicity? **[IIT (S) 2000]**

(a) F^- ☐ (b) OH^- ☐
(c) CH_3^- ☐ (d) NH_2^- ☐

108. Among the following, the strongest base is: **[illegible] (S) 2000]**

(a) $C_6H_5NH_2$ ☐ (b) *p*-NO_2—$C_6H_4NH_2$ ☐
(c) *m*-NO_2—$C_6H_4NH_2$ ☐ (d) $C_6H_5CH_2NH_2$ ☐

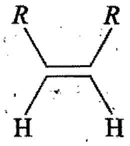
109. The order of reactivities of the following alkyl halides for a S_N2 reaction is: **[IIT (S) 2000]**

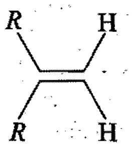
(a) $RF > RCl > RBr > RI$ ☐
(b) $RF > RBr > RCl > RI$ ☐
(c) $RCl > RBr > RF > RI$ ☐
(d) $RI > RBr > RCl > RF$ ☐

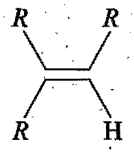
110. Which of the following has the most acidic hydrogen? **[IIT (S) 2000]**

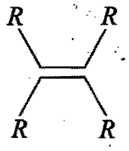
(a) 3-Hexanone ☐ (b) 2,4-Hexanedione ☐
(c) 2,5-Hexanedione ☐ (d) 2,3-Hexanedione ☐

111. Which of the following alkenes will react fastest with H_2 under catalytic hydrogenation conditions? **[IIT (S) 2000]**

(a)  ☐

(b)  ☐

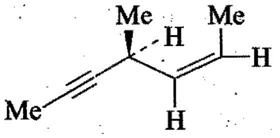
(c)  ☐

(d)  ☐

112. The set with correct order of acidity is: **[IIT (S) 2001; CBSE (Med.) 2005]**

(a) $HClO < HClO_2 < HClO_3 < HClO_4$ ☐
(b) $HClO_4 < HClO_3 < HClO_2 < HClO$ ☐
(c) $HClO < HClO_4 < HClO_3 < HClO_2$ ☐
(d) $HClO_4 < HClO_2 < HClO_3 < HClO$ ☐

113. Hydrogenation of the following compound in the presence of poisoned palladium catalyst gives: **[IIT (S) 2001]**



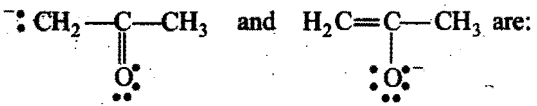
(a) optically active compound ☐
(b) an optically inactive compound ☐
(c) a racemic mixture ☐
(d) a distereomeric mixture ☐

114. Consider the following carbocations:

(I) $C_6H_5\overset{+}{C}H_2$ (II) $C_6H_5CH_2\overset{+}{C}H_2$
(III) $C_6H_5\overset{+}{C}HCH_3$ (IV) $C_6H_5\overset{+}{C}(CH_3)_2$

The correct sequence of the stability of these is: **[SCRA 2001]**

(a) II < I < III < IV ☐ (b) II < III < I < IV ☐
(c) III < I < II < IV ☐ (d) IV < III < I < II ☐

115. 
$\overset{-}{:}CH_2-\underset{\underset{\cdot\cdot}{\overset{\|}{O:}}}{C}-CH_3$ and $H_2C=\underset{\underset{\cdot\cdot}{\overset{|}{:O:^-}}}{C}-CH_3$ are:

[CBSE (Med.) 2002]

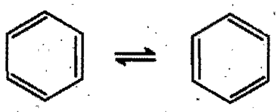
(a) resonating structures ☐ (b) tautomers ☐
(c) geometrical isomers ☐ (d) optical isomers ☐

116. The arrangement of $(CH_3)_3C-$, $(CH_3)_2CH-$, CH_3CH_2- when attached a benzene or an unsaturated group in increasing order of inductive effect is: [AIEEE 2002]

(a) $(CH_3)_3C- < (CH_3)_2CH- < CH_3CH_2-$ ☐
(b) $CH_3CH_2- < (CH_3)_2CH- < (CH_3)_3C-$ ☐
(c) $(CH_3)_2CH- < (CH_3)_3C- < CH_3CH_2-$ ☐
(d) $(CH_3)_3C- < CH_3CH_2- < (CH_3)_2CH-$ ☐

117. Which of the following statements regarding the resonance energy of benzene is correct? [UP SEAT 2002]

(a) The energy required to break the C—H bond in benzene ☐
(b) The energy required to break the C—C bond in benzene ☐
(c) The energy is a measure of stability of benzene ☐
(d) The energy required to convert ☐



118. The reaction,

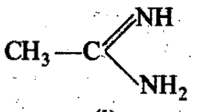
$(CH_3)_3C-Br \xrightarrow{H_2O} (CH_3)_3C-OH$ is: [AIEEE 2002]

(a) elimination reaction ☐
(b) substitution reaction ☐
(c) free radical reaction ☐
(d) displacement reaction ☐

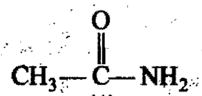
119. An S_N2 reaction at an asymmetric carbon of a compound always gives: [IIT(S) 2001]

(a) an enantiomer of the substrate ☐
(b) a product with opposite optical rotation ☐
(c) a mixture of diastereomers ☐
(d) a single stereoisomer ☐

120. The correct order of basicities of the following compounds is: [IIT (S) 2001]


(1)

, $CH_3CH_2NH_2$, (2) $(CH_3)_2NH$, (3)


$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$
(4)

(a) 2 > 1 > 3 > 4 ☐ (b) 1 > 3 > 2 > 4 ☐
(c) 3 > 1 > 2 > 4 ☐ (d) 1 > 2 > 3 > 4 ☐

121. Which of the following is not a Lewis base? [PMT (Delhi) 2002]

(a) $AlCl_3$ ☐ (b) $(CH_3)_2\ddot{N}H$ ☐
(c) C_2H_5OH ☐ (d) $C_2H_5-\underset{\cdot\cdot}{\ddot{O}}-C_2H_5$ ☐

122. Which of the following is the correct order of stability of free radicals? [PMT (Delhi) 2002]

(a) benzyl > allyl > 3° > 2° ☐
(b) allyl > benzyl > 3° > 2° ☐
(c) allyl > 3° > 2° > benzyl ☐
(d) benzyl > 3° > 2° > allyl ☐

123. The correct order of increasing basicity of the given conjugated bases ($R = CH_3$) is : [AIEEE 2010]

(a) $RCOO^- < HC\equiv C^- < NH_2^- < R^-$ ☐
(b) $RCOO^- < HC\equiv C^- < R^- < NH_2^-$ ☐
(c) $R^- < HC\equiv C^- < RCOO^- < NH_2^-$ ☐
(d) $RCOO^- < NH_2^- < HC\equiv C^- < R^-$ ☐

124. Which of the following is correct for stability of phenoxide ion? [CPMT 2002]

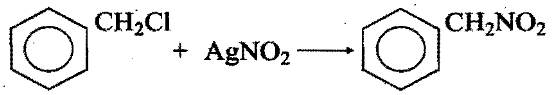
(a) Resonating structure of benzene ring ☐
(b) Localization of π-electrons in phenoxide ion ☐
(c) Delocalization of π-electrons in phenoxide ion ☐
(d) All of the above ☐

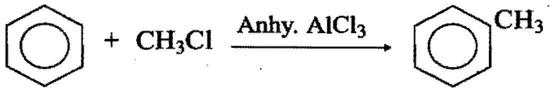
125. In the anion $HCOO^-$, the two carbon-oxygen bonds are found to be equal length. What is the reason for it? [AIEEE 2003]

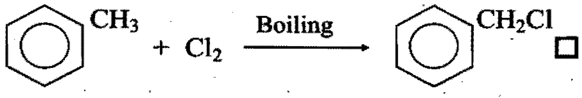
(a) The C=O bond is weaker than the C—O bond ☐
(b) The anion $HCOO^-$ has two resonating structures ☐
(c) The electronic orbitals of carbon atom are hybridized ☐
(d) The anion is obtained by removal of a proton from the acid molecule ☐

126. Which of the following is a free radical substitution reaction? [CBSE (Med.) 2003]

(a) $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$ ☐

(b)  ☐

(c)  ☐

(d)  ☐

127. Which of the following statements are correct for carbenes?

(a) Hybridisation of carbon in $\ddot{C}H_2$ may be sp^2 as well as sp ☐
(b) sp-hybrid carbene is triplet carbene ☐
(c) $\ddot{C}Cl_2$ always exist in singlet form ☐
(d) All are correct ☐

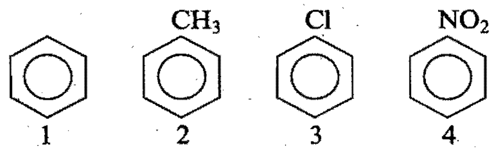
128. Arrange the following nucleophiles in the order of their nucleophilic strength: [MGIMS (Wardha) 2003]

(a) $OH^- > CH_3COO^- > CH_3O^- > C_6H_5O^-$ ☐
(b) $CH_3COO^- < C_6H_5O^- < CH_3O^- < OH^-$ ☐

(c) $C_6H_5O^- < CH_3COO^- < CH_3O^- < OH^-$ ☐

(d) $CH_3COO^- < C_6H_5O^- < OH^- < CH_3O^-$ ☐

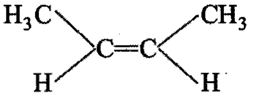
129. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds: **[IIT 2002]**



(a) 1 > 2 > 3 > 4 ☐ (b) 4 > 3 > 2 > 1 ☐

(c) 2 > 1 > 3 > 4 ☐ (d) 2 > 3 > 1 > 4 ☐

130. Which of the following hydrocarbons has the lowest dipole moment? **[IIT 2002]**

(a)  ☐

(b) $CH_3C{\equiv}C{-}CH_3$ ☐

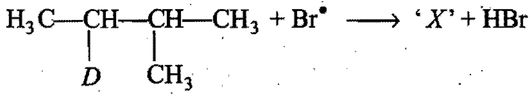
(c) $CH_3CH_2C{\equiv}CH$ ☐

(d) $H_2C{=}CH{-}C{\equiv}CH$ ☐

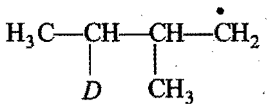
131. Which of the following acids has the smallest dissociation constant? **[IIT 2002]**

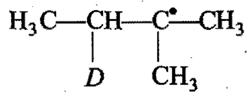
(a) $CH_3CHFCOOH$ ☐ (b) FCH_2CH_2COOH ☐

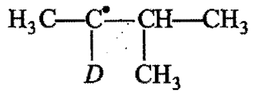
(c) $BrCH_2CH_2COOH$ ☐ (d) $CH_3CHBrCOOH$ ☐

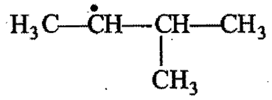
132. 
$H_3C{-}\underset{D}{CH}{-}\underset{CH_3}{CH}{-}CH_3 + Br^\bullet \longrightarrow \text{'}X\text{'} + HBr$

Identify the structure of the major product '*X*': **[IIT 2002]**

(a) 
$H_3C{-}\underset{D}{CH}{-}\underset{CH_3}{CH}{-}\dot{C}H_2$ ☐

(b) 
$H_3C{-}\underset{D}{CH}{-}\underset{CH_3}{C^\bullet}{-}CH_3$ ☐

(c) 
$H_3C{-}\underset{D}{C^\bullet}{-}\underset{CH_3}{CH}{-}CH_3$ ☐

(d) 
$H_3C{-}\dot{C}H{-}\underset{CH_3}{CH}{-}CH_3$ ☐

133. Identify the correct order of boiling points of the following compounds: **[IIT 2002]**

$\underset{(1)}{CH_3CH_2CH_2CH_2OH}$, $\underset{(2)}{CH_3CH_2CH_2CHO}$,

$\underset{(3)}{CH_3CH_2CH_2COOH}$

(a) 1 > 2 > 3 ☐ (b) 3 > 1 > 2 ☐

(c) 1 > 3 > 2 ☐ (d) 3 > 2 < 1 ☐

134. Among the following, the molecule with highest dipole moment is: **[IIT 2003]**

(a) CH_3Cl ☐ (b) CH_2Cl_2 ☐

(c) $CHCl_3$ ☐ (d) CCl_4 ☐

135. Which of the following represents the given mole of hybridization sp^2-sp^2-sp-sp from left to right? **[IIT 2003]**

(a) $H_2C{=}CH{-}C{\equiv}CH$ ☐

(b) $HC{\equiv}C{-}C{\equiv}CH$ ☐

(c) $H_3C{-}CH{=}CH{-}CH_3$ ☐

(d) $H_2C{=}CH{-}CH{=}CH_2$ ☐

136. Which of the following pK_a values, represents the strongest acid ? **[UPSEAT 2003]**

(a) 10^{-4} ☐ (b) 10^{-8} ☐

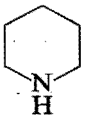
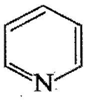
(c) 10^{-5} ☐ (d) 10^{-2} ☐

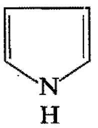
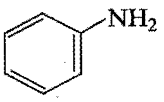
137. Which of the following orders regarding relative stability of free radicals is correct? **[UPSEAT 2004]**

(a) 3° < 2° < 1° ☐ (b) 3° > 2° > 1° ☐

(c) 1° < 2° > 3° ☐ (d) 3° > 2° < 1° ☐

138. Which of the following is the strongest base? **[AIIMS 2004; BHU 2004]**

(a)  ☐ (b)  ☐

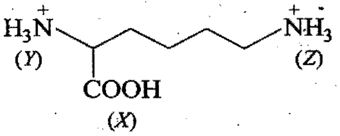
(c)  ☐ (d)  ☐

139. Which of the following is least reactive in a nucleophilic substitution reaction? **[CBSE (Med.) 2004]**

(a) $(CH_3)_3C{-}Cl$ ☐ (b) $CH_2{=}CHCl$ ☐

(c) CH_3CH_2Cl ☐ (d) $CH_2{=}CHCH_2Cl$ ☐

140. In the compound given below:



the correct order of acidity of the positions (X), (Y) and (Z) is: **[IIT 2004]**

(a) $(Z) > (X) > (Y)$ ☐ (b) $(X) > (Y) > (Z)$ ☐

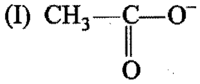
(c) $(X) > (Z) > (Y)$ ☐ (d) $(Y) > (X) > (Z)$ ☐

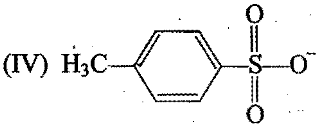
141. Due to the presence of an unpaired electron, free radicals are: **[AIEEE 2005; JCECE (Med.) 2008]**

(a) chemically reactive ☐ (b) chemically inactive ☐

(c) anions ☐ (d) cations ☐

142. The decreasing order of nucleophilicity among the nucleophiles is: **[AIEEE 2005]**

(I) 
$CH_3{-}\underset{\underset{O}{\|}}{C}{-}O^-$ (II) CH_3O^- (III) CN^-

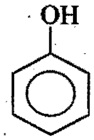
(IV) 

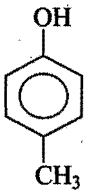
(a) I, II, III, IV ☐ (b) IV, III, II, I ☐
(c) II, III, I, IV ☐ (d) III, II, I, IV ☐

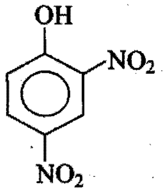
143. Among the following, the strongest nucleophile is: **[AIIMS 2005]**
(a) C_2H_5SH ☐ (b) CH_3COO^- ☐
(c) CH_3NH_2 ☐ (d) $NCCH_2^-$ ☐

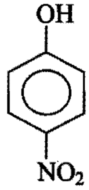
144. Which of the following is most reactive towards nucleophilic substitution reaction? **[DCE 2005]**
(a) $H_2C{=}CH{-}Cl$ ☐ (b) C_6H_5Cl ☐
(c) $CH_3CH{=}CHCl$ ☐ (d) $ClCH_2{-}CH{=}CH_2$ ☐

145. Strength of acidity is in order: **[DCE 2005]**


(I)


(II)


(III)


(IV)

(a) II > I > III > IV ☐ (b) III > IV > I > II ☐
(c) I > IV > III > II ☐ (d) IV > III > I > II ☐

146. Which is most stable carbocation? **[CET (J & K) 2005]**
(a) *n*-Propyl cation ☐
(b) iso-Propyl cation ☐
(c) Ethyl cation ☐
(d) Triphenylmethyl cation ☐

147. Which of the following undergoes nucleophilic substitution exclusively by S_N1 mechanism? **[CBSE (Med.) 2005; JIPMER 2007]**
(a) Ethyl chloride ☐ (b) Isopropyl chloride ☐
(c) Chlorobenzene ☐ (d) Benzyl chloride ☐

148. Which of the following is electron deficient molecule? **[CBSE (Med.) 2005; JIPMER 2007]**
(a) C_2H_6 ☐ (b) B_2H_6 ☐
(c) SiH_4 ☐ (d) PH_3 ☐

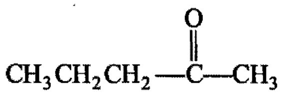
149. Which of the following compounds reacts slower than benzene in electrophilic bromination? **[JIPMER 2005]**
(a) $C_6H_5{-}CH_3$ ☐ (b) $C_6H_5{-}OH$ ☐
(c) $C_6H_5{-}NH_2$ ☐ (d) $C_6H_5{-}NO_2$ ☐

150. Which one of the following resonating structures of 1-methoxy-1,3-butadiene is least stable? **[IIT(S) 2005]**
(a) $\overset{\ominus}{C}H_2{-}CH{=}CH{-}CH{=}\overset{\oplus}{O}{-}CH_3$ ☐
(b) $H_2C{=}CH{-}\overset{\ominus}{C}H{-}CH{=}\overset{\oplus}{O}{-}CH_3$ ☐
(c) $\overset{\ominus}{C}H_2{-}\overset{\oplus}{C}H{-}CH{=}CH{-}O{-}CH_3$ ☐
(d) $H_2C{=}CH{-}\overset{\ominus}{C}H{-}\overset{\oplus}{C}H{-}O{-}CH_3$ ☐

151. $CH_3Br + Nu^- \longrightarrow CH_3Nu + Br^-$
The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) *A* to *D* is:
$[Nu^- = (A)\,PhO^-, (B)\,AcO^-, (C)\,HO^-, (D)\,CH_3O^-]$
[AIEEE 2006]
(a) $D > C > A > B$ ☐ (b) $D > C > B > A$ ☐
(c) $A > B > C > D$ ☐ (d) $B > D > C > A$ ☐

152. The increasing order of stability of the following free radicals is: **[AIEEE 2006]**
(a) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$ ☐
(b) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$ ☐
(c) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$ ☐
(d) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$ ☐

153. Which of the following is more basic than aniline? **[CBSE (Med.) 2006]**
(a) *p*-Nitroaniline ☐ (b) Benzyl amine ☐
(c) Diphenyl amine ☐ (d) Triphenyl amine ☐

154. Nucleophilic addition reaction will be most favoured in: **[CBSE (Med.) 2006]**
(a) CH_3CH_2CHO ☐
(b) CH_3CHO ☐
(c) 
$CH_3CH_2CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$ ☐
(d) $(CH_3)_2C{=}O$ ☐

155. The correct increasing order of the reactivity of halides for S_N1 reaction is: **[AIIMS 2006]**
(a) $CH_3CH_2{-}X < (CH_3)_2CH{-}X < H_2C{=}CHCH_2{-}X < PhCH_2{-}X$ ☐
(b) $(CH_3)_2CH{-}X < CH_3CH_2{-}X < H_2C{=}CHCH_2{-}X < PhCH_2{-}X$ ☐
(c) $PhCH_2{-}X < (CH_3)_2CH{-}X < CH_3CH_2{-}X < H_2C{=}CH{-}CH_2X$ ☐
(d) $H_2C{=}CHCH_2{-}X < PhCH_2{-}X < (CH_3)_2CH{-}X < CH_3CH_2{-}X$ ☐

156. Inductive effect involves: **[CET (Punjab) Engg. 2007; AFMC 2008]**
(a) displacement of σ-electrons ☐
(b) delocalisation of π-electrons ☐
(c) delocalisation of σ-electrons ☐
(d) displacement of π-electrons ☐

157. The basicity of aniline is less than that of cyclohexylamine. This is due to: **[KCET 2006; GGS Indraprastha Univ. (Engg.) 2007]**
(a) $-R$ effect of $-NH_2$ group ☐
(b) $-I$ effect of $-NH_2$ group ☐
(c) $+R$ effect of $-NH_2$ group ☐
(d) hyperconjugation effect ☐

158. In the solvolysis of 3-methyl-3-bromohexane, which of the following statements is not correct? **[PMT (Kerala) 2006]**
(a) It involves carbocation intermediate ☐
(b) The intermediate involves sp^2-carbon ☐
(c) Polar solvents accelerates the reaction ☐
(d) The rate of reaction depends upon 3-methyl-3- bromohexane concentration ☐

(e) It involves inversion of configuration ☐

159. Neopentyl bromide undergoes dehydrohalogenation to give alkene even though it has no β-hydrogen. This is due to: **[PMT (Kerala) 2006]**

(a) E_2 mechanism ☐
(b) E_1 mechanism ☐
(c) Hofmann elimination ☐
(d) rearrangement of carbocation by E_1 mechanism ☐
(e) E_1-Cb mechanism ☐

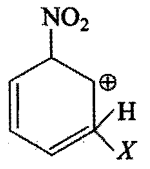
160. Which one is most reactive towards S_{N1} reaction ? **[CBSE (PMT) Prelims 2010]**

(a) $C_6H_5CH(C_6H_5)Br$ ☐
(b) $C_6H_5C(CH_3)(C_6H_5)Br$ ☐
(c) $C_6H_5CH(CH_3)Br$ ☐
(d) $C_6H_5CH_2Br$ ☐

161. Order of stability of vinyl, allyl and tertiary radical is: **[DPMT 2006]**

(a) tertiary, vinyl, allyl ☐ (b) vinyl, tertiary, allyl ☐
(c) tertiary, allyl, vinyl ☐ (d) allyl, tertiary, vinyl ☐

162. Which of the following carbocations is most stable? **[DPMT 2006]**

(a)


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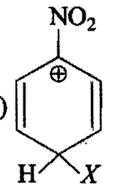
(b)


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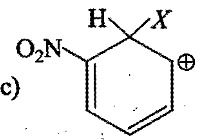
(c)


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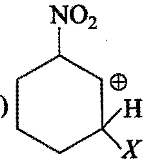
(d)


☐

163. $CH_3—O—CH_3$ is: **[AMU (Med.) 2006]**

(a) Lewis acid ☐ (b) Arrhenius acid ☐
(c) Lewis base ☐ (d) Bronsted acid ☐

164. Which one is ambidentate ligand? **[AMU (Med.) 2006]**

(a) SO_3^{2-} ☐ (b) CN^- ☐
(c) NH_3 ☐ (d) H_2O ☐

165. Which of the following is a Lewis acid? **[CET (J & K) 2006]**

(a) $AlCl_3$ ☐ (b) Cl^- ☐
(c) CO ☐ (d) C_2H_2 ☐

166. Which of the following intermediates have the complete octet around the carbon atom? **[GGS Indraprastha Univ. (Engg.) 2005]**

(a) Carbonium ion ☐ (b) Carbanion ☐
(c) Free radical ☐ (d) Carbene ☐

167. Which of the following is the correct order of decreasing S_{N2} reactivity? **[AIEEE 2007]**

(a) $R_2CHX > R_3CX > RCH_2X$ ☐
(b) $RCH_2X > R_3CX > R_2CHX$ ☐
(c) $RCH_2X > R_2CHX > R_3CX$ ☐
(d) $R_3CX > R_2CHX > RCH_2X$ (X is a halogen) ☐

168. Which of the following presents the correct order of the acidity in the given compounds? **[CBSE (Med.) 2007]**

(a) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$ ☐
(b) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$ ☐
(c) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$ ☐
(d) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$ ☐

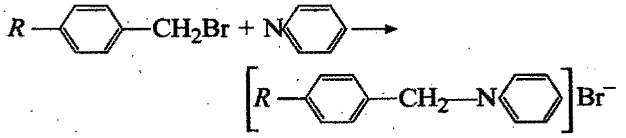
169. For the following
(i) I^- (ii) Cl^- (iii) Br^-
the increasing order of nucleophilicity would be: **[CBSE (Med.) 2007]**

(a) $I^- < Cl^- < Br^-$ ☐ (b) $Br^- < Cl^- < I^-$ ☐
(c) $I^- < Br^- < Cl^-$ ☐ (d) $Cl^- < Br^- < I^-$ ☐

170. Which one of the following is correct?
Formic acid has lower pK_a than that of CH_3COOH because: **[SCRA 2007]**

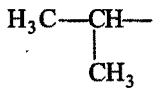
(a) formic acid does not dissociate ☐
(b) formic acid does not have an alkyl group ☐
(c) formic acid is smaller in size than acetic acid ☐
(d) formic acid is a strong reducing agent ☐

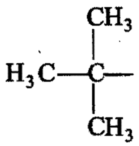
171. The rate of the reaction



is influenced by the hyperconjugation effect of group R. If R-sequentially is:

(i) $CH_3—$ (ii) $CH_3—CH_2—$

(iii) 
$H_3C—\underset{CH_3}{CH}—$

(iv) 
$H_3C—\underset{CH_3}{\overset{CH_3}{C}}—$

the increasing order of speed of the above reaction is: **[PMT (Kerala) 2007]**

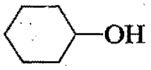
(a) (iv), (iii), (ii), (i) ☐ (b) (i), (ii), (iii), (iv) ☐
(c) (i), (iv), (iii), (ii) ☐ (d) (iii), (ii), (i), (iv) ☐
(e) (ii), (iii), (i), (iv) ☐

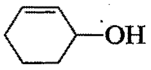
172. The S_{N1} reactivity of the following halides will be in the order:

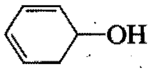
(i) $(CH_3)_3C—Br$ (ii) $(C_6H_5)_2CHBr$
(iii) $(C_6H_5)_2C(CH_3)Br$ (iv) $(CH_3)_2CHBr$
(v) C_2H_5Br **[PET (Kerala) 2007]**

(a) (v) > (iv) > (i) > (ii) > (iii) ☐
(b) (ii) > (i) > (iii) > (v) > (iv) ☐
(c) (i) > (iii) > (v) > (ii) > (iv) ☐
(d) (v) > (i) > (ii) > (iv) > (iii) ☐
(e) (iii) > (ii) > (i) > (iv) > (v) ☐

173. The correct order of case of dehydration of following is: **[AIIMS 2007]**


I


II


III

(a) I > II > III ☐ (b) III > II > I ☐
(c) I > III > II ☐ (d) III > I > II ☐

174. In which alkyl halide, S_N2 mechanism is favoured maximum? **[AFMC 2007]**
(a) CH_3Cl ☐ (b) CH_3CH_2Cl ☐
(c) $(CH_3)_2CHCl$ ☐ (d) $(CH_3)_3C-Cl$ ☐

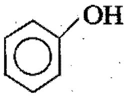
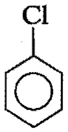
175. Which one of the following is least reactive in a nucleophilic substitution reaction? **[AMU (Med.) 2007]**
(a) CH_3CH_2Cl ☐ (b) $H_2C=CHCH_2Cl$ ☐
(c) $(CH_3)_3C-Cl$ ☐ (d) $H_2C=CHCl$ ☐

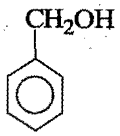
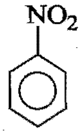
176. Which of the following is the most stable compound? **[BVC (Med.) 2007]**
(a) Ph_3C^+ ☐ (b) $Ph_2\overset{+}{C}H$ ☐
(c) $Ph_2\overset{+}{C}H_2$ ☐ (d) $Ph\overset{+}{C}H_2$ ☐

177. Hyperconjugation involves overlap of the following orbitals: **[IIT 2008]**
(a) $\sigma-\sigma$ ☐ (b) $\sigma-p$ ☐
(c) $p-p$ ☐ (d) $\pi-\pi$ ☐

178. Mesomeric effect involves the delocalisation of: **[CET (Karnataka) 2008]**
(a) protons ☐ (b) sigma electrons ☐
(c) pi electrons ☐ (d) none of these ☐

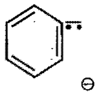
179. Which one of the following is most reactive towards electrophilic attack? **[CBSE (Med.) 2008]**

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

180. Which among the following statements are true with respect to electronic displacement in a covalent bond? **[PMT (Kerala) 2008]**
(1) Inductive effect operates through a π-bond
(2) Resonance effect operates through a σ-bond
(3) Inductive effect operates through a σ-bond
(4) Resonance effect operates through a π-bond
(5) Resonance and inductive effects operate through σ-bond
(a) 1 and 2 ☐ (b) 1 and 3 ☐
(c) 2 and 3 ☐ (d) 2 and 4 ☐
(e) 3 and 4 ☐

181. The stability of carbanions in the following:

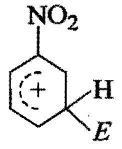
(i) $R-C\equiv C^{\ominus}$ (ii) 

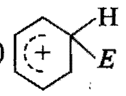
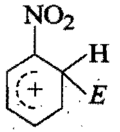
(iii) $R_2C=\overset{\ominus}{C}H$ (iv) $R_3C-\overset{\ominus}{C}H_2$

is in the order: **[CBSE (Med.) 2008]**
(a) (iv) > (ii) > (iii) > (i) ☐
(b) (i) > (iii) > (ii) > (iv) ☐
(c) (i) > (ii) > (iii) > (iv) ☐
(d) (ii) > (iii) > (iv) > (i) ☐

182. The hydrolysis of 2-bromo-3-methyl butane by S_N1 mechanism gives mainly: **[PMT (Kerala) 2008]**
(a) 3-methyl-2-butanol ☐
(b) 2-methyl-2-butanol ☐
(c) 2,2-dimethyl-2-propanol ☐
(d) 2-methyl-1-butanol ☐
(e) 1-pentanol ☐

183. The electrophile, E^+ attacks the benzene ring to generate the intermediate σ-complex of the following, which σ-complex is of lowest energy? **[AIEEE 2008]**

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

184. Which one of the following carbanions is the least stable? **[PET (Kerala) 2008]**
(a) $CH_3CH_2^-$ ☐ (b) $HC\equiv C^-$ ☐
(c) $(C_6H_5)_3C^-$ ☐ (d) CH_3^- ☐
(e) $(CH_3)_3\bar{C}$ ☐

185. CH_3CH_2Cl undergoes homolytic fission produces: **[BCECE (Med.) 2008]**
(a) $CH_3\dot{C}H_2$ and $Cl^{\bullet}$ ☐ (b) $CH_3\overset{+}{C}H_2$ and Cl^- ☐
(c) $CH_3\overset{+}{C}H_2$ and $Cl^{\bullet}$ ☐ (d) $CH_3\dot{C}H_2$ and Cl^- ☐

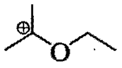
186. Tertiary butyl chloride preferably undergo hydrolysis by: **[CPMT 2008; PMET (Punjab) 2008]**
(a) S_N1 mechanism ☐ (b) S_N2 mechanism ☐
(c) any of (a) and (b) ☐ (d) none of these ☐

187. In a S_N2 substitution reaction of the type

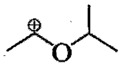
$$R-Br + Cl^- \xrightarrow{DMF} R-Cl + Br^-$$

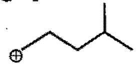
Which one of the following has the highest relative rate? **[CBSE (Med.) 2008]**
(a) $(CH_3)_3C-CH_2Br$ ☐ (b) CH_3CH_2Br ☐
(c) $CH_3CH_2CH_2Br$ ☐ (d) $(CH_3)_2CH-CH_2Br$ ☐

188. The correct stability order for the following species is:


I


II


III


IV

[IIT 2008]
(a) II > IV > I > III ☐ (b) I > II > III > IV ☐
(c) II > I > IV > III ☐ (d) I > III > II > IV ☐

189. Arrange the carbanions,

$(CH_3)_3\bar{C}$, $\bar{C}Cl_3$, $(CH_3)_2\bar{C}H$, $C_6H_5\bar{C}H_2$ in order of their decreasing stability: **[AIEEE 2009]**

(a) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$ ☐
(b) $(CH_3)_2\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$ ☐
(c) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$ ☐
(d) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > C_6H_5\bar{C}H_2 > \bar{C}Cl_3$ ☐

190. Which of the following carbocations will be more stable? **[JEE (WB) 2009]**

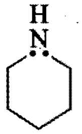
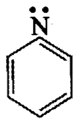
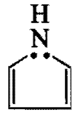
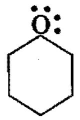
(a) Ph_3C^+ ☐ (b) $CH_3-\overset{+}{C}H_2$ ☐
(c) $(CH_3)_2\overset{+}{C}H$ ☐ (d) $CH_2=CH-\overset{+}{C}H_2$ ☐

191. Arrange the following free radicals in order of decreasing stability: **[DPMT 2009]**

Methyl (I), Vinyl (II), Allyl (III), Benzyl (IV)

(a) I > II > III > IV ☐ (b) III > II > I > IV ☐
(c) II > I > IV > III ☐ (d) IV > III > I > II ☐

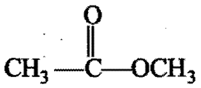
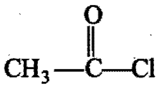
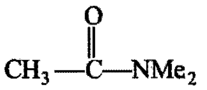
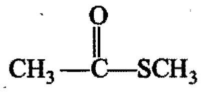
192. Strongest base is: **[DCE 2009]**

(a)  ☐
(b)  ☐
(c)  ☐
(d)  ☐

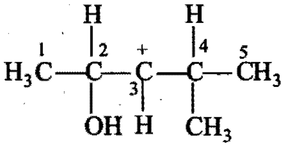
193. The most easily hydrolysed molecule under S_N1 condition is: **[CET (J&K) 2009]**

(a) allyl chloride ☐ (b) benzyl chloride ☐
(c) ethyl chloride ☐ (d) isopropyl chloride ☐

194. Least active electrophile is : **[DCE 2009]**

(a)  $CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$ ☐
(b)  $CH_3-\overset{\overset{O}{\|}}{C}-Cl$ ☐
(c)  $CH_3-\overset{\overset{O}{\|}}{C}-NMe_2$ ☐
(d)  $CH_3-\overset{\overset{O}{\|}}{C}-SCH_3$ ☐

195. In the following carbocation, H/CH_3 that is most likely to migrate to the positive charged carbon is: **[IIT 2009]**



(a) CH_3 at C-4 ☐ (b) H at C-4 ☐
(c) CH_3 at C-2 ☐ (d) H at C-2 ☐

196. The correct stability order of the following resonance structures is: **[IIT 2009]**

(I) $H_2C=\overset{+}{N}=\overset{-}{N}$ (II) $H_2\overset{+}{C}-N=\overset{-}{N}$
(III) $H_2\overset{-}{C}-\overset{+}{N}\equiv N$ (IV) $H_2\overset{-}{C}-N=\overset{+}{N}$

(a) I > II > IV > III ☐ (b) I > III > II > IV ☐
(c) II > I > III > IV ☐ (d) III > I > IV > II ☐

SET II : The following questions have more than one correct answer(s) for each of them.

197. Compound which shows positive mesomeric effect : **[AMU (Engg.) 2010]**

(a) $H_2C=CH-Cl$ ☐ (b) $C_6H_5-\overset{+}{N}-Me_3$ ☐
(c) $H_2C=CH-CH_2Cl$ ☐ (d) $C_6H_5-CH=CHCl$ ☐

198. Which of the following are nucleophile?

(a) NH_3 ☐ (b) OH^- ☐
(c) $R-O-R$ ☐ (d) $AlCl_3$ ☐

199. Which of the following are electrophile?

(a) CN^- ☐ (b) BF_3 ☐
(c) NO_2^+ ☐ (d) $AlCl_3$ ☐

200. Which types of mechanism take place in *sec.*-halides, $(CH_3)_2CH-X$?

(a) S_N1 ☐ (b) S_N2 ☐
(c) S_N1 and S_N2 ☐ (d) None of these ☐

201. Anti-Markownikoff's addition of HBr can be observed in:

(a) propene ☐ (b) but-1-ene ☐
(c) but-2-ene ☐ (d) pent-2-ene ☐

202. Which gives nucleophilic addition reactions?

(a) Methanal ☐ (b) Ethanal ☐
(c) Propanone ☐ (d) Propene ☐

203. Acetyl nitrene has been proposed as possible intermediate in:

(a) Reimer-Tiemann reaction ☐
(b) Hofmann's rearrangement ☐
(c) Lossen's rearrangement ☐
(d) Curtius rearrangement ☐

204. Carbenes are the reactive intermediates in:

(a) Carbylamine reaction ☐
(b) Reimer-Tiemann reaction ☐
(c) Hofmann's bromamide reaction ☐
(d) Wittig reaction ☐

205. Which of the statements are correct?

(a) $-NH_2$ is *ortho-para* directing group ☐
(b) $-CHO$ is *meta* directing group ☐
(c) $:CCl_2$ is an electrophile ☐
(d) $-\ddot{\underset{\cdot\cdot}{O}}H$ is (*–M*) group ☐

206. Which of the following are aprotic solvents?

(a) DMSO ☐ (b) DMF ☐
(c) H_2O ☐ (d) CH_3COOH ☐

207. On treatment with strong NaOH at 340°C, *p*-chlorotoluene gives:

(a) *ortho*-cresol ☐ (b) *meta*-cresol ☐
(c) *para*-cresol ☐ (d) none of these ☐

208. In which of the following reactions is there a possibility of rearrangement?

(a) S_N1 ☐ (b) S_N2 ☐
(c) E_1 ☐ (d) E_2 ☐

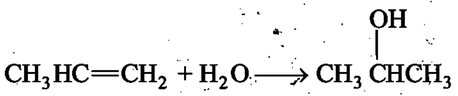
209. In the reaction,

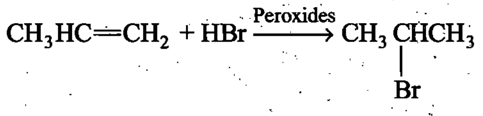
$$\underset{}{CH_3—CH{=}CH_2} \xrightarrow[\text{Benzoyl peroxide}]{HX} \underset{(A)}{CH_3CH_2CH_2X}$$

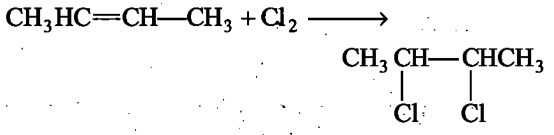
The product (*A*) cannot be obtained by using:

(a) HBr ☐ (b) HCl ☐
(c) HI ☐ (d) HF ☐

210. Which of the following are examples of electrophilic addition?


(a) $CH_3HC{=}CH_2 + H_2O \longrightarrow CH_3\overset{\overset{OH}{|}}{C}HCH_3$ ☐


(b) $CH_3HC{=}CH_2 + HBr \xrightarrow{\text{Peroxides}} CH_3\underset{\underset{Br}{|}}{C}HCH_3$ ☐


(c) $CH_3HC{=}CH—CH_3 + Cl_2 \longrightarrow CH_3\underset{\underset{Cl}{|}}{C}H—\underset{\underset{Cl}{|}}{C}HCH_3$ ☐

(d) None of the above ☐

211. Which of the following statements are correct?

(a) The addition of HBr to propene gives 2-bromo propane ☐
(b) The addition of HBr to propene gives 1-bromo propane ☐
(c) The addition of HCl to vinyl chloride gives ethylidene chloride ☐
(d) The addition of HCl to vinyl chloride gives ethylene chloride ☐

212. Which of the following is an example of nucleophilic addition to acetone?

(a) Ketal formation ☐
(b) Reduction with hydrogen gas ☐
(c) Cyanohydrin formation ☐
(d) Bisulphite addition ☐

213. Which of the following are correct for S_N1 reaction ?

(a) The reaction intermediate is carbocation ☐
(b) In this reaction the complete inversion takes place ☐
(c) It is favoured by polar solvents ☐
(d) It is favoured by stability of carbocation ☐

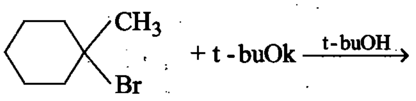
214. Which of the following statement regarding anti-Markownikoff's rule is correct ?

(a) It is catalysed by peroxide ☐
(b) Only HBr shows this effect ☐
(c) Br adds to more substituted radical ☐
(d) $CF_3—CH{=}CH_2$ forms anti-Markownikoff's product ☐

215. Reaction involving carbanion formation is/are :

(a) Cannizaro's reaction ☐
(b) Addition reaction of Grignard reagent ☐
(c) Perkin's reaction ☐
(d) Beckmann's reaction ☐

216. Which of the following statement are incorrect regarding following reaction ?



(a) Product is exocyclic alkene formed according to saytzeff ☐
(b) Product is exocyclic alkene formed according to Hofmann ☐
(c) Product is endocyclic alkene formed according to Saytzeff ☐
(d) Product is endocyclic alkene formed according to Hofmann ☐

217. Which is/are correctly linked here?

List I		List II	
(a) E_1Cb	(a)	Carbanion formation	☐
(b) E_2	(b)	Stereo specific	☐
(c) S_N1	(c)	Presence of non-polar solvent	☐
(d) E_1	(d)	Carbocation formation	☐

218. Toluene when treated with Br_2/Fe, give *p*-bromotoluene as the major product because the $—CH_3$ group :

(a) is *p*-directing ☐
(b) deactivates the ring ☐
(c) is *m*-directing ☐
(d) activates the ring by hyperconjugation ☐

219. $—CX_3$ group is associated with :

(a) *m*-directing ☐
(b) increasing acidic ☐
(c) ring deactivation ☐
(d) increase of stability of carbocation ☐

ASSERTION-REASON TYPE QUESTIONS

Following questions consist of an **Assertion (A)** and **Reason (R).** Use the following keys to select an appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.
(e) If both (A) and (R) are incorrect.

1. (A) S_N2 reaction takes place in single step.
(R) S_N2 reaction involves transition state intermediate.

2. (A) Ethyl chloride is more reactive than vinyl chloride towards nucleophilic substitution reactions.
(R) Vinyl chloride is +*I* electron pushing group.

3. (A) $—NO_2, —CN, —CNO$ act as ambident nucleophiles.

(R) These consist atoms of same period.

4. (A) Nucleophiles attack the regions of high electron density.
   (R) Nucleophiles act as Lewis bases.
5. (A) Cation carriers, *e.g.*, H—Br, Cl—OH and Br—Br and oxidising agents such as O_3 and R—O—O—R, etc. act as electrophilic reagents.
   (R) Electrophiles are Lewis acids.
6. (A) Inductive and electromeric effects require polar nature in the molecule.
   (R) Polar nature in inductive effect is a must but not necessarily in electromeric effect.
7. (A) Singlet carbenes have opposite spin (antiparallel).
   (R) They have a bent structure.
8. (A) Carbenes act as free radicals.
   (R) Only triplet carbenes act as biradical (divalent free radical).
9. (A) Tertiary carbocations are generally formed more easily than primary carbocations.
   (R) Hyperconjugation as well as inductive effect due to additional alkyl groups stabilize tertiary carbocations.
10. (A) Allyl free radical is more stable than simple alkyl free radical.
    (R) The allyl free radical is stabilized by resonance.
11. (A) Heterolytic fission involves the breaking of a covalent bond in such a way that both the electrons of the shared pair are carried away by one of the atoms.
    (R) Heterolytic fission occurs readily in polar covalent bonds.
12. (A) Tertiary butyl carbanion is more stable than methyl carbanion.
    (R) $+I$ effect of the three methyl groups in tertiary butyl carbanion tends to make it more stable than methyl carbanion.
13. (A) In S_N2 reactions, complete inversion of configuration takes place.
    (R) In S_N1 reactions, retention but not the inversion takes place.
14. (A) In allylic substitution propene gives allyl bromide.
    (R) NBS is a selective brominating agent and gives substitution at the alpha carbon with respect to the double bond.

ANSWERS

OBJECTIVE QUESTIONS

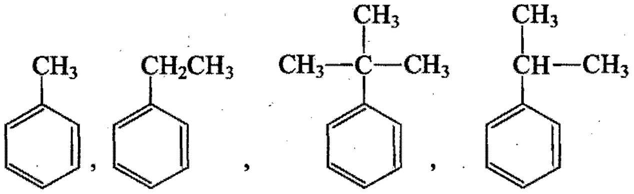
1.	(a)	**2.**	(d)	**3.**	(a)	**4.**	(e)	**5.**	(c)	**6.**	(c)	**7.**	(d)	**8.**	(b)	**9.**	(a)	**10.**	(c)
11.	(d)	**12.**	(b)	**13.**	(d)	**14.**	(a)	**15.**	(c)	**16.**	(d)	**17.**	(b)	**18.**	(c)	**19.**	(a)	**20.**	(b)
21.	(b)	**22.**	(c)	**23.**	(a)	**24.**	(d)	**25.**	(a)	**26.**	(c)	**27.**	(b)	**28.**	(d)	**29.**	(b)	**30.**	(a)
31.	(c)	**32.**	(d)	**33.**	(b)	**34.**	(c)	**35.**	(d)	**36.**	(a)	**37.**	(c)	**38.**	(c)	**39.**	(b)	**40.**	(a)
41.	(d)	**42.**	(b)	**43.**	(d)	**44.**	(a)	**45.**	(c)	**46.**	(b)	**47.**	(d)	**48.**	(a)	**49.**	(a)	**50.**	(d)
51.	(b)	**52.**	(c)	**53.**	(a)	**54.**	(b)	**55.**	(c)	**56.**	(b)	**57.**	(c)	**58.**	(b)	**59.**	(a)	**60.**	(b)
61.	(d)	**62.**	(c)	**63.**	(b)	**64.**	(d)	**65.**	(b)	**66.**	(a)	**67.**	(c)	**68.**	(b)	**69.**	(d)	**70.**	(d)
71.	(a)	**72.**	(c)	**73.**	(a)	**74.**	(d)	**75.**	(c)	**76.**	(b)	**77.**	(d)	**78.**	(c)	**79.**	(c)	**80.**	(b)
81.	(a)	**82.**	(b)	**83.**	(d)	**84.**	(a)	**85.**	(a)	**86.**	(c)	**87.**	(a)	**88.**	(d)	**89.**	(c)	**90.**	(a)
91.	(b)	**92.**	(c)	**93.**	(a)	**94.**	(d)	**95.**	(d)	**96.**	(c)	**97.**	(b)	**98.**	(d)	**99.**	(a)	**100.**	(d)
101.	(c)	**102.**	(a,d)	**103.**	(c)	**104.**	(d)	**105.**	(c)	**106.**	(a)	**107.**	(c)	**108.**	(d)	**109.**	(d)	**110.**	(b)
111.	(a)	**112.**	(a)	**113.**	(b)	**114.**	(a)	**115.**	(a)	**116.**	(a)	**117.**	(c)	**118.**	(b)	**119.**	(d)	**120.**	(b)
121.	(a)	**122.**	(a)	**123.**	(a)	**124.**	(c)	**125.**	(b)	**126.**	(d)	**127.**	(d)	**128.**	(c)	**129.**	(c)	**130.**	(b)
131.	(c)	**132.**	(b)	**133.**	(b)	**134.**	(a)	**135.**	(a)	**136.**	(d)	**137.**	(b)	**138.**	(a)	**139.**	(b)	**140.**	(b)
141.	(a)	**142.**	(c)	**143.**	(a)	**144.**	(d)	**145.**	(b)	**146.**	(d)	**147.**	(d)	**148.**	(b)	**149.**	(d)	**150.**	(c)
151.	(a)	**152.**	(a)	**153.**	(b)	**154.**	(b)	**155.**	(a)	**156.**	(a)	**157.**	(c)	**158.**	(e)	**159.**	(d)	**160.**	(b)
161.	(c)	**162.**	(a)	**163.**	(c)	**164.**	(b)	**165.**	(a)	**166.**	(b)	**167.**	(c)	**168.**	(b)	**169.**	(a)	**170.**	(b)
171.	(a)	**172.**	(e)	**173.**	(b)	**174.**	(a)	**175.**	(d)	**176.**	(a)	**177.**	(b)	**178.**	(c)	**179.**	(a)	**180.**	(e)
181.	(c)	**182.**	(b)	**183.**	(c)	**184.**	(e)	**185.**	(a)	**186.**	(a)	**187.**	(b)	**188.**	(d)	**189.**	(c)	**190.**	(a)
191.	(d)	**192.**	(a)	**193.**	(b)	**194.**	(c)	**195.**	(d)	**196.**	(b)	**197.**	(a,d)	**198.**	(a,b,c)	**199.**	(b,c,d)	**200.**	(a,b,c)
201.	(a,b,d)	**202.**	(a,b,c)	**203.**	(b,c,d)	**204.**	(a,b,d)	**205.**	(a,b)	**206.**	(a,b)	**207.**	(b,c)	**208.**	(a,c)	**209.**	(b,c,d)	**210.**	(a,c)
211.	(a,c)	**212.**	(a,c,d)	**213.**	(a,c,d)	**214.**	(a,b,c,d)	**215.**	(b,c)	**216.**	(a,c,d)	**217.**	(a,b,d)	**218.**	(a,d)	**219.**	(a,b,c)		

ASSERTION-REASON TYPE QUESTIONS

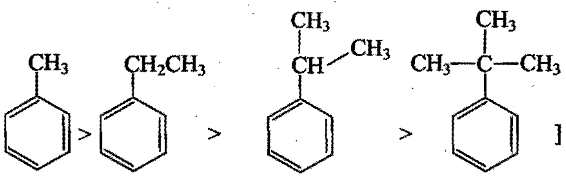
1.	(b)	**2.**	(c)	**3.**	(a)	**4.**	(d)	**5.**	(b)	**6.**	(d)	**7.**	(a)	**8.**	(d)	**9.**	(a)	**10.**	(a)
11.	(b)	**12.**	(e)	**13.**	(c)	**14.**	(a)												

BRAIN STORMING PROBLEMS

1. Arrange the following in decreasing order of reactivity towards electrophilic substitution:



[**Ans.** Greater is the number of hyperconjugative forms more will be reactivity towards electrophilic substitution.

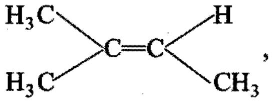


]

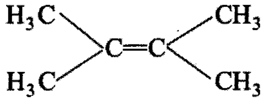
2. Arrange the following in decreasing order of stability:

$H_2C{=}CH_2$, $CH_3—CH{=}CH_2$,

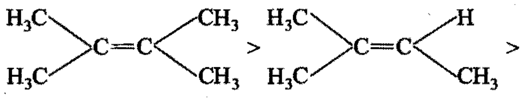
$CH_3—CH{=}CH—CH_3$,



,



[**Ans.** "More the alkyl groups are attached to the double bonded carbon atom more is the stability of alkene" Known as Saytzeff's rule due to hyperconjugation.



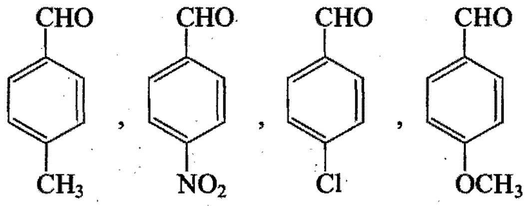
$CH_3—CH{=}CH—CH_3 > CH_3—CH{=}CH_2 > H_2C{=}CH_2$]

3. Arrange the following carbonyl compounds in decreasing order of reactivity towards nucleophilic addition:

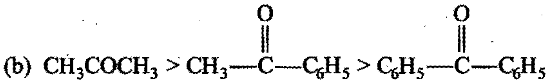
(a) HCHO, CH_3CHO, CH_3COCH_3, CCl_3CHO

(b) $C_6H_5COC_6H_5$, $CH_3COC_6H_5$, CH_3COCH_3

(c)

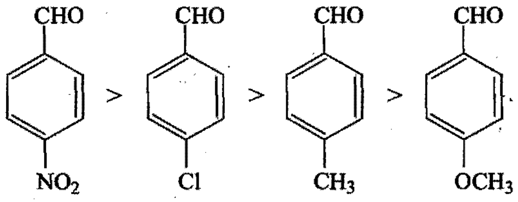


[**Ans.** (a) $CCl_3CHO > HCHO > CH_3CHO > CH_3COCH_3$



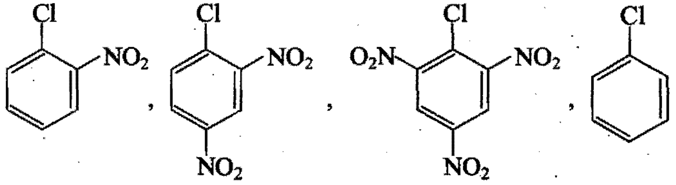
(b) $CH_3COCH_3 > CH_3—\overset{O}{\overset{\|}{C}}—C_6H_5 > C_6H_5—\overset{O}{\overset{\|}{C}}—C_6H_5$

(c)

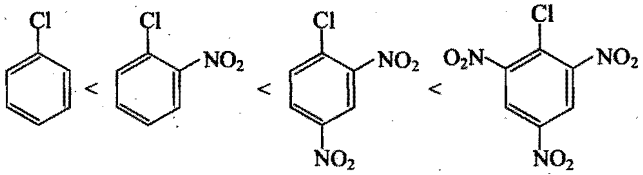


Ring with —OCH_3 group is less reactive than ring with —CH_3 group because —OCH_3 group has +*M* effect which is more effective than +*I* effect of alkyl group. So, that speed of attack of nucleophile decreases. –*I* and –*M* effect increases the nucleophilic reactivity.]

4. Arrange the following compounds in increasing order of reactivity towards nucleophilic substitution:

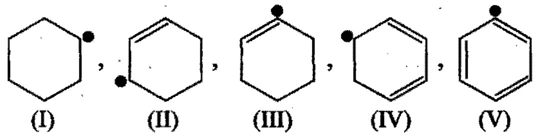


[**Ans.**



Electron withdrawing groups increase the reactivity of aryl halide towards nucleophilic substitution.]

5. Arrange the following free radicals in increasing order of stability:



[**Ans.** V < III < I < II < IV]

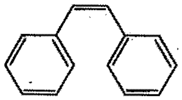
6. Which compound in each of the following pairs will add HCl readily?

I II

(a) $H_2C{=}CH_2$ OR $CH_3—CH{=}CH—CH_3$

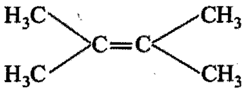
(b) $CH_3—CH{=}CH—CH_3$ OR $H_2C{=}CH—CH{=}CH_2$

(c)



OR $CH_3—CH{=}CH—CH_3$

(d) $CH_3—CH{=}CH—CH_3$ OR



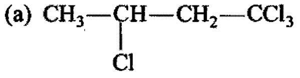
[**Ans.** (a) II (b) II (c) I (d) II]

7. Complete the following reactions:

(a) $CH_3—CH{=}CH_2 + CCl_4 \xrightarrow{\text{Peroxide}} ?$

(b) $H_2C{=}CH—(CH_2)_5—CH_3 + CHCl_3 \xrightarrow{\text{Peroxide}} ?$

[**Ans.** (a)

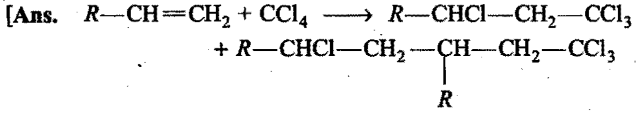


$CH_3—\underset{Cl}{\underset{|}{C}H}—CH_2—CCl_3$

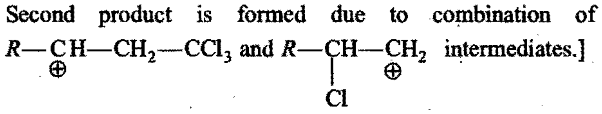
(b) $CCl_3—(CH_2)_7—CH_3$]

1,1,1-Trichlorononane

8. Which products will be obtained when CCl_4 adds on $R-CH=CH_2$? Give the mechanism of formation of the products.

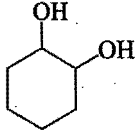


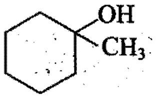
[**Ans.** $R-CH=CH_2 + CCl_4 \longrightarrow R-CHCl-CH_2-CCl_3 + R-CHCl-CH_2-\underset{R}{\underset{|}{CH}}-CH_2-CCl_3$

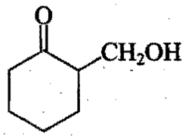


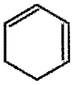
Second product is formed due to combination of $R-\underset{\oplus}{C}H-CH_2-CCl_3$ and $R-\underset{Cl}{\underset{|}{CH}}-\underset{\oplus}{CH_2}$ intermediates.]

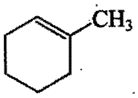
9. Write down the dehydration products of the following alcohols:

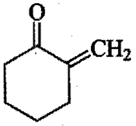
(a) 

(b) 

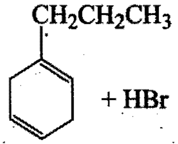
(c) 

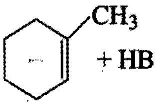
[**Ans.** (a) 

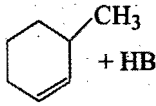
(b) 

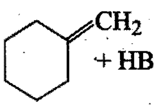
(c) ]

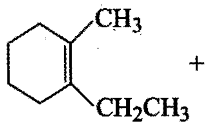
10. Give the major product of the following electrophilic addition reactions:

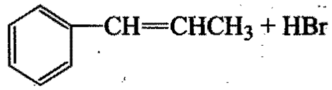
(a)  + HBr ⟶ ?

(b)  + HBr ⟶ ?

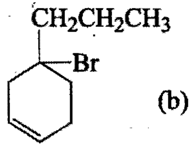
(c)  + HBr ⟶ ?

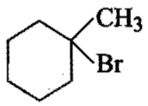
(d)  + HBr ⟶ ?

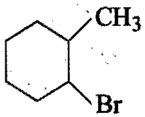
(e)  + HBr ⟶ ?

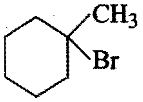
(f)  + HBr ⟶ ?

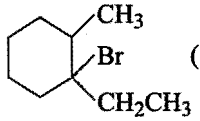
[**Ans.**

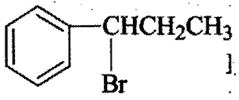
(a) 

(b) 

(c) 

(d) 

(e) 

(f) ]

11. Why does the potential effectiveness as leaving group, in nucleophilic substitution, decreases in the following order: $C_6H_5SO_3^- > Cl_3C-CO\bar{O} > CH_3CO\bar{O} > C_6H_5\bar{O}$?

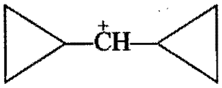
[**Ans.** The pK_a values of their conjugated acids of these anions are:

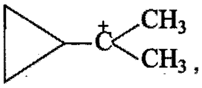
$C_6H_5SO_3H$	$Cl_3C-COOH$	CH_3COOH	C_6H_5OH
pK_a = −2.6	0.9	4.5	10.0

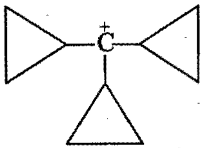
The strongest acid has the smallest pK_a. Therefore, its conjugate base is the weakest and is the best leaving group. Hence, the potential effectiveness of anions as leaving groups (fugacity) decreases in the following order:

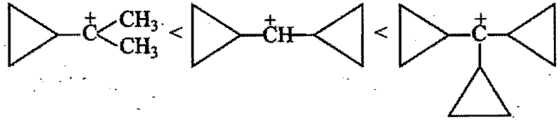
$C_6H_5SO_3^-$ >	Cl_3C-COO^- >	CH_3COO^- >	$C_6H_5O^-$]
Benzene sulphonate anion	Trichloro acetate anion	Acetate anion	Phenoxide anion

12. Arrange the following carbocations in increasing order of stability:

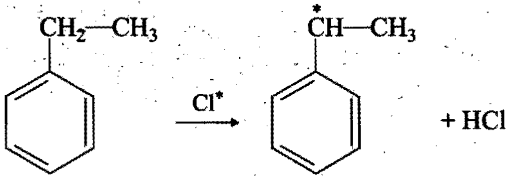
,

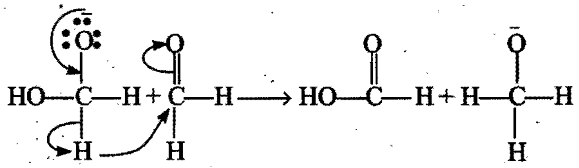
,

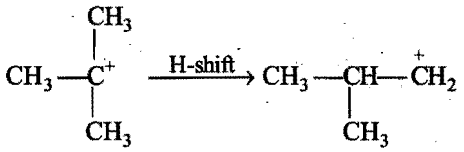


[**Ans.** ]

13. Which of the following is incorrect?

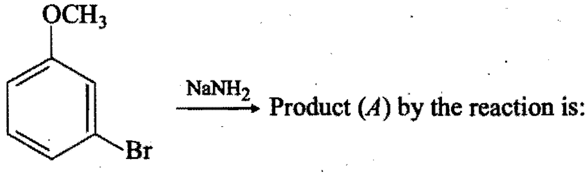
(a)  ☐

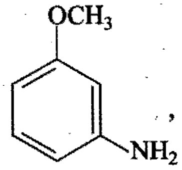
(b)  ☐

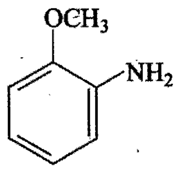
(c)  ☐

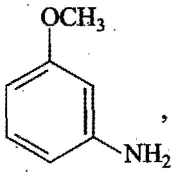
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C^+}}}} \xrightarrow{\text{H-shift}} CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{+}{C}H_2$

(d) $CH_3CH_2CHO \xrightarrow{\bar{O}H} CH_3-\bar{C}H-CHO + H_2O$ ☐

14.  Product (A) by the reaction is:

(a)  , elimination addition ☐

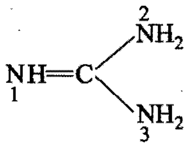
(b)  , elimination addition ☐

(c)


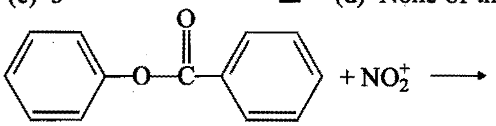
, substitution ☐

(d) none of these ☐

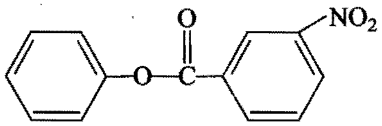
15. Which nitrogen is protonated readily in the guanidine?



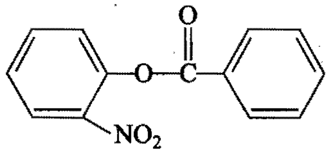
(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) None of these ☐

16.


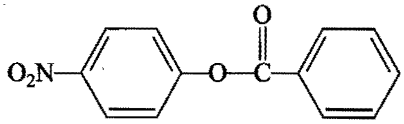
Product of this reaction by single (S_E) electrophilic substitution is:

(a)


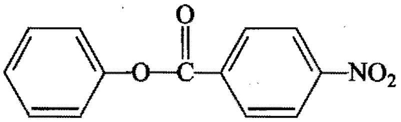
☐

(b)


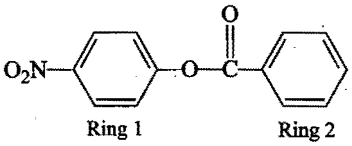
☐

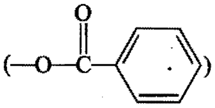
(c)


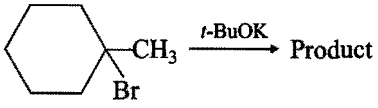
☐

(d)


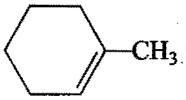
☐

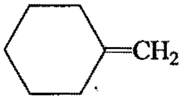
[Hint :


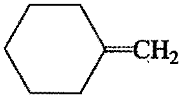
Ring 1 is activated (

) by group, thus nitration takes place at *para*-position of the ring 1.]

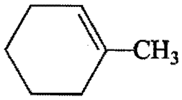
17.


Which is/are correct statement(s) about the product?

I

—CH₃ is an endocyclic Saytzeff product

II

=CH₂ is an exocyclic Saytzeff product

III

=CH₂ is an exocyclic Hofmann product

IV

—CH₃ is an endocyclic Hofmann product

Codes:

(a) I, II and III are correct ☐
(b) I and II are correct ☐
(c) II and IV are correct ☐
(d) I and III are correct ☐

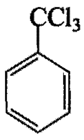
18. Which of the following can undergo nucleophilic substitution under ordinary conditions?

I Allyl chloride II Benzyl chloride
III *n*-Propyl chloride IV Vinyl chloride

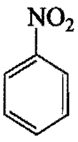
Codes:

(a) I, II and III are correct ☐
(b) I and II are correct ☐
(c) II and IV are correct ☐
(d) I and III are correct ☐

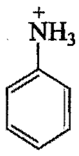
19. Electrophile NO_2^+ attacks on the following:



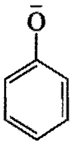
(I)



(II)



(III)



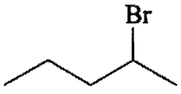
(IV)

In which cases will NO_2^+ be at *meta*-position?

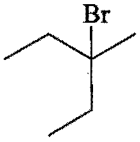
(a) II and IV ☐ (b) I, II and III ☐
(c) II and III ☐ (d) I only ☐

20. Dehydrobromination (—HBr) of the following in increasing order will be:

I



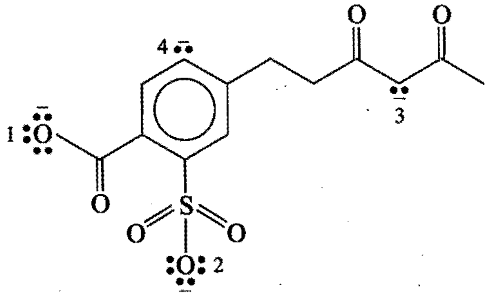
II



III

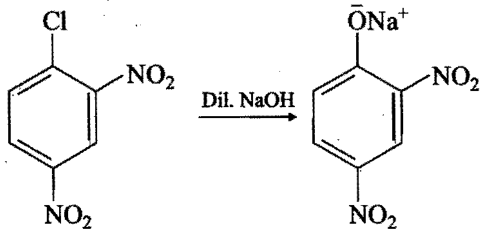
(a) I < II < III ☐ (b) III < II < I ☐
(c) I = II < III ☐ (d) III < I = II ☐

21. Which of the following is the strongest nucleophilic site in the following species?



(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) 4 ☐

22.

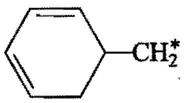


The above transformation proceeds through:
(a) electrophilic addition ☐
(b) benzyne intermediate ☐
(c) activated nucleophilic substitution ☐
(d) elimination ☐

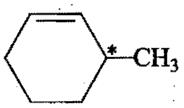
23. Maximum stability will be in which of the following free radicals?

(a) $H_2C{=}\overset{*}{C}H$ ☐ (b) $H_2C{=}CH{-}\overset{*}{C}H_2$ ☐

(c)

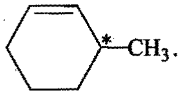


☐ (d)



☐

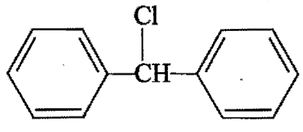
[Hint:



. It is 3° allyl free radical, hence it will be most stable.]

24. Which of the following structures correspond to the product expected, when excess of C_6H_6 reacts with CH_2Cl_2 in presence of anhydrous $AlCl_3$?

(a)



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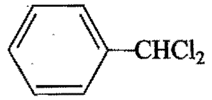
(b)



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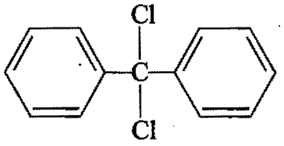
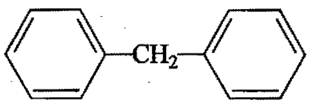
(c)



☐

(d)



☐

25. The intermediate during the addition of HCl to propene in presence of peroxide is:

(a) $CH_3-\overset{*}{C}H-CH_2Cl$ ☐ (b) $CH_3-\overset{+}{C}H-CH_3$ ☐
(c) $CH_3-CH_2-\overset{*}{C}H_2$ ☐ (d) $CH_3-CH_2-\overset{+}{C}H_2$ ☐

26. A covalently strated host group present in the benzene nucleus is *ortho* and *para*-directing; if unsaturated group is present, it is *meta*-directing. This rule is known as:
(a) Vorlander's rule ☐
(b) Crum Brown Gibson rule ☐
(c) Korner's rule ☐
(d) Huckel rule ☐

27. Select the incorrect statement among the following.
(a) Benzene undergoes predominant reactions by electrophilic substitution ☐
(b) Toluene is more easily sulphonated than benzene ☐
(c) Benzene reacts with CCl_4 in the presence of anhydrous $AlCl_3$ to give triphenyl methyl chloride ☐
(d) Benzene reacts with chlorine (Cl_2) in presence of light to give benzyl chloride ☐

28. Kharasch effect regarding addition of HBr is not observed in:
(a) hex-1-ene ☐ (b) hex-2-ene ☐
(c) hex-3-ene ☐ (d) pent-1-ene ☐

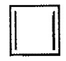
29. Among the following the aromatic compound is:

(a)

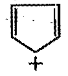
☐ (b)

☐

(c)



☐ (d)



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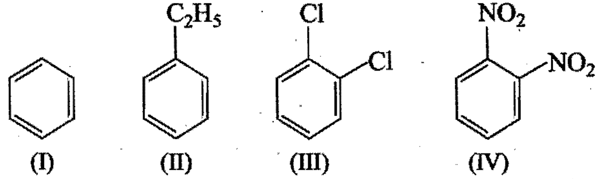
30. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:



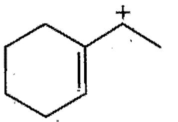
(a) I > II > III > IV ☐ (b) IV > III > II > I ☐
(c) II > I > III > IV ☐ (d) II > III > I > IV ☐

31. In which of the following, first member is more stable than second?
(a) $(C_6H_5)_2\overset{*}{C}CH_3, (C_6H_5)_3\overset{*}{C}$ ☐
(b) $:CH_2, \bullet CH_2\bullet$ ☐
(c) $(C_6H_5)_3\bar{C}, \bar{C}H_3$ ☐
(d) $(C_2H_5)_3\overset{*}{C}, (CH_3)_3\overset{*}{C}$ ☐

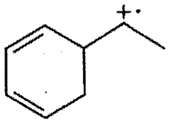
[Hint: $(C_6H_5)_3\bar{C}$ is more stable than $\bar{C}H_3$ because three phenyl groups not only decrease the electron density but also stabilise it by the phenomena of resonance].

32. Most stable carbocation is:

(a)



☐ (b)



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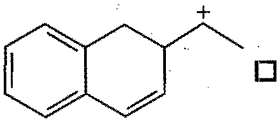
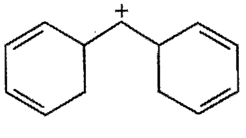
(c)



☐ (d)



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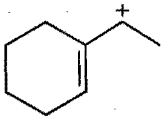
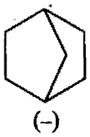
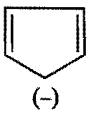
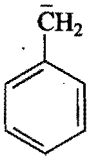
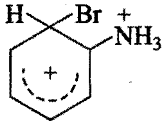
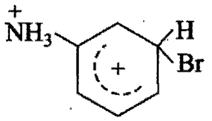
[**Hint:**  is most stable, since it is secondary allylic carbonium ion].

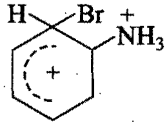
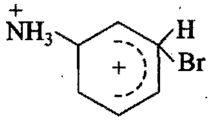
33. Which of the following is least stable?

(a)  ☐ (b)  ☐

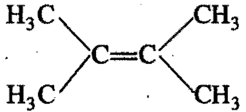
(c) $HC\equiv\bar{C}$ ☐ (d)  ☐

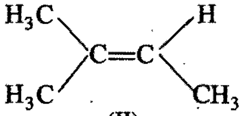
34. The structure of Wheland intermediate obtained after the attack of Br^+ on anilinium ion is:

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

35. The relative rates of addition of


(I)

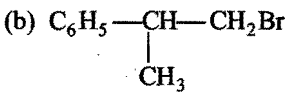

(II)

$\underset{(III)}{CH_3CH_2CH{=}CH_2}$ $\underset{(IV)}{H_2C{=}CH_2}$ $\underset{(V)}{H_2C{=}CH{-}COOH}$ is:

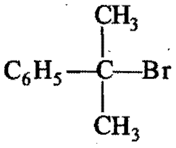
(a) I > II > III > IV > V ☐ (b) V > IV > III > II > I ☐
(c) II > III > I > IV > V ☐ (d) IV > III > II > V > I ☐

36. Which of the following halides will be most reactive towards S_N2 reaction?

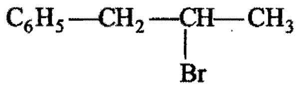
(a) $C_6H_5CH_2CH_2CH_2Br$ ☐

(b)  ☐

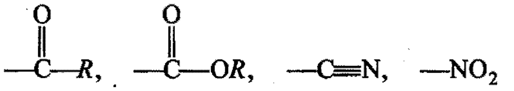
$C_6H_5{-}\underset{CH_3}{\underset{|}{C}H}{-}CH_2Br$

(c)  ☐

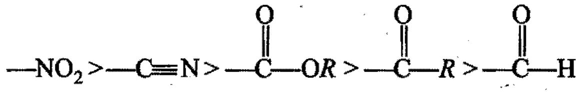
$C_6H_5{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}Br$

(d)  ☐

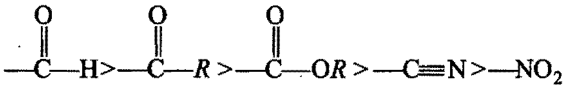
$C_6H_5{-}CH_2{-}\underset{Br}{\underset{|}{C}H}{-}CH_3$

37. Conjugation of electron withdrawing groups, *e.g.*, —CHO,  activates nucleophilic addition. The order of reactivity of these groups is:

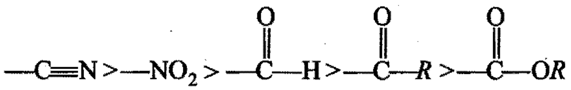
$\overset{O}{\overset{\|}{-C-}}R$, $\overset{O}{\overset{\|}{-C-}}OR$, $-C\equiv N$, $-NO_2$

(a)  ☐

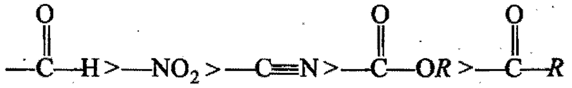
$-NO_2 > -C\equiv N > \overset{O}{\overset{\|}{-C-}}OR > \overset{O}{\overset{\|}{-C-}}R > \overset{O}{\overset{\|}{-C-}}H$

(b)  ☐

$\overset{O}{\overset{\|}{-C-}}H > \overset{O}{\overset{\|}{-C-}}R > \overset{O}{\overset{\|}{-C-}}OR > -C\equiv N > -NO_2$

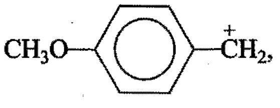
(c)  ☐

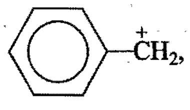
$-C\equiv N > -NO_2 > \overset{O}{\overset{\|}{-C-}}H > \overset{O}{\overset{\|}{-C-}}R > \overset{O}{\overset{\|}{-C-}}OR$

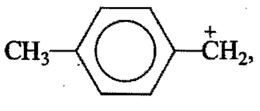
(d)  ☐

$\overset{O}{\overset{\|}{-C-}}H > -NO_2 > -C\equiv N > \overset{O}{\overset{\|}{-C-}}OR > \overset{O}{\overset{\|}{-C-}}R$

38. Relative stabilities of the following carbocations will be in the order:


(I)


(II)


(III)

$CH_3\overset{+}{C}H_2$
(IV)

(a) I < II < III < IV ☐ (b) IV < III < II < I ☐
(c) IV < II < III < I ☐ (d) II < IV < III < I ☐

ANSWERS : BRAIN STORMING PROBLEMS

13. (c)	**14.** (c)	**15.** (a)	**16.** (c)	**17.** (d)	**18.** (a)	**19.** (b)	**20.** (a)	**21.** (d)	**22.** (c)
23. (d)	**24.** (d)	**25.** (b)	**26.** (a)	**27.** (d)	**28.** (c)	**29.** (b)	**30.** (c)	**31.** (c)	**32.** (a)
33. (a)	**34.** (b)	**35.** (a)	**36.** (a)	**37.** (b)	**38.** (c)				

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

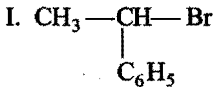
Nucleophilic substitution reaction is given by those compounds which have nucleophilic groups as leaving groups. The weaker the basicity of a group of the substrate, the better is its leaving ability.

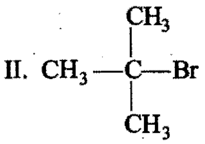
In nucleophilic substitution reactions, the basicity of leaving group should be less than the incoming nucleophilic group. Nucleophilic substitution reaction at *sp*^{3}-hybridised carbon is either bimolecular (S_N2) or unimolecular (S_N1). Bimolecular reaction takes place in single step, involving transition state intermediate. In S_N2 reaction, inversion in configuration takes place. In case of optically active alkyl halides, the inversion in configuration is called Walden inversion. S_N2 reaction is preferred if the compound has less steric hindrance.

Unimolecular (S_N1) reaction involves two steps and carbonium ion intermediate. Optically active substrates give racemic mixture in these reactions.

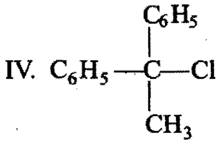
Answer the following questions:

1. Which compound will give Walden inversion in S_N2 reaction?
   (a) CH_3CH_2Br (b) $CH_3-CHD-Br$
   (c) CH_3-Br (d) $C_6H_5CH_2CH_2Cl$
2. Which among the following will give S_N1 reaction?


I. $CH_3-\underset{C_6H_5}{CH}-Br$

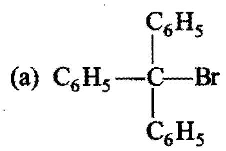

II. $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$

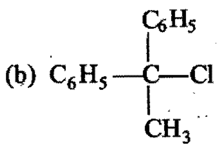
III. CH_3-CH_2-I

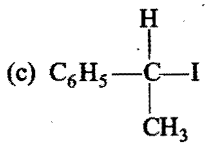

IV. $C_6H_5-\overset{C_6H_5}{\underset{CH_3}{C}}-Cl$

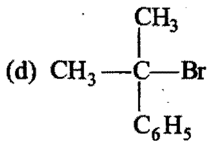
Codes :
(a) I, II, III (b) I, II, IV
(c) III (d) II and IV

3. Which among the following will give enantiomeric pair on treatment with HOH?


(a) $C_6H_5-\overset{C_6H_5}{\underset{C_6H_5}{C}}-Br$


(b) $C_6H_5-\overset{C_6H_5}{\underset{CH_3}{C}}-Cl$

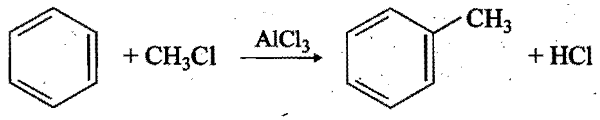

(c) $C_6H_5-\overset{H}{\underset{CH_3}{C}}-I$


(d) $CH_3-\overset{CH_3}{\underset{C_6H_5}{C}}-Br$

4. Select the correct statements among the following:
   (a) carbocation rearrangement takes place in S_N1 reaction
   (b) S_N2 is a two step reaction
   (c) S_N1 mechanism is favoured when nucleophile is neutral
   (d) tertiary alkyl halides give only S_N1 reaction
5. S_N2 reaction involves transition state intermediate, hence it is favoured in which of the following solvents?
   (a) Polar protic solvent (b) Non-polar solvent
   (c) Polar aprotic solvent (d) All of these

Passage 2

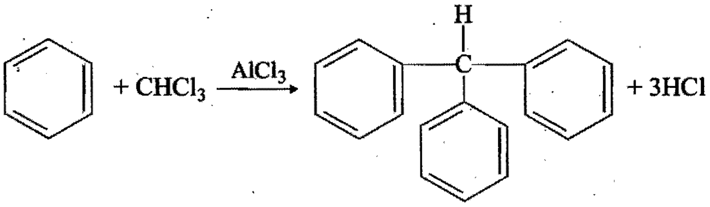
Alkylation of aromatic compounds with aliphatic compounds like halides in presence of Lewis acid catalyst is known as Friedel-Crafts alkylation. It is an example of electrophilic substitution.



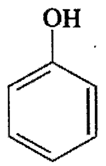
In the process of acylation, $R-\overset{O}{\overset{\|}{C}}-$ group is introduced to the ring. Compounds having (+ mesomeric groups) like $-NH_2$ do not give Friedel-Crafts reaction because these compounds undergo conjugation with the catalyst. In the alkylation process, most branched alkyl group is substituted because isomerisation of carbonium ion takes place. In some Friedel-Crafts reactions, the nature of product changes with the solvent used in the reaction.

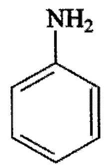
Predict whether the following statements are **true** or **false**:

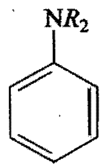
1. $AlCl_3$(aq.) is used as catalyst in Friedel-Crafts reaction:
   (a) True (b) False
2. When benzene is treated with $CHCl_3$ in presence of $AlCl_3$ catalyst, the following reaction takes place:



   (a) True (b) False
3. Carbocations undergo isomerisation in Friedel-Crafts reaction. In each of the following alkyl halides the isomerisation takes place:
   $CH_3-CH_2-CH_2-Cl$,
   $CH_3-CH_2-CH_2-CH_2-Cl$
   (a) True (b) False
4. Following compounds easily give Friedel-Crafts reaction:







(a) True (b) False

5. Diphenyl methane is obtained when benzene is treated with dichloro methane in presence of anhydrous $AlCl_3$:
(a) True (b) False

Passage 3

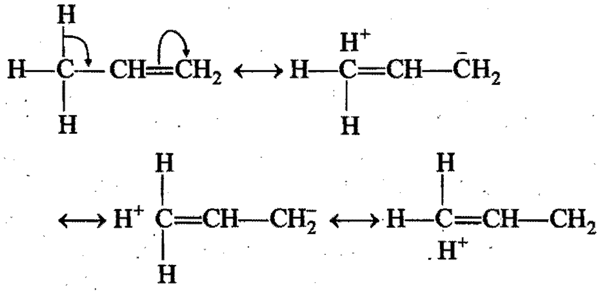
Hyperconjugation describes the orbital interactions between the π-systems and the adjacent σ-bond of the substituent group(s) in organic compounds. Hyperconjugation is also called as Baker and Nathan effect. The necessary and sufficient conditions for the hyperconjugation are:

(i) Compound should have at least one sp^2-hybrid carbon of either alkene, carbocation or alkyl free radical.

(ii) α-carbon with respect to sp^2-hybrid carbon should have at least one hydrogen.

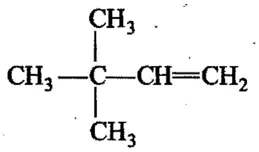
Hyperconjugation are of three types:
(i) σ(C—H), π-conjugation,
(ii) σ(C—H); positive charge conjugation,
(iii) σ(C—H); odd electron conjugation.

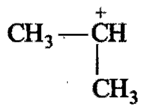
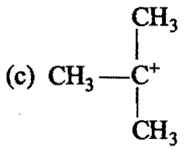
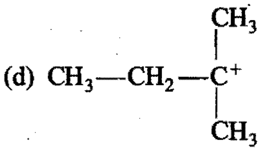
The hyperconjugation may be represented as,

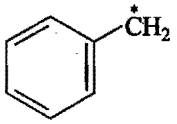
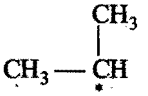


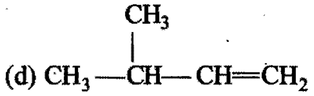
Number of resonating structures due to hyperconjugation $= (n+1)$, where n is the number of α-hydrogen. Greater is the number of such forms, more is the stability of the species under consideration.

Answer the following questions:

1. Hyperconjugation is possible in which of the following species?
(a) CH_3-CH_2 (b) $C_6H_5-CH_3$
(c) $H_2C=CH_2$ (d)

$CH_3-C(CH_3)_2-CH=CH_2$

2. Which of the following carbocations will show highest number of hyperconjugative forms?
(a) $CH_3-\overset{+}{C}H_2$ (b)

$CH_3-\overset{+}{C}H-CH_3$
(c)

$CH_3-C^+(CH_3)_2$
(d)

$CH_3-CH_2-C^+(CH_3)_2$

3. Which of the following free radicals will not show the phenomena of hyperconjugation?
(a) $\dot{C}H_3$ (b)

(c) $CH_3-\dot{C}H_2$ (d)

$CH_3-\dot{C}H-CH_3$

4. Which of the following alkenes will show maximum number of hyperconjugation forms?
(a) $H_2C=CH_2$
(b) $CH_3-CH=CH_2$
(c) $CH_3-CH_2-CH=CH_2$
(d)

$CH_3-CH(CH_3)-CH=CH_2$

5. Stability of alkyl carbocations can be explained by:
(a) inductive effect
(b) hyperconjugation
(c) both inductive effect and hyperconjugation
(d) electromeric effect

Passage 4

Free radical halogenation takes place in the presence of light or at high temperature (above 500°C). Formation of halogen free radical intermediate takes place in first step called chain initiation step.

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$$

This reaction is mainly given by those compounds which have at least one hydrogen atom present at sp^3-hybrid carbon. Reactivity of sp^3-hybrid carbon depends on the reactivity of reaction intermediate.

The relative rate of formation of alkyl radicals by a chlorine radical is:

$$\underset{(5)}{\text{Tertiary}} > \underset{(3.8)}{\text{Secondary}} > \underset{(1)}{\text{Primary}}$$

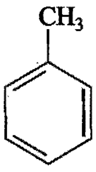
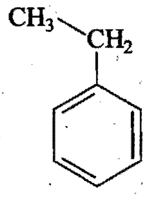
$$\text{Percentage yield of the product} = \frac{\text{Relative amount} \times 100}{\text{Sum of relative amounts}}$$

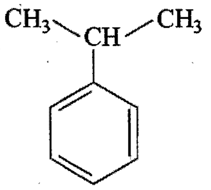
Relative amount = Number of hydrogen atoms on the respective carbon × relative reactivity.

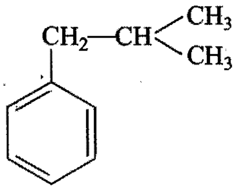
NBS (N-bromosuccinimide) is used for bromination at allylic and benzylic carbon, whereas $Br_2/h\nu$ gives bromination at benzylic, allylic and alkyl carbons.

Answer the following questions:

1. Select most reactive compound for chlorination in presence of light:

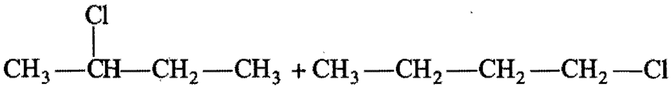
(a)

(b)


(c) 

(d) 

2. Chlorination of butane takes place as;

$CH_3—CH_2—CH_2—CH_3 + Cl_2 \xrightarrow[\text{Light}]{h\nu}$



$CH_3—CH(Cl)—CH_2—CH_3 + CH_3—CH_2—CH_2—CH_2—Cl$

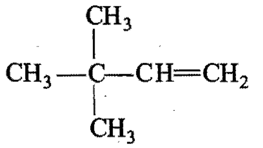
2-Chlorobutane 1-Chlorobutane

Percentage yield of 2-chlorobutane will be:

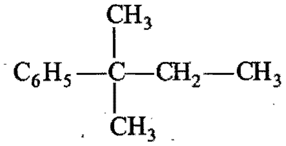
(a) $\frac{15}{21} \times 100$ (b) $\frac{21}{21} \times 100$

(c) $\frac{6}{21} \times 100$ (d) $\frac{3}{21} \times 100$

3. Which one of the following compounds will react with NBS?

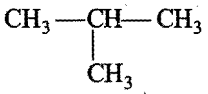
(a) 

$CH_3—C(CH_3)_2—CH{=}CH_2$

(b) 

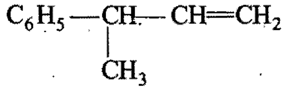
$C_6H_5—C(CH_3)_2—CH_2—CH_3$

(c) $C_6H_5—CH_2—CH{=}CH_2$

(d) 

$CH_3—CH(CH_3)—CH_3$

4. Arrange decreasing order of reactivity of given compounds with NBS (N-bromosuccinimide).

I. $C_6H_5—CH_3$
II. $C_6H_5—CH_2—CH_2—CH_3$
III. $C_6H_5—CH_2—CH{=}CH_2$
IV. 

$C_6H_5—CH(CH_3)—CH{=}CH_2$

Select the correct answer from the codes given below:

Codes :

(a) IV, III, I, II (b) IV, III, II, I

(c) I, II, III, IV (d) I, III, II, IV

5. Chlorinating agent for free radical chlorination may be taken as:

(a) Cl_2 (b) SO_2Cl_2

(c) $(CH_3)_3C—O—Cl$ (d) PCl_5

Passage 5

The electronic displacements in covalent bonds may occur either in the ground state under the influence of an atom or a substituent group or in presence of an appropriate attacking reagent. As a result of these electron displacements, centres of different electron densities are created and these centres are susceptible to attack by the reagents. These electron displacements occur through inductive electromeric, resonance and hyperconjugation effects. Whereas inductive effect involves displacement of σ-electrons towards the substituent, resonance effect involves delocalization of π-electrons transmitted through the chain and both are permanent effects. Electromeric effect is the complete transfer of a shared pair of π-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. Hyperconjugation effects on the other hand involve delocalization of σ-electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system (*i.e.*, σ-π-conjugation). Both inductive and hyperconjugation effects can be used to explain the stability of carbocations and free radicals which follow the stability order: 3° > 2° > 1°. The stability of carbanions, however, follows the reverse order.

An organic reaction occurs through making and breaking of bonds. The breaking of a covalent bond may occur either homolytic leading to the formation of free radicals or heterolytic forming positively (carbocations) or negatively (carbanions) charged species. Most of the attacking reagents carry either a positive or a negative charge. The positively charged species with electron deficient centre or neutral species (free radicals, carbenes, nitrene) are collectively called electrophiles, while negatively charged species with electron rich centre or neutral species (like water, alcohol, ammonia, etc.) are called nucleophiles.

Answer the following questions:

1. Which of the following groups has highest inductive effect?

(a) $CH_3—$ (b) $CH_3CH_2—$

(c) $(CH_3)_2CH—$ (d) $(CH_3)_3C—$

2. The decreasing order of basic strength in

$C_6H_5NH_2$, $(C_6H_5)_2NH$, CH_3NH_2, NH_3
(I) (II) (III) (IV)

is:

(a) (IV) > (III) > (II) > (I) (b) (I) > (II) > (III) > (IV)

(c) (III) > (IV) > (I) > (II) (d) (II) > (I) > (III) > (IV)

3. Out of the following series, the one containing only electrophiles is:

(a) H_2O, Cl^+, NH_3 (b) H_2O, RNH_2, H_3O^+

(c) BF_3, SO_3, NO_2^+ (d) $AlCl_3, NH_3, H_2O$

4. Consider the following alkenes and what is correct decreasing order of stability?

$CH_3CH_2CH{=}CH_2$, $(CH_3)_2C{=}C(CH_3)_2$,
But-1-ene 2,3-Dimethyl but-2-ene
(I) (II)

$(CH_3)_2C{=}CHCH_3$,	$(CH_3)_2C{=}CH_2$
2-Methyl but-2-ene	2-Methyl propene
(III)	(IV)

(a) (I) > (II) > (III) > (IV) (b) (II) > (III) > (IV) > (I)
(c) (IV) > (III) > (II) > (I) (d) (III) > (IV) > (I) > (II)

5. Which of the following is most stable cation?
(a) $(CH_3)_2\overset{+}{C}H$ (b) $\overset{+}{C}H_3$
(c) $\overset{+}{C}F_3$ (d) $F_3C{-}\overset{+}{C}H_2$

[CET (J&K) 2004]

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	**1.** (b)	**2.** (b)	**3.** (c)	**4.** (a,c,d)	**5.** (c)
Passage 2	**1.** (b)	**2.** (a)	**3.** (a)	**4.** (b)	**5.** (a)
Passage 3	**1.** (b)	**2.** (c)	**3.** (a,b)	**4.** (b)	**5.** (c)
Passage 4	**1.** (c)	**2.** (a)	**3.** (c)	**4.** (b)	**5.** (a,b,c)
Passage 5	**1.** (d)	**2.** (c)	**3.** (c)	**4.** (b)	**5.** (a)

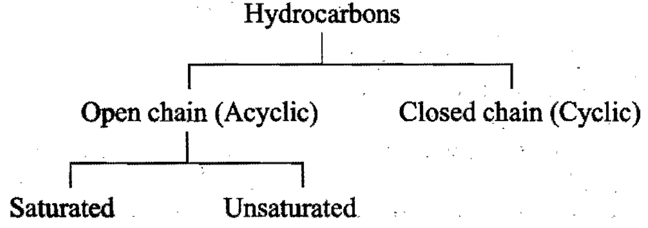
6

SATURATED ALIPHATIC HYDROCARBONS

(Alkanes or Paraffins)

6.1 HYDROCARBONS

Organic compounds composed of only carbon and hydrogen are called hydrocarbons. On the basis of structure, hydrocarbons are divided into two main classes; open chain (acyclic) and closed chain (cyclic). Open chain hydrocarbons are called **aliphatic hydrocarbons.** Aliphatic hydrocarbons are further classified into two groups depending on the types of carbon-carbon bonds in the carbon chain. Hydrocarbons which contain only single covalent C—C and C—H bonds are termed **saturated hydrocarbons** and those in which carbon atoms are linked by multiple bonds (at least one double or one triple bond) besides single covalent bonds between C—C and C—H, are termed **unsaturated hydrocarbons.**



6.2 SATURATED HYDROCARBONS

These constitute a homologous series having general formula C_nH_{2n+2} (n may have value 1, 2, 3, 4, . . .). The simplest member of the series is methane (CH_4). The formulae of few members of the series are:

C_2H_6 Ethane	C_3H_8 Propane	C_4H_{10} Butane
C_5H_{12} Pentane	C_6H_{14} Hexane	C_7H_{16} Heptane
C_8H_{18} Octane	C_9H_{20} Nonane	$C_{10}H_{22}$ Decane
$C_{11}H_{24}$ Undecane	$C_{12}H_{26}$ Dodecane	and so on . . .

The saturated hydrocarbons are called **paraffins** (Latin: *parum* = little; *affinis* = affinity) as they are relatively inert towards chemical reagents. In IUPAC nomenclature, paraffins are termed **alkanes.** Nomenclature of alkanes has already been described in chapter 3. Alkanes have following structural characteristics.

1. Every carbon atom is sp^3 hybridized, its four bonding orbitals are directed towards the four corners of a regular tetrahedron.
2. All the carbon-carbon and carbon-hydrogen bonds are strong sigma bonds. The carbon-carbon bond is formed from the overlap of sp^3 orbitals, one from each carbon atom. All carbon-hydrogen bonds result in overlap of sp^3 hybrid orbital from carbon and s-orbital from hydrogen.
3. The bond lengths between carbon-carbon and carbon-hydrogen are 1.54 Å and 1.112 Å respectively.
4. The bond angles in alkanes are tetrahedral angles having a value of 109.5° (109°28′).
5. Carbon-carbon chain in alkanes consisting more than two carbon atoms is not linear but *zig-zag*. The usual depiction of carbon chain as straight chain is only for convenience of presentation. Thus, alkanes have three-dimensional, rather than planar structure.
6. Carbon-carbon bond dissociation energy is 83 kcal/mol while carbon-hydrogen bond dissociation energy is 99 kcal/mol.

The structure of methane molecule can be represented by Figs. 6.1 (a), 6.1 (b) and 6.1 (c).

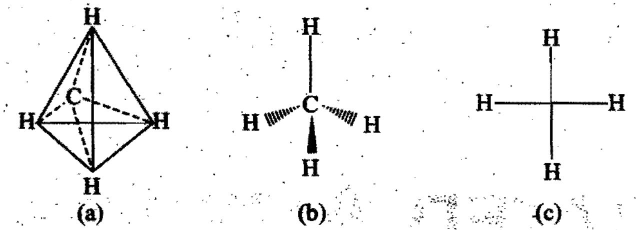


Fig. 6.1 Representation of methane molecule

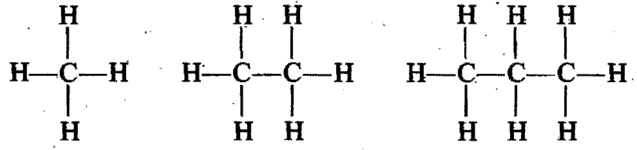
Fig. 6.1 (a) is the **tetrahedral structure** of methane in which carbon atom lies in the centre of the regular tetrahedron and the four hydrogen atoms attached to it are present at the corners or the vertices of the tetrahedron. Thus, each face of a tetrahedron is an equilateral triangle and has three hydrogen atoms.

Fig. 6.1 (b) is the **Wedge** and **Dash** representation (three dimensional, **3-D**) in which the *solid wedge* (◀) or a thick solid (or heavy) line is used to indicate a bond projecting above the plane of the paper and projecting towards the observer. The *dashed wedge* (⋯) or a dashed line is used to represent a bond lying below the plane of the paper and projecting away from the observer. The bonds lying in the plane of the paper are shown by a normal (ordinary) line. As this representation describes the actual positions of various atoms present in the molecule in space, it is termed a **spatial formula.**

Fig. 6.1 (c) is the two-dimensional (2-D) representation of a methane molecule. This is called **graphic** or **displayed formula.** This formula does not reveal the true tetrahedral geometry of the molecule; however, this is most commonly used **(Fischer Projection Formula).**

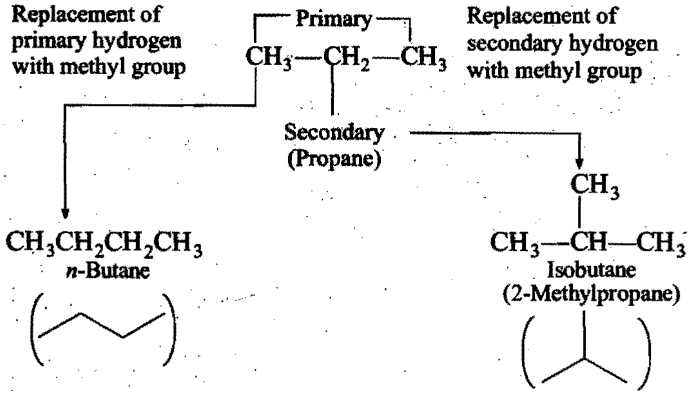
6.3 STRUCTURAL ISOMERISM IN ALKANES

Alkanes exhibit chain isomerism. The first three members, *viz.*, methane, ethane and propane do not exhibit isomerism as they can be represented by only one structural formula.



Methane Ethane Propane

However, propane consists of two types of carbon atoms; primary and secondary. If hydrogen of primary carbon or secondary carbon is replaced by a methyl group, two possible structures result.

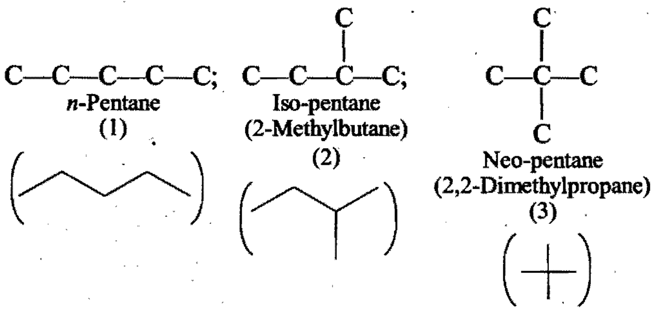


Thus, butane has two chain isomers. With increase in the number of carbon atoms in the molecule, the number of chain isomers also increases.

Alkane	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	$C_{10}H_{22}$
No. of possible isomers	3	5	9	18	75

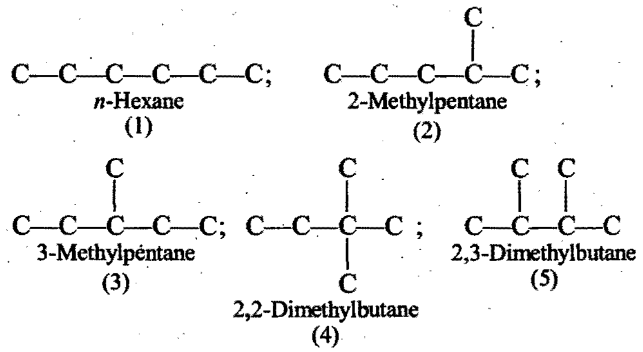
The carbon skeletons of isomeric pentanes and hexanes are shown below:

Pentanes :



Greater the branching greater the stability; so increasing order of stability is: *n*-pentane < iso-pentane < neo-pentane.

Hexanes :



6.4 NATURAL SOURCES (OCCURRENCE) OF ALKANES

Two main sources of alkanes are:

(a) Petroleum and (b) Natural gas.

Petroleum contains large quantities of liquid hydrocarbons along with little solid paraffin wax dissolved in it. It is the main source of alkanes containing upto 40 carbon atoms.

Natural gas contains mainly lower alkanes. It contains about 80% methane, 10% ethane and the remaining 10% being a mixture of higher members. It also consists of small amounts of hydrogen, nitrogen, carbon dioxide, etc.

The natural wax, called *ozokerite,* found near petroleum wells, is a mixture of higher solid hydrocarbons. Bee's wax, which is mainly myricyl palmitate (an ester), also contains small quantities of $C_{27}H_{56}$ and $C_{31}H_{64}$. Fuel gas obtained from coal contains about 32% methane. Methane **(Marsh gas)** is found at marshy places where it is formed by the decomposition of vegetable and animal waste with bacteria.

6.5 GENERAL METHODS OF PREPARATION

To obtain an alkane in pure form from a natural source is not an easy task. Therefore, usually synthetic methods are preferred for the preparation of alkanes in pure form. It is one of the characteristics of a homologous series that various members can be prepared by similar methods. The similar methods are termed as general methods of preparation of a particular homologous series. The general methods of preparation of the alkanes are given below:

1. By hydrogenation of unsaturated hydrocarbons : Alkanes are obtained by hydrogenation of unsaturated hydrocarbons (alkenes and alkynes) in presence of finely divided nickel* at 200–300°C. This is known as **Sabatier** and **Senderen's** reaction.

$$\underset{\text{Alkene}}{C_nH_{2n}} + H_2 \xrightarrow[\text{Heat}]{\text{Ni or Raney Ni}} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

$$\underset{\text{Alkyne}}{C_nH_{2n-2}} + 2H_2 \xrightarrow[\text{Heat}]{\text{Ni or Pt or Pd}} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

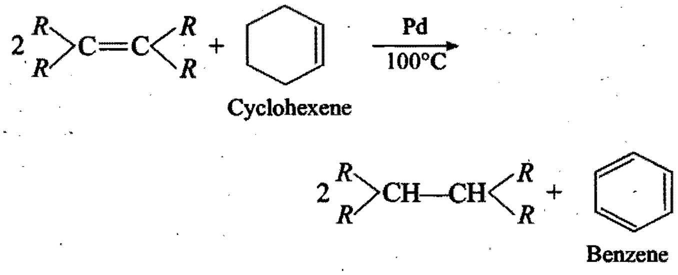
$$\underset{\text{Ethene}}{H_2C{=}CH_2} + H_2 \xrightarrow[200°C]{\text{Ni}} \underset{\text{Ethane}}{H_3C{-}CH_3}$$

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + H_2 \xrightarrow[200°C]{\text{Ni}} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

$$\underset{\substack{\text{Ethyne}\\\text{(Acetylene)}}}{HC{\equiv}CH} + 2H_2 \xrightarrow[300°C]{\text{Ni}} \underset{\text{Ethane}}{H_3C{-}CH_3}$$

When platinum, palladium, rhodium, ruthenium or B_2H_6 in THF are used as catalysts, the hydrogenation takes place at room temperature. Catalytic hydrogenation proceeds very smoothly and quantitatively.

Transfer hydrogenation : The hydrogen is supplied by a donor such as cyclohexene or hydrazine.



The driving force in the case of cyclohexene is the gain in aromatic stabilization energy when benzene is formed. With hydrazine ($H_2N{-}NH_2$), the strongly bonded N_2 molecule is formed.

Limitation : No unsaturated hydrocarbon contains only one carbon atom, hence this method cannot be used for the preparation of methane.

2. By the reduction of alkyl halides : Alkyl halides undergo reduction with nascent hydrogen to form alkanes.

$$\underset{\text{Alkyl halide}}{R{-}X} + 2H \longrightarrow \underset{\text{Alkane}}{R{-}H} + HX$$

The yields are generally good and the hydrocarbons obtained are pure. The nascent hydrogen for reduction may be obtained by using any one of the following:

(a) Zinc and dilute hydrochloric acid,
(b) Zinc and acetic acid; Zn and NaOH,
(c) Zinc-copper couple in ethanol,
(d) Red phosphorus and hydrogen iodide,
(e) Al–Hg in ethanol.

$$\underset{\text{Methyl iodide}}{CH_3I} + 2H \xrightarrow[\text{or Zn–Cu}/C_2H_5OH]{\text{Zn + HCl}} \underset{\text{Methane}}{CH_4} + HI$$

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + 2H \xrightarrow[\text{or Zn–Cu}/C_2H_5OH]{\text{Zn + HCl}} \underset{\text{Ethane}}{C_2H_6} + HI$$

$$\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} + Zn + H^+ \longrightarrow \underset{\text{Propane}}{CH_3CH_2CH_3} + Zn^{2+} + Br^-$$

$$3C_2H_5I + 3HI \xrightarrow{150°C} 3C_2H_6 + 3I_2$$

$$2P + 3I_2 \longrightarrow 2PI_3$$

$$\underset{\text{Ethyl iodide}}{3C_2H_5I} + 3HI + \underset{\text{(Red)}}{2P} \longrightarrow \underset{\text{Ethane}}{3C_2H_6} + 2PI_3$$

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + 2HI \xrightarrow[150°C]{\text{Red P}} \underset{\text{Ethane}}{CH_3CH_3} + HBr + I_2$$

The purpose of use of red phosphorus is to remove iodine.

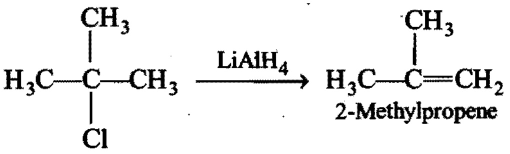
Alkyl halides may also be reduced catalytically by hydrogen using catalysts like nickel, palladium, platinum, etc.

$$R{-}X + H_2 \xrightarrow{\text{Pd}} R{-}H + HX$$

Primary and secondary alkyl halides may be conveniently reduced with lithium aluminium hydride in a dry organic solvent.

$$4RX + LiAlH_4 \xrightarrow[\text{solvent}]{\text{Organic}} 4RH + LiAlX_4\ (LiX + AlX_3)$$

$LiAlH_4$ is not useful for 3° alkyl halide which is converted into alkenes. In such cases $NaBH_4$ or TPH is used.



$$H_3C{-}C(CH_3)(Cl){-}CH_3 \xrightarrow{LiAlH_4} \underset{\text{2-Methylpropene}}{H_3C{-}C(CH_3){=}CH_2}$$

3° 2-Methylpropane

Alkyl halides (1°, 2°, 3°) can also be reduced to alkanes with TPH (Triphenyl tin hydride, Ph_3SnH).

3. By Wurtz reaction : This method was discovered by the French chemist Wurtz in 1855 and is very convenient for preparing paraffins of high molecular mass.

An ether solution of an alkyl halide is treated with sodium which removes the halogen of alkyl halide and the two alkyl radicals join together to form an alkane.

$$\underset{\text{Alkyl halide}}{R\,X} + 2Na + \underset{\text{Alkyl halide}}{X\,R} \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R{-}R} + 2NaX$$

$$\underset{\text{Methyl iodide}}{CH_3\,I} + 2Na + \underset{\text{Methyl iodide}}{I\,CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaI$$

---

*Raney nickel is often used as an effective catalyst at room temperature and atmospheric pressure. It is obtained by boiling Ni–Al alloy with NaOH, when aluminium dissolves leaving nickel in finally divided state. It is filtered, washed, dried and stored under H_2O or C_2H_5OH.

Note : Alkyl bromides and iodides are preferred in this reaction. The net result in this reaction is the formation of symmetrical alkane ($R—R$) having an **even number of carbon atoms.**

When a mixture of two different alkyl halides is used, a mixture of three alkanes is obtained.

$$\underset{\text{Methyl bromide}}{CH_3Br} + 2Na + \underset{\text{Ethyl bromide}}{BrC_2H_5} \xrightarrow{\text{Dry Ether}} \underset{\text{Propane}}{CH_3—C_2H_5} + 2NaBr$$

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{Dry Ether}} \underset{\text{Ethane}}{CH_3—CH_3} + 2NaBr$$

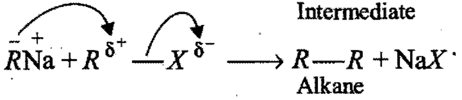
$$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{Dry Ether}} \underset{\text{Butane}}{C_2H_5—C_2H_5} + 2NaBr$$

The separation of the mixture into individual members is not always easy. **Thus, Wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atoms but the method is useful for the preparation of symmetrical alkanes.**

Mechanism : The mechanism of Wurtz reaction is not fully understood. Two mechanisms are proposed for this reaction.

(a) Intermediate formation of an organometallic compound :

$$RX + 2Na \longrightarrow \underset{\text{Intermediate}}{[\overset{-}{R}\overset{+}{Na}]} + NaX$$



$$\overset{-}{R}\overset{+}{Na} + R^{\delta+} — X^{\delta-} \longrightarrow \underset{\text{Alkane}}{R—R} + NaX$$

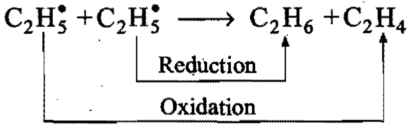
(b) Intermediate formation of free radicals :

$$RX + Na \longrightarrow \underset{\text{Free radical}}{[\dot{R}]} + NaX$$

$$\dot{R} + \dot{R} \longrightarrow \underset{\text{Alkane}}{R—R}$$

Other hydrocarbons are also obtained as a result of disproportionation, *i.e.*, intermolecular hydrogenation of free radicals.

e.g.,



$$C_2H_5^{\bullet} + C_2H_5^{\bullet} \longrightarrow C_2H_6 + C_2H_4$$

Reduction

Oxidation

Wurtz reaction is useful in ascending the series of organic compounds, because it leads to the formation of carbon-carbon bond. For example, methane can be converted into ethane.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

$$CH_3Cl + 2Na + ClCH_3 \longrightarrow CH_3 — CH_3 + 2NaCl$$

Limitations : (i) Methane cannot be obtained by this method.

(ii) The reaction fails with *tert.* alkyl halides.

(iii) The reaction is suitable for symmetrical alkanes (even number of carbon atoms).

4. By Frankland's reaction : The method is similar to Wurtz reaction. The alkyl halide is heated with zinc in inert solvent, higher alkane is formed.

$$RX + Zn + XR \xrightarrow{\text{Ether}} \underset{\text{Alkane}}{R—R} + ZnX_2$$

$$\underset{\text{Ethyl iodide}}{C_2H_5}\boxed{I + Zn + I}\underset{\text{Ethyl iodide}}{C_2H_5} \longrightarrow \underset{\text{Butane}}{C_2H_5—C_2H_5} + ZnI_2$$

Methane cannot be prepared by this method. When two different alkyl halides are used, a mixture of three alkanes is obtained as in Wurtz reaction.

5. By decarboxylation of carboxylic acid (Laboratory method) : When the sodium salt of a fatty acid is heated at 360°C with sodalime (mixture of NaOH and CaO), a molecule of carbon dioxide is eliminated as carbonate and an alkane is formed.

$$R\boxed{COONa + NaO}H \xrightarrow[\text{CaO}]{\text{Heat}} \underset{\text{Alkane}}{R—H} + Na_2CO_3$$

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \xrightarrow[\text{CaO}]{\text{Heat}} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

However, pure methane can be obtained if barium oxide is used in place of sodalime.

$$\underset{\text{Sodium propionate}}{C_2H_5COONa} + NaOH \xrightarrow[\text{CaO}]{\text{Heat}} \underset{\text{Ethane}}{C_2H_6} + Na_2CO_3$$

The purpose of CaO in sodalime is to keep NaOH dry since it is quite hygroscopic in nature.

In this process, one molecule of carbon dioxide is eliminated from a carboxylic acid and hence called **decarboxylation.**

A good yield of alkanes has also been obtained from the photochemical decarboxylation of primary carboxylic acids by lead tetraacetate in chloroform.

$$R—COOH \xrightarrow[\text{CHCl}_3]{\text{Pb(OAc)}_4} \underset{\text{Alkane}}{R—H} + CO_2$$

Note : The alkane formed always contains one carbon atom less than the original acid. The yield is usually good in the case of lower members but poor for higher members. The method is used for reducing the carbon atoms in the carbon chain.

6. By electrolysis of sodium or potassium salts of fatty acids (Kolbe's method or Kolbe's electrolysis) : Electrolysis of a concentrated aqueous solution of either sodium or potassium salts of saturated monocarboxylic acids yields higher alkanes at anode.

$$2RCOOK + 2H_2O \xrightarrow{\text{Electrolysis}} R—R + 2CO_2 + 2KOH + H_2$$

$$\underset{\text{Potassium acetate}}{2CH_3COOK} + 2H_2O \longrightarrow \underset{\text{Ethane}}{CH_3—CH_3} + 2CO_2 + 2KOH + H_2$$

$$\underset{\text{Potassium propionate}}{2C_2H_5COOK} + 2H_2O \longrightarrow \underset{\text{Butane}}{C_2H_5—C_2H_5} + 2CO_2 + 2KOH + H_2$$

In the electrolysis of potassium propionate, small amounts of ethane, ethene and ethyl propionate are also formed.

Mechanism : The formation of alkane follows free radical mechanism.

$$CH_3COONa \rightleftharpoons \underset{\underset{\text{Anode}}{\downarrow}}{CH_3COO^-} + \underset{\underset{\text{Cathode}}{\downarrow}}{Na^+}$$

At anode :

$$2CH_3COO^- \longrightarrow \underset{\text{Acetate free radical}}{2CH_3CO\dot{O}} + 2e^-.$$

$$2CH_3CO\dot{O} \longrightarrow \underset{\text{Methyl free radical}}{2\dot{C}H_3} + 2CO_2\uparrow$$

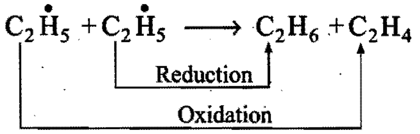
$$2\dot{C}H_3 \longrightarrow CH_3{-}CH_3$$

At cathode :

$$2Na^+ + 2e^- \longrightarrow 2Na$$
$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

If mixture of two salts R_1COOK and R_2COOK are taken then hydrocarbons $R_1{-}R_1$, $R_2{-}R_2$ are also obtained. Esters, lower alkanes and alkenes are also obtained as side products.

$$C_2H_5COONa \longrightarrow C_2H_5COO^- + Na^+$$
$$C_2H_5COO^- \longrightarrow C_2H_5CO\dot{O} + e^-$$
$$C_2H_5COO^- \longrightarrow C_2\dot{H}_5 + CO_2$$
$$C_2H_5CO\dot{O} + C_2\dot{H}_5 \longrightarrow \underset{\text{Ester}}{C_2H_5COOC_2H_5}$$



$$C_2\dot{H}_5 + C_2\dot{H}_5 \longrightarrow C_2H_6 + C_2H_4$$

Note : (i) This method is applicable for the preparation of only symmetrical alkanes of the type $R{-}R$.
(ii) Methane cannot be prepared by this method.

---

7. From Grignard reagents : Alkyl magnesium halides ($RMgX$) are called Grignard reagents. These undergo double decomposition reactions with water or ammonia or alcohol or amines having active H atom (attached to strongly electronegative O, N, S or F and triple bond . . ., etc.) to give alkane corresponding to alkyl (R-) group of Grignard reagent. Since, carbon is more electronegative (electronegativity = 2.5) than magnesium (electronegativity = 1.2), therefore, C-Mg bond is quite polar.

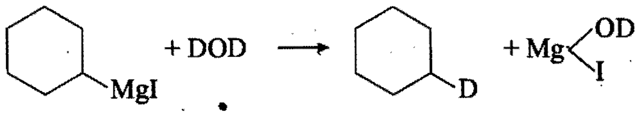
$$[\ \underset{\text{Alkyl halide}}{RX} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Alkyl mag. halide}}{R{-}Mg{-}X}\ ]$$

$$\underset{\text{Grignard reagent}}{RMgX} + HOH \xrightarrow{H^+} \underset{\text{Alkane}}{R{-}H} + Mg\left\langle\begin{matrix}OH\\X\end{matrix}\right.$$

$$\underset{\text{Ethyl magnesium bromide}}{C_2H_5MgBr} + HOH \xrightarrow{H^+} \underset{\text{Ethane}}{C_2H_5H} + Mg\left\langle\begin{matrix}OH\\Br\end{matrix}\right.$$

If heavy water, D_2O is used, then the product formed is RD, deutero alkane.

$$R{-}MgX + D_2O \longrightarrow \underset{\text{Deuteroalkane}}{R{-}D} + Mg\left\langle\begin{matrix}OD\\X\end{matrix}\right.$$



$$\underset{\text{Methyl magnesium bromide}}{CH_3MgBr} + \underset{\text{Ethanol}}{HOC_2H_5} \longrightarrow \underset{\text{Methane}}{CH_3H} + Mg\left\langle\begin{matrix}Br\\OC_2H_5\end{matrix}\right.$$

$$C_2H_5MgI + \underset{\text{Ethanthiol}}{HSC_2H_5} \longrightarrow \underset{\text{Ethane}}{C_2H_5H} + Mg\left\langle\begin{matrix}I\\SC_2H_5\end{matrix}\right.$$

$$\underset{\text{Alkyl magnesium halide}}{Mg\left\langle\begin{matrix}\boxed{R+H}\underset{\text{Ammonia}}{NH_2}\\X\end{matrix}\right.} \longrightarrow \underset{\text{Alkane}}{RH} + Mg\left\langle\begin{matrix}NH_2\\X\end{matrix}\right.$$

$$\underset{\text{Ethyl magnesium bromide}}{Mg\left\langle\begin{matrix}\boxed{C_2H_5+H}\underset{\substack{\text{Methyl amine}\\(1^\circ\text{ amine})}}{\overset{H\atop|}{-N-}CH_3}\\Br\end{matrix}\right.} \longrightarrow \underset{\text{Ethane}}{C_2H_5H} + Mg\left\langle\begin{matrix}HNCH_3\\Br\end{matrix}\right.$$

$$Mg\left\langle\begin{matrix}\boxed{C_2H_5+\ H}\underset{\substack{\text{Dimethylamine}\\(2^\circ\text{ amine})}}{N(CH_3)_2}\\I\end{matrix}\right. \longrightarrow \underset{\text{Ethane}}{C_2H_6} + Mg\left\langle\begin{matrix}I\\N(CH_3)_2\end{matrix}\right.$$

This method gives quantitative yield of alkane (pure).

$$Mg\left\langle\begin{matrix}\boxed{C_2H_5+H}\underset{\text{Propyne}}{C{\equiv}C{-}CH_3}\\I\end{matrix}\right. \longrightarrow \underset{\text{Ethane}}{C_2H_6} + Mg\left\langle\begin{matrix}I\\C{\equiv}C{-}CH_3\end{matrix}\right.$$

$$C_2H_5MgBr + \underset{\text{Acetic acid}}{CH_3COOH} \longrightarrow \underset{\text{Ethane}}{C_2H_6} + Mg\left\langle\begin{matrix}Br\\OOCCH_3\end{matrix}\right.$$

8. By reduction of alcohols, aldehydes, ketones or fatty acids and their derivatives : Alkanes are formed when alcohols, aldehydes, ketones or fatty acids and their derivatives are reduced with hot conc. hydroiodic acid and red phosphorus at 150–200°C in a sealed tube. Phosphorus and iodine react to form PI_3 which again produces HI.

$$\underset{\text{Methyl alcohol}}{CH_3OH} + 2HI \xrightarrow[150^\circ C]{\text{Red P}} \underset{\text{Methane}}{CH_4} + H_2O + I_2$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 4HI \xrightarrow[150^\circ C]{\text{Red P}} \underset{\text{Ethane}}{C_2H_6} + H_2O + 2I_2$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 4HI \xrightarrow[150^\circ C]{\text{Red P}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + 2I_2$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + 6HI \xrightarrow[200^\circ C]{\text{Red P}} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2H_2O + 3I_2$$

$$\underset{\text{Acetyl chloride}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}Cl} + 6HI \xrightarrow[200^\circ C]{\text{Red P}} \underset{\text{Ethane}}{CH_3{-}CH_3} + H_2O + HCl + 3I_2$$

$$\underset{\text{Acetamide}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}NH_2} + 6HI \xrightarrow[200^\circ C]{\text{Red P}} \underset{\text{Ethane}}{CH_3{-}CH_3} + H_2O + NH_3 + 3I_2$$

Higher fatty acids undergo reduction more readily as compared to the lower ones. This method is thus, useful for the preparation of higher alkanes. However, the yield is usually poor.

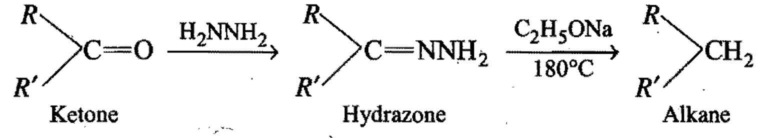
Aldehydes and ketones when reduced with amalgamated zinc and conc. HCl also yield alkanes. This process is known as **Clemmensen reduction.**

$$>C{=}O \xrightarrow[\text{Conc. HCl}]{\text{Zn–Hg}} >CH_2$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2H_2 \xrightarrow[\text{Conc. HCl}]{\text{Zn—Hg}} \underset{\text{Ethane}}{CH_3{—}CH_3} + H_2O$$

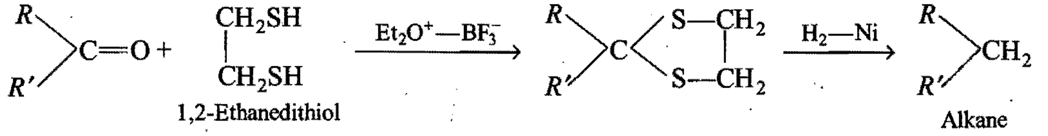
$$\underset{\text{Acetone}}{CH_3COCH_3} + 2H_2 \xrightarrow[\text{Conc. HCl}]{\text{Zn—Hg}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$

Aldehydes and ketones ($>C{=}O$) can be reduced to hydrocarbons in presence of excess of hydrazine and sodium alkoxide on heating.



This is called **Wolff-Kishner reduction.**

In **Mozingo method,** the $>C{=}O$ is converted into its dithioacetal or ketol using ethanedithiol in the presence of a Lewis acid. Dithioacetal is then hydrogenolysed over Raney Nickel.

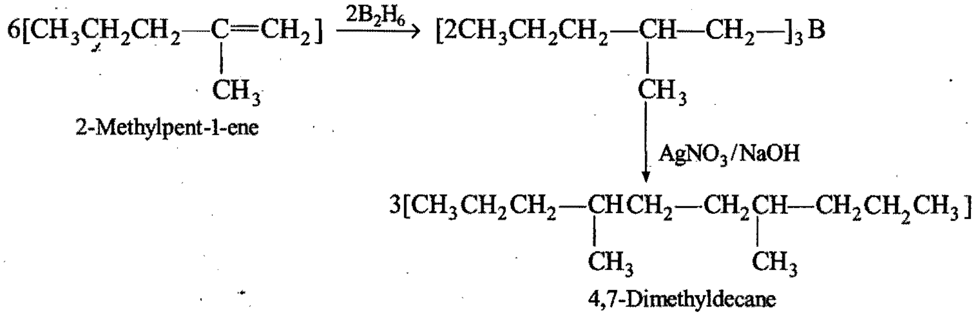


9. Hydroboration of Alkenes : Diborane (B_2H_6) adds to an olefinic bond forming trialkyl borane which on treatment with acetic acid or propionic acid yields corresponding alkane.

$$\underset{\text{Alkene}}{R{—}CH{=}CH_2} \xrightarrow[\text{In Diglyme}]{B_2H_6} \underset{\text{Trialkyl borane}}{(R{—}CH_2{—}CH_2{—})_3B} \xrightarrow[(H^+)]{CH_3COOH} \underset{\text{Alkane}}{R{—}CH_2{—}CH_3}$$

This provides a method of reducing alkene into alkane. This method cannot be used to prepare methane, but is very useful for preparing long chain alkanes. It involves coupling of alkyl boranes by means of silver nitrate in presence of sodium hydroxide at 25°C.

$$6[R{—}CH{=}CH_2] \xrightarrow{2B_2H_6} [2R{—}CH_2{—}CH_2{—}]_3B \xrightarrow[NaOH]{AgNO_3} 3[RCH_2CH_2{—}CH_2CH_2R]$$



$$\underset{\text{2-Methylpent-1-ene}}{6[CH_3CH_2CH_2{—}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2]} \xrightarrow{2B_2H_6} [2CH_3CH_2CH_2{—}\underset{\displaystyle CH_3}{\underset{|}{C}H}{—}CH_2{—}]_3B$$

$$\xrightarrow{AgNO_3/NaOH} \underset{\text{4,7-Dimethyldecane}}{3[CH_3CH_2CH_2{—}\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2{—}CH_2\underset{\displaystyle CH_3}{\underset{|}{C}H}{—}CH_2CH_2CH_3]}$$

10. Corey-House alkane synthesis : An alkyl halide is first converted into lithium alkyl which reacts with cuprous iodide to form lithium dialkyl cuprate, LiR_2Cu. It is then treated with an alkyl halide to give an alkane.

(i) $$CH_3Br + 2Li \xrightarrow{\text{Dry ether}} \underset{\text{Methyl lithium}}{CH_3Li} + LiBr$$

(ii) $$2CH_3Li + CuI \longrightarrow \underset{\text{Lithium dimethyl cuprate}}{Li(CH_3)_2Cu} + LiI'$$

(iii) $$\underset{\text{Ethyl bromide}}{C_2H_5Br} + Li(CH_3)_2Cu \longrightarrow \underset{\text{Propane}}{C_2H_5{—}CH_3} + CH_3Cu + LiBr$$

For the third step to give a good yield of alkane, the alkyl halide must be either CH_3X, or a primary alkyl halide or a secondary cycloalkyl halide. The alkyl group of the lithium dialkyl cuprate (also called **Gilman reagent**) may be methyl 1°, 2° or 3°. Moreover, the two alkyl groups being coupled need not to be different.

This method is particularly suitable for the preparation of unsymmetrical alkanes of the type, $R—R'$ (via S_N2 mechanism).

$$\underset{\text{Isopropyl bromide}}{(CH_3)_2CHBr} \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} \underset{\text{Lithium isopropyl cuprate}}{[(CH_3)_2CH]_2LiCu}$$

$$\xrightarrow{CH_3CH_2Br} \underset{\text{2-Methylbutane}}{(CH_3)_2CH—CH_2CH_3}$$

11. By the action of water (or dil. HCl) an aluminium and beryllium carbide : Both these carbides on treatment with water or dilute HCl at room temperature yield methane.

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$

$$\underset{\text{Beryllium carbide}}{Be_2C} + 4H_2O \longrightarrow \underset{\text{Methane}}{CH_4} + 2Be(OH)_3$$

12. Industrial preparation : Methane is formed by passing a mixture of hydrogen sulphide and carbon disulphide vapours through red hot copper tube.

$$CS_2 + 2H_2S + 8Cu \xrightarrow{\text{High temperature}} CH_4 + 4Cu_2S$$

6.6 GENERAL CHARACTERISTICS OF ALKANES

Physical : The physical properties (boiling point, melting point, solubility, density, etc.) of hydrocarbons depend upon the *intermolecular forces of attraction*. Since alkanes are almost non-polar and therefore, their molecules are held only by weak *van der Waals' forces* which mainly depend upon the size (surface area) and the structure of the molecule.

(i) State : Due to weak forces, the alkanes upto four carbon atoms, *i.e.*, methane, ethane, propane and butane are colourless, odourless gases, the next thirteen members (from C_5 to C_{17}) are colourless, odourless liquids. Alkanes from C_{18} onwards are colourless and odourless solids.

(ii) Density : The density of alkanes increases very slowly with the rise of molecular mass until it becomes constant at about 0.8. Thus, all alkanes are lighter than water.

(iii) Solubility : They are generally insoluble in polar solvents such as water but soluble in non-polar solvents like ether, carbon tetrachloride, benzene, etc. The solubility decreases with increase in molecular mass.

However, the liquid hydrocarbons themselves are good non-polar solvents for other non-polar organic compounds.

(iv) Boiling points : The boiling points of straight chain or *n*-alkanes increase regularly with increasing number of carbon atoms. In general, the boiling point difference between two successive members of the series (except for the first few members) is about 20 –30°C. **Among the isomeric alkanes, the normal isomer has a higher boiling point than the branched chain isomer. The greater the branching of the chain, the lower is the boiling point.**

Physical Constants of Some Alkanes

Name	Formula	B.pt. (°C)	M.pt. (°C)	Density (as liquids)
Methane	CH_4	−161.5	−182.5	0.4240
Ethane	CH_3CH_3	−88.6	−172.0	0.5462
Propane	$CH_3CH_2CH_3$	−42.1	−187.7	0.5824
n-Butane	$CH_3(CH_2)_2CH_3$	−0.5	−138.4	0.5788
n-Pentane	$CH_3(CH_2)_3CH_3$	36.1	−129.7	0.6264
n-Hexane	$CH_3(CH_2)_4CH_3$	68.7	−95.3	0.6594

For example, the following boiling point values of various isomers of butane and pentane justify the above statement.

	n-Butane	>	Isobutane		
b.pt.	−0.5°C		−12°C		
	n-Pentane	>	Isopentane	>	Neopentane
b.pt.	36.1°C		28°C		9.5°C

The trend in boiling points can be explained in terms of intermolecular (dipole-dipole) forces of attraction. These forces act along the surface of the molecules and their magnitude increases with increase in surface area. As the molecular size increases in the series, the surface area increases and with that the boiling points also increase. This has been depicted in Fig. 6.2.

The *n*-alkanes have most extended structure and larger surface area in comparison to branched chain isomers having compact structure (as the shape approaches that of a sphere in the branched chain isomers). Thus, intermolecular forces are weaker in branched chain isomers, therefore, they have lower boiling points in comparison to straight chain isomers.

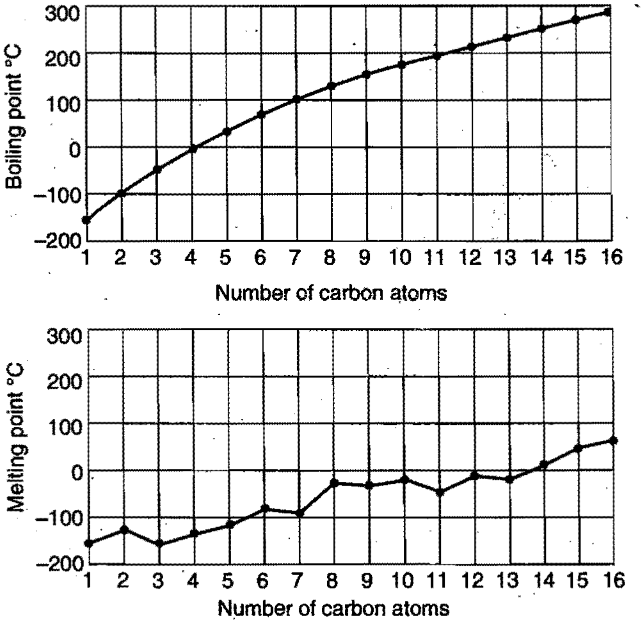
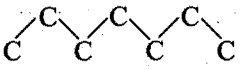
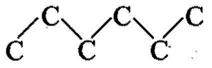


Fig. 6.2

(v) Melting points : The melting points of alkanes do not follow a very smooth gradation with the increase of molecular size. **Alkanes with even number of carbon atoms have higher melting point than the next lower and next higher alkanes having odd number of carbon atoms** (Fig. 6.2).

It is explained by the fact that alkanes with an odd number of carbon atoms have their end-carbon atoms on the same side of the molecule and the even-numbered carbon atom alkanes have their end-carbon atoms on the opposite sides of the molecules. Thus, alkanes with even number of carbon atoms pack closely in such a manner as to permit greater intermolecular attraction and therefore have slightly higher melting point.


Odd number of carbon atoms

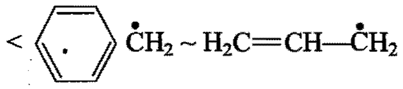

Even number of carbon atoms

Chemical : Alkanes are quite inert towards common reagents such as acids, alkalies, oxidising and reducing agents, etc., at ordinary conditions because of their saturated character. The electronegativity difference between carbon (2.6) and hydrogen (2.1) is small and thus, C—H bond is almost non-polar. The C—C bond is completely non-polar. Therefore, the polar reagents (electrophiles and nucleophiles) do not find reaction sites (electron-rich or electron-deficient centres) on alkane molecules. The C—C and C—H bonds are strong sigma bonds and cannot break under ordinary conditions. At high temperature, energies of collisions are sufficient for breaking C—H and C—C bonds resulting the formation of free radicals.

$$R\mathrm{CH_2{-}H} \longrightarrow R\dot{\mathrm{C}}\mathrm{H_2} + \dot{\mathrm{H}}$$

and stability of free radicals is in the order:

$$\mathrm{H_2C{=}\dot{C}H < \dot{C}H_3 < CH_3\dot{C}H_2 < (CH_3)_2\dot{C}H < (CH_3)_3\dot{C}}$$



$$< \mathrm{C_6H_5\dot{C}H_2 \sim H_2C{=}CH{-}\dot{C}H_2}$$

However, alkanes do show some reactions under special conditions. Some of the important reactions of alkanes are described below:

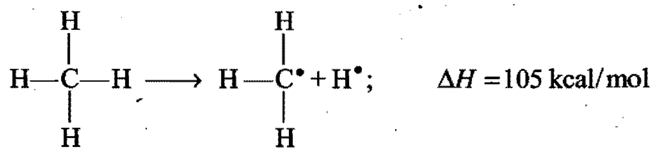
1. Substitution reactions : These are most characteristic reactions of the alkanes.

(a) Halogenation : When the alkanes are treated with halogens (particularly chlorine or bromine) in presence of light (sunlight or UV) or at elevated temperatures 250–400°C, the hydrogen atoms of alkanes are successively replaced by halogen atoms. This process is known as **halogenation.** The extent of halogenation depends on the amount of halogen used. For example, methane undergoes chlorination in excess of chlorine in presence of UV light giving the mixture of methyl chloride, methylene chloride, chloroform and carbon tetrachloride.

$$\underset{\text{Methane}}{\mathrm{CH_4}} \xrightarrow[h\nu]{\mathrm{Cl_2}} \underset{\substack{\text{Monochloromethane}\\\text{(Methyl chloride)}}}{\mathrm{CH_3Cl}} \xrightarrow[h\nu]{\mathrm{Cl_2}} \underset{\substack{\text{Dichloromethane}\\\text{(Methylene chloride)}}}{\mathrm{CH_2Cl_2}}$$

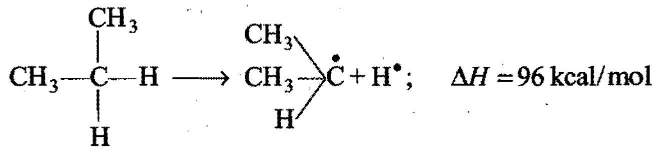
$$\xrightarrow[h\nu]{\mathrm{Cl_2}} \underset{\substack{\text{Trichloromethane}\\\text{(Chloroform)}}}{\mathrm{CHCl_3}} \xrightarrow[h\nu]{\mathrm{Cl_2}} \underset{\substack{\text{Tetrachloromethane}\\\text{(Carbon tetrachloride)}}}{\mathrm{CCl_4}}$$

For chlorination reactivity of 1°, 2° and 3° hydrogen is in the ratio 1° : 2° : 3° : : 1 : 3.8 : 5

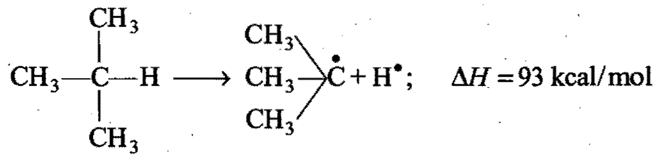


$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H \longrightarrow H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C^{\bullet}}} + H^{\bullet}}; \quad \Delta H = 105\ \text{kcal/mol}$$

$$\mathrm{CH_3{-}CH_3 \longrightarrow CH_3{-}\dot{C}H_2 + H^{\bullet}}; \quad \Delta H = 100\ \text{kcal/mol}$$



$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}{-}H \longrightarrow (CH_3)_2(H)\dot{C} + H^{\bullet}}; \quad \Delta H = 96\ \text{kcal/mol}$$

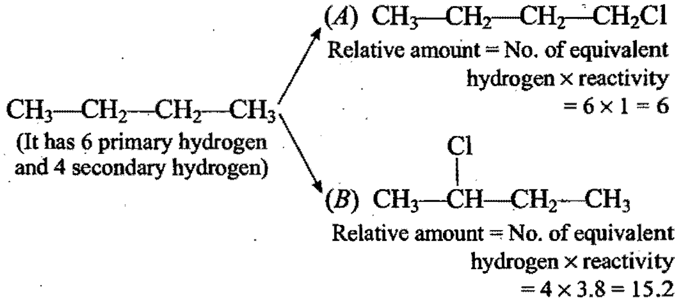


$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}H \longrightarrow (CH_3)_3\dot{C} + H^{\bullet}}; \quad \Delta H = 93\ \text{kcal/mol}$$

Bond energy for extraction of hydrogen lies in following sequence.

$\mathrm{CH_3^{\circ}} > 1° > 2° > 3°$, hence, the reactivity order will be $\mathrm{CH_4} < 1° < 2° < 3°$.

On the basis of relative reactivity of different types of hydrogen, the percentage of the products in mixture can be calculated, *e.g.*,



CH₃—CH₂—CH₂—CH₃ (It has 6 primary hydrogen and 4 secondary hydrogen)

(*A*) $\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2Cl}$
Relative amount = No. of equivalent hydrogen × reactivity = 6 × 1 = 6

(*B*) $\mathrm{CH_3{-}\overset{\displaystyle Cl}{CH}{-}CH_2{-}CH_3}$
Relative amount = No. of equivalent hydrogen × reactivity = 4 × 3.8 = 15.2

$$\text{Total amount} = 6 + 15.2 = 21.2$$

$$\%\ \text{of}\ A = \frac{6}{21.2} \times 100 = 28.3\ ;$$

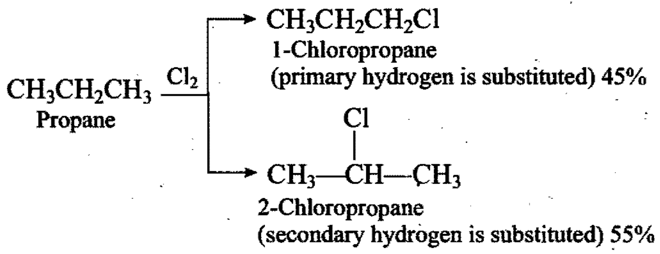
$$\%\ \text{of}\ B = \frac{15.2}{21.2} \times 100 = 71.7$$

Note: The relative reactivity of 1°, 2°, 3° hydrogen to bromination is 1 : 82 : 1600.

Ethane and higher alkanes react with chlorine in a similar way and all possible substitution products are obtained. However, propane and higher members contain hydrogen atoms of two or three types, *i.e.*, primary, secondary or tertiary, which differ in reactivity. The order of reactivity is:

Tert. hydrogen > Sec. hydrogen > Primary hydrogen

Propane gives two monochloro substituted products on chlorination.



$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow{Cl_2} \underset{\substack{\text{1-Chloropropane} \\ \text{(primary hydrogen is substituted) 45\%}}}{CH_3CH_2CH_2Cl} + \underset{\substack{\text{2-Chloropropane} \\ \text{(secondary hydrogen is substituted) 55\%}}}{CH_3—\overset{\overset{\displaystyle Cl}{|}}{C}H—CH_3}$$

The bromination proceeds in almost identical manner but the reaction is less vigorous than chlorination. Reaction with fluorine is very violent. Iodine does substitute as the reaction is very slow and reversible but iodination can occur in presence of an oxidising agent such as iodic acid or nitric acid, etc., which decomposes HI into iodine.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI \quad \text{(reducing agent)}$$

$$5HI + HIO_3 \xrightarrow{\text{Heat}} 3I_2 + 3H_2O$$

or $$2HI + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + I_2$$

Halogenation of alkanes proceeds through free radical mechanism (See Chapter 5).

Note : (i) Fluorination can be achieved without violence when alkane is treated with fluorine diluted with an inert gas or by the action of inorganic fluorides such as AsF_3, SbF_3, AgF, HgF_2 or Hg_2F_2 etc. on bromo or iodo derivatives.

$$2C_2H_5I + HgF_2 \longrightarrow 2C_2H_5F + HgI_2$$

$$2CH_3CH_2Cl + Hg_2F_2 \longrightarrow \underset{\text{Fluoroethane}}{2CH_3CH_2F} + Hg_2Cl_2$$

This reaction is called **Swarts reaction.**

(ii) Iodo compounds are obtained by treating chloro or bromo derivatives with sodium iodide (concentrated solution in acetone). It is a halide exchange reaction. **(Finkelstein reaction).**

$$C_2H_5Br + \underset{\text{(Excess)}}{NaI} \xrightarrow{\text{Acetone}} C_2H_5I + NaBr$$

Points to remember : (i) Relative reactivities of halogens on alkanes follow the following order:

$$F_2 > Cl_2 > Br_2 > I_2$$

The reactivity decreases with decrease in the electronegativity of the halogens.

(ii) The replacement of hydrogen atom by halogen follows the following order.

Tertiary hydrogen > Secondary hydrogen > Primary hydrogen > Methane H

(iii) Halogenation takes place in presence of sunlight, UV light or in dark at high temperatures (250–400°C). The reaction may be initiated by peroxide (dibenzoyl peroxide).

(iv) Laboratory chlorination of alkanes is often done with SO_2Cl_2 (Sulphuryl chloride), instead of Cl_2 and an organic peroxide, $ROOR$ is used as an initiator.

(v) Tetra-ethyl lead, $Pb(C_2H_5)_4$, initiates the chlorination of methane in the dark at 150°C.

(vi) Small amount of oxygen slow down the reaction for a period of time, which depends upon the amount of oxygen. Oxygen is believed to react with methyl free radical to form less reactive free radical.

$$\dot{C}H_3 + O_2 \longrightarrow CH_3—O—\dot{O}$$

Here, oxygen acts as inhibitor.

(b) Nitration : Nitration is a substitution reaction in which a hydrogen atom of alkane is replaced by nitro (—NO_2) group.

$$\underset{\text{Alkane}}{R—H} + \underset{\text{(Fuming)}}{HONO_2} \xrightarrow[\text{temp.}]{\text{High}} \underset{\text{Nitroalkane}}{R—NO_2} + H_2O$$

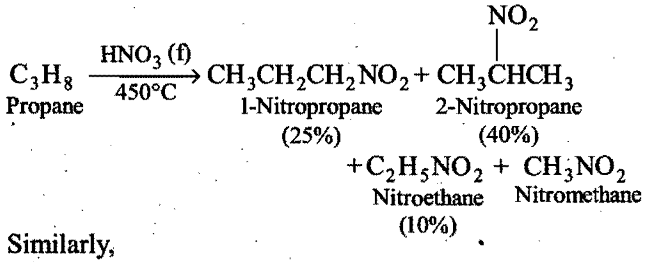
Lower members do not react with concentrated nitric acid at ordinary temperatures but long chain members on heating with fuming nitric acid yield nitroalkanes.

$$\underset{n\text{-Hexane}}{C_6H_{13}—H} + \underset{\text{(Fuming)}}{HONO_2} \xrightarrow{400°C} \underset{\text{Nitrohexane}}{C_6H_{13}NO_2} + H_2O$$

However, when a mixture of vapours of an alkane and nitric acid is heated at 400 – 500°C, nitroalkane is formed readily. This is known as **vapour phase nitration.** By this process lower as well as higher alkanes can be converted into nitroalkanes.

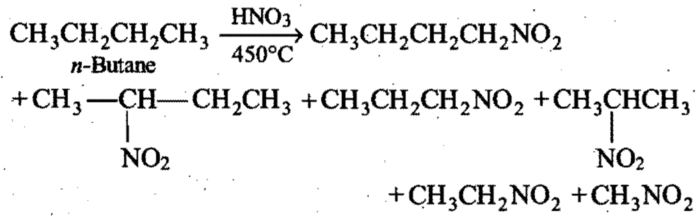
$$\underbrace{CH_3—H + HONO_2}_{\text{Vapour state}} \xrightarrow{450°C} \underset{\text{Nitromethane}}{CH_3—NO_2} + H_2O$$

In alkanes having two or more carbon atoms, there is always a possibility that the C—C bonds may break at high temperatures and a mixture of nitro alkanes is formed. For example, in the nitration of propane, the following products are obtained:



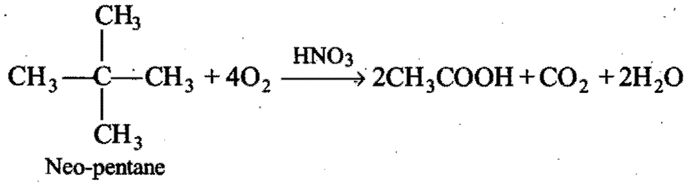
$$\underset{\text{Propane}}{C_3H_8} \xrightarrow[450°C]{HNO_3\,(f)} \underset{\substack{\text{1-Nitropropane} \\ (25\%)}}{CH_3CH_2CH_2NO_2} + \underset{\substack{\text{2-Nitropropane} \\ (40\%)}}{CH_3\overset{\overset{\displaystyle NO_2}{|}}{C}HCH_3} + \underset{\substack{\text{Nitroethane} \\ (10\%)}}{C_2H_5NO_2} + \underset{\text{Nitromethane}}{CH_3NO_2}$$

Similarly,



$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[450°C]{HNO_3} CH_3CH_2CH_2CH_2NO_2 + CH_3—\underset{\underset{\displaystyle NO_2}{|}}{C}H—CH_2CH_3 + CH_3CH_2CH_2NO_2 + CH_3\underset{\underset{\displaystyle NO_2}{|}}{C}HCH_3 + CH_3CH_2NO_2 + CH_3NO_2$$

Higher alkanes yield even more complex mixtures. Alkanes containing neo-skeleton are easily oxidised with HNO_3 to form carboxylic acids and no nitro compounds.



$$\underset{\text{Neo-pentane}}{CH_3—\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}—CH_3} + 4O_2 \xrightarrow{HNO_3} 2CH_3COOH + CO_2 + 2H_2O$$

Nitration like halogenation also follows **free radical mechanism.**

$$HONO_2 \xrightarrow{150\text{–}400°C} \dot{H}O + \dot{N}O_2$$

$$\underset{\text{Propane}}{C_3H_7—H} + H\dot{O} \longrightarrow C_3\dot{H}_7 + H_2O$$

$$C_3\dot{H}_7 + \dot{N}O_2 \longrightarrow C_3H_7NO_2$$

(c) Sulphonation : The replacement of hydrogen atom by sulphonic acid group ($—SO_3H$) is known as **sulphonation.** Lower alkanes do not undergo sulphonation but higher members (from hexane onwards) are sulphonated slowly when treated with fuming sulphuric acid (oleum) at about 400°C.

$$\underset{\text{Alkane}}{R—H} + HOSO_3H \xrightarrow[\text{Prolonged heating}]{SO_3} \underset{\text{Alkane sulphonic acid}}{R—SO_3H} + H_2O$$

$$\underset{\text{Hexane}}{C_6H_{13}—H} + HOSO_3H \xrightarrow{SO_3} \underset{\text{Hexane sulphonic acid}}{C_6H_{13}SO_3H} + H_2O$$

However, lower members such as propane, butane, pentane, etc., react with SO_3 in vapour phase to form sulphonic acids.

Ease of replacement of H atoms is:

$$3° > 2° > 1°$$

Sulphonation also follows free radical mechanism.

$$HOSO_3H \xrightarrow[\text{Homolytic fission}]{400°C} \dot{H}O + \dot{S}O_3H$$

$$C_6H_{13}—H + \dot{O}H \longrightarrow C_6\dot{H}_{13} + H_2O$$

$$C_6\dot{H}_{13} + \dot{S}O_3H \longrightarrow C_6H_{13}SO_3H$$

2. Oxidation : Oxidation of alkanes gives different products under different conditions.

(a) Combustion or complete oxidation : Alkanes readily burn with non-luminous flame in excess of air or oxygen to form carbon dioxide and water. The combustion of alkanes is an exothermic reaction, *i.e.*, large quantity of heat is evolved and heat of combustion increases with molecular weight. It forms the basis of the use of alkanes as fuel in the internal combustion engines. The cooking gas, which is often called **LPG** (Liquefied Petroleum Gas) is a mixture of propane and butane.

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O + Q$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) + 213 \text{ kcal/mol}$$

$$2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O + 746 \text{ kcal/mol}$$

(b) Incomplete combustion or oxidation :

(i) When alkane is burnt in insufficient supply of oxygen, carbon monoxide or carbon black may be formed.

$$2CH_4 + \underset{\text{(Limited)}}{3O_2} \xrightarrow{\text{Burn}} 2CO + 4H_2O$$

$$CH_4 + \underset{\text{(Limited)}}{O_2} \xrightarrow{\text{Burn}} \underset{\text{Carbon black}}{C} + 2H_2O$$

Carbon black is used for making printing ink, black paints, polishes and as a filler in rubber vulcanisation.

(ii) Reaction with steam : Methane reacts with steam over nickel suspended on alumina at 1073 K, hydrogen gas is formed with carbon monoxide.

$$CH_4 + \underset{\text{Steam}}{H_2O} \xrightarrow[1073K]{Ni/Al_2O_3} CO + 3H_2$$

(c) Catalytic oxidation : Lower alkanes undergo restricted oxidation in presence of metallic catalysts such as copper at high temperature and pressure to form alcohols, aldehydes, ketones and acids.

(i) When methane and oxygen mixed in the ratio of 9 : 1 are compressed to 100 atmospheres and passed through copper tube at 200°C, methyl alcohol is formed,

$$\underset{9}{2CH_4} + \underset{:\ 1}{[O]_2} \xrightarrow[100 \text{ atm}/200°C]{\text{Cu-tube}} 2CH_3OH$$

(This is the industrial method for the manufacture of methyl alcohol.)

(ii) When a mixture of methane and oxygen is passed over heated molybdenum oxide under pressure or in air at 543 K, it is oxidised to formaldehyde.

$$\underset{\text{Methane}}{CH_4} + O_2 \xrightarrow[543 \text{ K, } 100 \text{ atm.}]{MoO} \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

Higher alkanes are oxidised to carboxylic acids in presence of manganese stearate or silver oxide.

$$CH_3(CH_2)_nCH_3 \xrightarrow[100\text{–}160°C]{O_2} CH_3(CH_2)_nCOOH$$

$$2R—CH_3 + 3[O]_2 \xrightarrow[\text{Heat}]{Ag_2O} 2R—COOH + 2H_2O$$

The controlled partial oxidation of methane at 1773 K yields acetylene.

$$6CH_4 + 2O_2 \xrightarrow{1773 \text{ K}} \underset{\text{Ethyne}}{2HC{\equiv}CH} + 2CO_2 + 10H_2\uparrow$$

(d) Chemical oxidation : Alkanes are usually not affected by oxidising agents like $KMnO_4$ or $K_2Cr_2O_7$. However, alkanes having tertiary hydrogen are oxidised by these oxidising agents to the corresponding alcohols.

$$\underset{\text{Isobutane}}{(CH_3)_3CH} + [O] \xrightarrow[\text{(Alk.)}]{KMnO_4} \underset{\text{Tertiary butyl alcohol}}{(CH_3)_3COH}$$

3. Thermal decomposition or Fragmentation (pyrolysis or cracking) : The decomposition of a compound by heat is called pyrolysis (Greek: *pyro* = fire; *lysis* = loosening). **When pyrolysis occurs in alkanes, the process is termed cracking.** The alkanes, on heating under high temperature in absence of air, are broken down into a mixture of lower alkanes, alkenes and hydrogen. During cracking of alkanes, either rupture of carbon-hydrogen bonds or rupture of carbon-carbon bonds (Occurs by a free radical mechanism) takes place. The rupture of C—H bonds is catalysed by the oxides of chromium, vanadium, molybdenum, etc., and the rupture of C—C bonds is catalysed by silica, alumina, zinc oxide, etc. The following are some of the examples of pyrolysis.

$$\underset{\text{Methane}}{CH_4} \xrightarrow{1000°C} C + 2H_2$$

$$\underset{\text{Ethane}}{C_2H_6} \xrightarrow[Cr_2O_3 + Al_2O_3]{500°C} \underset{\text{Ethylene}}{H_2C{=}CH_2} + H_2$$

$$\underset{\text{Propane}}{C_3H_8} \xrightarrow{\Delta} CH_3CH{=}CH_2 + H_2 \text{ (C—H fission)}$$

$$\underset{\text{Propane}}{C_3H_8} \xrightarrow{\Delta} H_2C{=}CH_2 + CH_4 \text{ (C—C fission)}$$

$$\underset{\text{Hexane}}{C_6H_{14}} \longrightarrow \underset{\text{Hexene}}{C_6H_{12}} + H_2$$

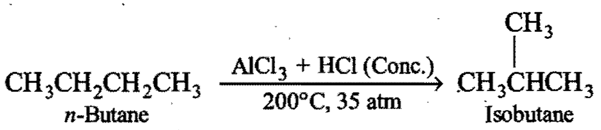
$$\underset{\text{Hexane}}{C_6H_{14}} \longrightarrow \underset{\text{Butene}}{C_4H_8} + \underset{\text{Ethane}}{C_2H_6}$$

$$\underset{\text{Hexane}}{C_6H_{14}} \longrightarrow \underset{\text{Propene}}{C_3H_6} + \underset{\text{Ethene}}{C_2H_4} + \underset{\text{Methane}}{CH_4}$$

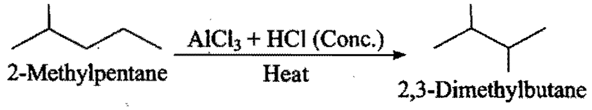
$$\underset{\text{Octane}}{C_8H_{18}} \longrightarrow \begin{cases} C_4H_{10} + C_4H_8 \\ C_6H_{14} + C_2H_4 \\ C_4H_{10} + CH_4 + C_2H_4 + C \\ C_8H_{16} + H_2 \\ C_6H_{12} + C_2H_6 \\ C_7H_{14} + CH_4 \end{cases}$$

The pyrolysis or cracking of alkanes involves breaking of C—C and C—H bonds and occurs by a free radical mechanism. It is of great importance to the petroleum industry.

4. Isomerisation : The process of conversion of one isomer into another isomer is called isomerisation. Alkanes when heated in presence of anhydrous aluminium chloride and concentrated hydrochloric acid or anhydrous aluminium bromide and hydrobromic acid at about 200°C under a pressure of 35 atmospheres are converted into one or more other isomers.



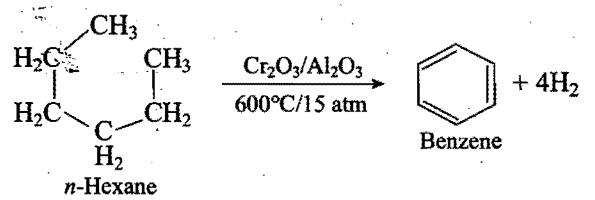
$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[200°C,\ 35\ atm]{AlCl_3 + HCl\ (Conc.)} \underset{\text{Isobutane}}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_3}$$

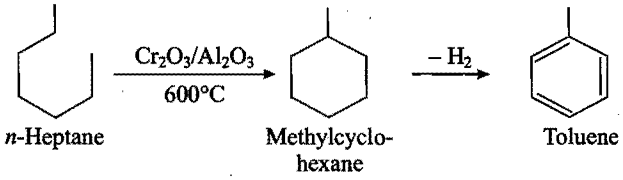


This isomerisation involves 1,2 shift of hydride or methyl group.

The branched chain alkanes have lower b.pts. than straight chain, hence isomerisation is important in petroleum industry.

5. Aromatisation : The conversion of aliphatic compounds into aromatic compounds is known as aromatisation. Alkanes having 6 to 10 carbon atoms are converted into benzene or its homologous at high temperatures and in presence of a catalyst.

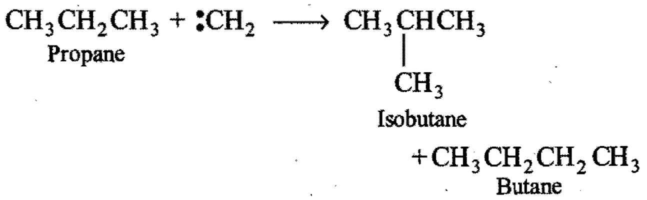




6. Insertion reaction : Diazomethane or ketene acts as insertion reagent because on photolysis they easily give carbene intermediate. So, due to introduction of methylene (—CH_2—) group, the lower alkanes are converted into higher homologues. This process is known as methylation.

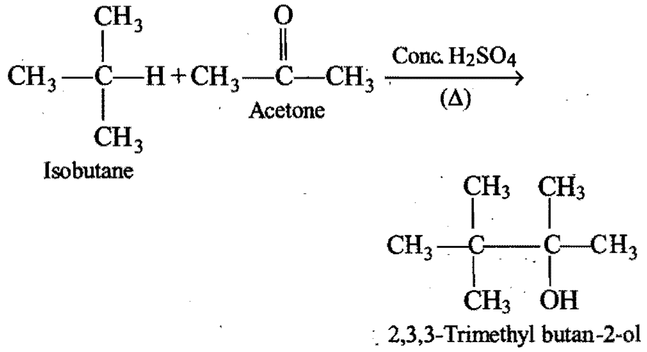
$$\underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow{h\nu} {:}CH_2 + N_2$$

$$\underset{\text{Ketene}}{CH_2{=}C{=}O} \xrightarrow{h\nu} {:}CH_2 + CO$$



$$\underset{\text{Propane}}{CH_3CH_2CH_3} + {:}CH_2 \longrightarrow \underset{\text{Isobutane}}{CH_3\underset{\underset{CH_3}{|}}{C}HCH_3} + \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$

7. Reaction with ketones: When isoalkane is heated with a ketone in the presence of conc. H_2SO_4, we get a tertiary alcohol (3°).



$$\underset{\text{Isobutane}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-H} + \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[(\Delta)]{Conc.\ H_2SO_4} \underset{\text{2,3,3-Trimethyl butan-2-ol}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3}$$

Uses of alkanes

(i) Methane is used in the manufacture of compounds like CH_3OH, HCHO, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 etc.

(ii) Methane is used in the preparation of carbon black which is used for making printing ink, black paints and automobile tyres.

(iii) Methane in the form of natural gas is used for running the cars, buses, etc. **LPG** (mixture of butane and isobutane) is used as a fuel.

(iv) Ethane is used for making hexachloroethane which is an artificial camphor.

(v) Higher alkanes in the form of gasoline, kerosene oil, diesel, lubricating oils and paraffin wax are widely used.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. A compound with no tertiary hydrogen is:
   (a) $(CH_3)_3C—CH(CH_3)_2$
   (b) $(CH_3)_3C—CH_2CH_3$
   (c) $(CH_3)_2CH—CH_2CH_2CH_3$
   (d) none of the above
   [Ans. (b)]
2. Which of the following gives methane on hydrolysis?
   (a) Al_2O_3 (b) CaC_2
   (c) Fe_3O_4 (d) Al_4C_3
   [Ans. (d)]
3. Which of the following has highest octane number?
   (a) *n*-Hexane (b) *n*-Heptane
   (c) *n*-Pentane (d) 2,2,4-Trimethylpentane
   [Ans. (d)]
4. Relative reactivity of halogens on alkanes follow the order:
   (a) $F_2 > Cl_2 > Br_2 > I_2$ (b) $Cl_2 > Br_2 > I_2 > F_2$
   (c) $F_2 > I_2 > Br_2 > Cl_2$ (d) $I_2 > Br_2 > Cl_2 > F_2$
   [Ans. (a)]
5. The reaction,
   $$C_2H_5Br \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} [X] \xrightarrow{CH_3Br} [Y]\text{; is called:}$$
   (a) Wurtz synthesis
   (b) Wolff-Kishner reduction
   (c) Corey-House synthesis
   (d) Kolbe's synthesis
   [Ans. (c)]
6. What are $[X]$ and $[Y]$ in the following reaction?
   $$(CH_3)_2CHBr \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} [X] \xrightarrow{CH_3CH_2Br} [Y]$$
   (a) $[(CH_3)_2CH]_2LiCu$ and $(CH_3)_2CHCH_3$
   (b) $[(CH_3)_2CH]_2LiCu$ and $(CH_3)_2CHCH_2CH_3$
   (c) $[(CH_3)_2CH]_2LiCu$ and $CH_3CH_2CH_3$
   (d) $[(CH_3)_2CH]LiBr$ and $(CH_3)_2CHCH_2CH_3$
   [Ans. (b)]
7. Propane is obtained from propene by which of the following method?
   (a) Wurtz reaction (b) Dehydration
   (c) Frankland reaction (d) Catalytic hydrogenation
   [Ans. (d)]
8. When these compounds are arranged in order of increasing boiling point,
   $\underset{\text{(I)}}{CH_3CH_2CH_2CH_2CH_3}$, $\underset{\text{(II)}}{CH_3CH_2CH(CH_3)CH_3}$,
   $\underset{\text{(III)}}{CH_3C(CH_3)_2CH_3}$
   what is the correct order?
   (a) I < II < III (b) II < I < III
   (c) II < III < I (d) III < II < I
   [Ans. (d)]

Ascent and descent of series : When a higher homologue is prepared from a lower homologue, it is called **ascent of series.** Similarly the preparation of lower homologue is called **descent of series.**

Ascent of alkane series : Use of Wurtz reaction is made.

(i) Methane to ethane :

$$\underset{\text{Methane}}{CH_4} \xrightarrow[UV]{Cl_2} CH_3Cl \xrightarrow[\text{Wurtz reaction}]{\text{Heat with Na in ether}} \underset{\text{Ethane}}{CH_3—CH_3}$$

(ii) Butane from ethane :

$$\underset{\substack{\text{Ethane}\\ \text{(excess)}}}{C_2H_6} \xrightarrow[UV]{Cl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} \xrightarrow[\text{Wurtz reaction}]{\text{Heat with Na in ether}} \underset{\text{Butane}}{C_2H_5—C_2H_5}$$

Descent of alkane series : Use of decarboxylation reaction is made. It is a multistep conversion.

Ethane to methane :

$$\underset{\substack{\text{Ethane}\\ \text{(excess)}}}{C_2H_6} \xrightarrow[UV]{Cl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} \xrightarrow{KOH\,(aq.)} \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} \underset{\text{Sodium acetate}}{CH_3COONa} \xrightarrow[\text{Heat}]{NaOH/CaO} \underset{\text{Methane}}{CH_4}$$

$$\underset{\text{alkane}}{\text{Higher}} \xrightarrow[UV]{Cl_2} \underset{\text{halide}}{\text{Alkyl}} \xrightarrow{KOH\,(aq.)} \text{Alcohol} \xrightarrow{[O]} \text{Aldehyde} \xrightarrow{[O]} \text{Acid} \xrightarrow{NaOH} \underset{\text{the acid}}{\text{Sodium salt of}} \xrightarrow[\text{Heat}]{NaOH/CaO} \text{Lower alkane}$$

SOME SOLVED PROBLEMS

Problem 1. *Why are alkanes relatively unreactive?*

Solution : Alkanes are inert substances at room temperature as they are not affected by acids, alkalies and oxidising agents. This is due to the fact that the C—C and C—H bonds in alkanes are non-polar, *i.e.*, they have no reaction sites where the polar reagents can attack.

Problem 2. *Why do the C—C bonds rather than the C—H bonds break during pyrolysis of alkanes?*

Solution : Bond energy of C—C bond is lower than the bond energy of C—H bond. The C—C bond energy is 83.0 kcal/mol while C—H bond energy is 98.8 kcal/mol. Thus, C—C bonds break more easily than C—H bonds.

Problem 3. *Methane does not react with chlorine in dark. Explain by giving reason.*

Solution : Chlorination of methane is a free radical substitution. To convert Cl_2 molecules into chlorine-free radicals, energy is required which is not available in dark. Thus, methane does not react with Cl_2 in dark due to absence of free radicals.

Problem 4. *The fire of burning liquid paraffin cannot be extinguished by throwing water over this. Explain by giving reason.*

Solution : The liquid paraffin is lighter than water. It flows over water surface and continues burning.

Problem 5. *How will you obtain? Give equations only :*

(*a*) *methane from acetone.*

(*b*) *ethane from acetic acid.*

(*c*) *methane and ethane from sodium acetate.*

Solution :

(a) (i) $$\underset{\text{Acetone}}{CH_3COCH_3} + 4[O] \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + CO_2 + H_2O$$

(ii) $$CH_3COOH + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

(iii) $$CH_3COONa + NaOH \xrightarrow[\text{Heat}]{\text{CaO}} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

(b) (i) $$\underset{\text{Acetic acid}}{CH_3COOH} + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

(ii) $$\begin{array}{l} CH_3 \vdots COO \vdots Na \\ + \\ CH_3 \vdots COO \vdots Na \end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} \overset{\text{Anode}}{+ 2CO_2},$$

$$\overset{\text{Cathode}}{2Na + 2H_2O} \longrightarrow 2NaOH + H_2$$

(c) Apply a (iii) and b (ii) equations for obtaining methane and ethane respectively.

Problem 6. *Why is the Wurtz synthesis not a good method for preparing propane?*

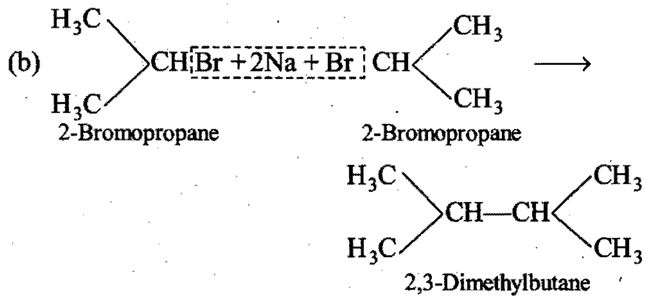
Solution : Two different alkyl halides (methyl chloride and ethyl chloride) are to be used to prepare propane. Thus, three reactions may occur giving a mixture containing ethane, butane and propane.

Problem 7. *Write the structural formulae and IUPAC names of the different alkanes formed when a mixture of 1-bromopropane and 2-bromopropane is reacted with sodium in presence of ether. What is the name of the reaction?*

Solution : (a) $$\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2} \boxed{Br + 2Na + Br} \underset{\text{1-Bromopropane}}{CH_2CH_2CH_3}$$

$$\longrightarrow \underset{\text{Hexane}}{CH_3(CH_2)_4CH_3}$$

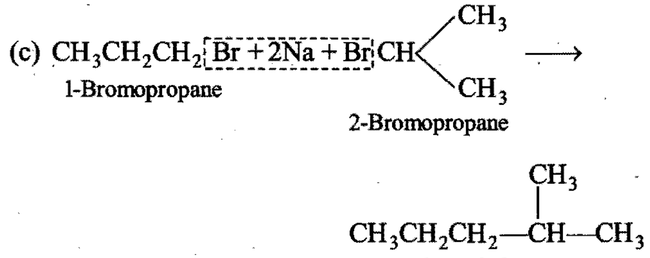
(b)



2-Bromopropane 2-Bromopropane

2,3-Dimethylbutane

(c)



1-Bromopropane 2-Bromopropane

2-Methylpentane

$$CH_3CH_2CH_2 \boxed{Br + 2Na + Br} CH(CH_3)_2 \longrightarrow CH_3CH_2CH_2-\overset{\overset{\large CH_3}{|}}{C}H-CH_3$$

The name of the reaction is Wurtz reaction.

Problem 8. *An alkane with molecular mass 72 formed only one substitution product. Suggest a structure for the alkane.* **[BCECE 2006]**

Solution : Let the molecular formula of the alkane be C_nH_{2n+2}.

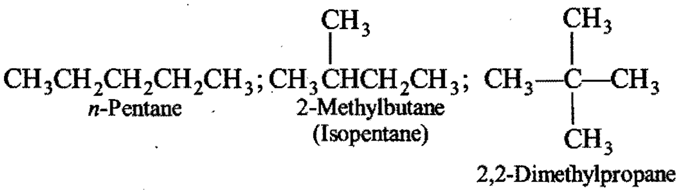
$$\begin{aligned} \text{Molecular mass of the alkane} &= nC + (2n+2)H \\ &= n \times 12 + (2n+2) \times 1 \\ &= 14n + 2 \end{aligned}$$

Thus, $14n + 2 = 72$

or $14n = 72 - 2 = 70$

So, $n = \frac{70}{14} = 5$

Thus, the molecular formula of the alkane is C_5H_{12}. It can have three isomers.



$$\underset{n\text{-Pentane}}{CH_3CH_2CH_2CH_2CH_3};\ \underset{\substack{\text{2-Methylbutane}\\\text{(Isopentane)}}}{CH_3\overset{\overset{\large CH_3}{|}}{C}HCH_2CH_3};\ \underset{\substack{\text{2,2-Dimethylpropane}\\\text{(Neopentane)}}}{CH_3-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-CH_3}$$

2,2-Dimethylpropane (Neopentane)

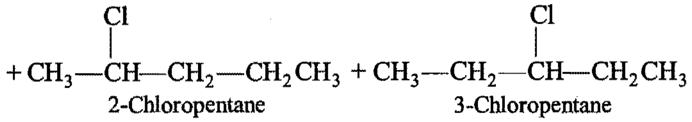
Since, the alkane forms only one mono substituted product, it must have only one type of hydrogen atoms. Therefore, the alkane is 2,2-dimethylpropane.

Problem 9. *Give reason why chlorination of ethane to ethyl chloride is more practicable than the chlorination of n-pentane to 1-chloropentane.*

Solution : Ethane forms only one mono chloroderivative (ethyl chloride) on chlorination while *n*-pentane forms three isomers on mono-chlorination and the yield of 1-chloropentane is low as it is formed by replacement of primary hydrogen while other two isomers are formed by replacement of secondary hydrogen atoms respectively.

$$\underset{\text{Ethane}}{CH_3—CH_3} \xrightarrow{Cl_2} \underset{\text{Ethyl chloride}}{CH_3—CH_2Cl}$$

$$\underset{n\text{-Pentane}}{CH_3CH_2CH_2CH_2CH_3} \xrightarrow{Cl_2} \underset{\text{1-Chloropentane}}{CH_3CH_2CH_2CH_2CH_2Cl}$$



$$+ \underset{\text{2-Chloropentane}}{CH_3—\overset{Cl}{\overset{|}{C}}H—CH_2—CH_2CH_3} + \underset{\text{3-Chloropentane}}{CH_3—CH_2—\overset{Cl}{\overset{|}{C}}H—CH_2CH_3}$$

Problem 10. *Prepare butane from chloroethane using the Corey-House synthesis.*

Solution : Chloroethane is first converted into lithium diethyl cuprate which then reacts with chloroethane to form butane.

(i) $CH_3CH_2Cl + 2Li \xrightarrow{\text{Ether}} CH_3CH_2Li + LiCl$

(ii) $2CH_3CH_2Li + CuI \longrightarrow \underset{\text{Lithium diethyl cuprate}}{Li(CH_3CH_2)_2Cu} + LiI$

(iii) $Li(CH_3CH_2)_2Cu + CH_3CH_2Cl \longrightarrow \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + CH_3CH_2Cu + LiCl$

6.7 PETROLEUM

The term petroleum (Latin: *Petra* = rock; *Oleum* = oil) is applied to the dark-coloured oily liquid with offensive odour found at various depths in many regions below the surface of the earth. It is also called rock oil, mineral oil or crude oil. It is generally found under the rocky strata of the earth's crust and often floats over salted water. It is covered by an atmosphere of a gaseous mixture known as **natural gas.**

The chief oil producing centres in India are: Rudrasagar and Lakwa in Assam; Ankleshwar, Cambay and Kalol in Gujarat and Mumbai high (offshore area).

Composition : The composition of crude petroleum varies with places of occurrence but essentially it is a mixture of hydrocarbons. It contains mainly the following:

(i) Alkanes : The percentage of alkanes can vary from 30 to 70. Alkanes containing upto 40 carbon atoms are present. Alkanes are mainly straight chain but few are branched chain isomers.

(ii) Cycloalkanes : The percentage of cycloalkanes varies from 16 to 64. The cycloalkanes mainly present in petroleum are: Methyl cyclopentane, cyclohexane and methyl cyclohexane. The oil rich in cycloalkanes is known as **asphaltic oil.**

(iii) Aromatic hydrocarbons : The percentage of aromatic hydrocarbons varies from 8 to 15. The chief aromatic compounds present in petroleum are: Benzene, toluene, xylenes and naphthalene.

(iv) Sulphur, nitrogen and oxygen compounds : Besides hydrocarbons, there are also present certain organic compounds containing oxygen, nitrogen and sulphur. The sulphur compounds are present to the extent of 6% and these include mercaptans (*R*—SH) and sulphides (*R*—S—*R*). The disagreeable smell of petroleum is due to these sulphur compounds. Their removal from petroleum products is very necessary, otherwise these will get oxidised to sulphurous and sulphuric acids during combustion in internal combustion engine and will cause corrosion of metal.

The chief nitrogen compounds are alkyl pyridines, quinolines and pyrroles. The oxygen compounds present in petroleum include alcohols, phenols and resins. Compounds like chlorophyll, haemin (green and red colouring matter of plants and animals, respectively) are also present in petroleum.

(v) Natural gas : The gas found above the petroleum deposits is referred to as natural gas. It is a mixture of low molecular weight alkanes, namely methane (80%), ethane (13%), propane (3%), butane (1%), the vapours of low boiling pentanes and hexanes (0.5%) and nitrogen (1.3%). The natural gas in liquid form under pressure mainly consisting propane, and butanes is used as cooking gas (**LPG** = liquefied petroleum gas). It is highly inflammable. The gas burns with blue flame producing lot of heat. The gas containing methane, nitrogen and ethane is sold as bottled gas in compressed state in steel cylinders.

Theories of origin of petroleum : Many theories have been proposed to explain the origin of petroleum below the crust of the earth but none is satisfactory in itself. Any theory proposed must explain the following characteristics associated with petroleum:

(i) its association with brine (sodium chloride solution),
(ii) the presence of nitrogen and sulphur compounds in it,
(iii) the presence of chlorophyll and haemin in it,
(iv) its optically active nature.

Mining of petroleum : Petroleum deposits occur at varying depths at different places ranging from 500 to 15000 feet. This is brought to the surface by artificial drilling. The oil well is drilled till the oil bearing region is reached and pipes are fitted. Sometimes, the oil rushes out through these pipes due to the pressure exerted by the natural gas. As the gas pressure subsides, air pressure is applied to raise the oil from the well.

The crude oil thus, obtained is either stored in big steel tanks or sent to refineries by pipelines for processing.

Petroleum refining : The petroleum obtained by mining contains impurities such as sand, brine or sea water, sulphur compounds and resins. It is technically called as **crude oil.** The crude oil is mechanically freed from sand and brine and then subjected to fractional distillation in a refinery because crude oil as such is not suitable for most technical purposes.

The process of dividing crude oil into useful fractions with different boiling ranges and free from undesirable impurities is termed refining.

The fractional distillation of crude oil is carried out continuously in a specially designed tall fractionating tower or column, made of steel. The crude oil is heated in a furnace to about 400°C and introduced in this tower. Higher boiling fractions condense first whereas the low boiling fractions rise upward and are collected as soon as they condense. The gases which do not condense at all (low boiling points such as methane, ethane, propane and butane) are collected at the top of the column. Some portion of the crude oil does not vaporise and is obtained as a residue or pitch.

The main fractions obtained are:

Fraction	Approximate composition	Boiling point range upto room temperature
1. Uncondensed gases	$C_1 - C_4$	—
2. Crude naphtha (16%)	$C_5 - C_{10}$	30–150°C
3. Kerosene (25–30%)	$C_{11} - C_{16}$	150–250°C
4. Heavy oil (25–30%)	$C_{16} - C_{18}$	250–400°C
5. Residual oil (about 30%)	$C_{17} - C_{40}$	Above 400°C
6. Non-volatile residue	—	—

Different fractions are further refined and subjected to refractionation to yield various useful products.

Purification : The fractions obtained above are called sour fractions. These fractions are purified in order to improve odour, stability to air oxidation, corrosiveness and other properties. The actual process of purification differs from one fraction to the other depending upon its commercial utility and nature of unwanted substances present.

(i) Treatment with concentrated sulphuric acid : The gasoline or kerosene fraction is shaken with sulphuric acid to remove aromatic compounds like thiophene and other sulphur compounds which impart offensive odour to gasoline and kerosene and also make them corrosive. It is then allowed to settle and the upper layer is withdrawn. It is treated with sodium hydroxide to remove excess of acid and finally washed with water several times. It is then redistilled.

(ii) Doctor sweetening process : Sometimes sodium plumbite is used in presence of alkali and calculated quantity of sulphur to remove mercaptans. Mercaptans are oxidised to disulphides.

$$2RSH + Na_2PbO_2 + S \longrightarrow \underset{\text{Disulphide}}{RSSR} + PbS + 2NaOH$$

(iii) Treatment with adsorbents : Various fractions are passed over adsorbents like alumina or silica or clay, etc., when the undesirable compounds get adsorbed.

A complete list of petroleum products, approximate composition, boiling range and their uses is given below:

Table : Petroleum Products

S. No.	Fraction	Boiling range (°C)	Approximate composition	Uses
1.	Uncondensed gases	Upto room temperature	$C_1 - C_4$	Fuel gases; refrigerants; production of carbon black; hydrogen; synthesis of organic chemicals.
2.	Crude naphtha on refractionation yields:	30–150°	$C_5 - C_{10}$	
	(i) Petroleum ether	30–70°	$C_5 - C_6$	Solvent.
	(ii) Petrol or gasoline	70–120°	$C_6 - C_8$	Motor fuel; drycleaning; petrol gas.
	(iii) Benzene derivatives	120–150°	$C_8 - C_{10}$	Solvent; drycleaning.
3.	Kerosene	150–250°	$C_{11} - C_{16}$	Fuel; illuminant; oil gas.
4.	Heavy oil	250–400°	$C_{15} - C_{18}$	As fuel for diesel engines; converted to gasoline by cracking.
	Refractionation gives:			
	(i) Gas oil			
	(ii) Fuel oil			
	(iii) Diesel oil			
5.	Residual oil on fractionation by vacuum distillation gives:	Above 400°C	$C_{17} - C_{40}$	
	(i) Lubricating oil		$C_{17} - C_{20}$	Lubrication.
	(ii) Paraffin wax		$C_{20} - C_{30}$	Candles; boot polish; wax paper; etc.
	(iii) Vaseline		$C_{20} - C_{30}$	Toilets; ointments; lubrication.
	(iv) Pitch		$C_{30} - C_{40}$	Paints, road surfacing.
6.	Petroleum coke (or redistilling tar).			As fuel.

LPG and CNG (Petroleum Gases)

1. Liquefied petroleum gas (LPG) : The petroleum gas liquefied under pressure is called liquefied petroleum gas (LPG). It is chiefly a mixture of butane and isobutane with a small amount of propane and is easily compressed under pressure as liquid and stored in iron cylinders. It is supplied in liquid form, so that a cylinder of even small volume may contain an appreciable amount of the gas. A domestic gas cylinder contains about 14 kg of LPG. A strong foul smelling substance called ethyl mercaptan (C_2H_5SH) is added to LPG cylinders to help in the detection of gas leakage. The gas used for domestic cooking is called **Liquefied Petroleum Gas (LPG).** It is mainly used as a pollution free household neat and clean **good fuel** because the combustion of butane and isobutane is complete. When we turn the knob of the gas cylinder, the pressure is released resulting decrease of pressure inside the cylinder, so that highly volatile LPG changes into gas. When ignited, the gas burns with a blue flame producing a lot of heat. It has a high calorific value (about 50 kJ/g). The major sources of LPG are natural gas and from refining and cracking of petroleum.

2. Compressed natural gas (CNG) : The natural gas compressed at very high pressure is called compressed natural gas (CNG). It consists mainly of methane (95%) which is a relatively unreactive hydrocarbon and makes it nearly complete combustion possible. The other 5% is made up of various gases such as ethane, propane and butane including small amounts of other gases nitrogen, helium, carbon dioxide, hydrogen sulphide and water vapours, etc. Because of the gaseous nature of this fuel, it must be stored in either a compressed natural gas **(CNG)** state or in a liquefied natural gas **(LNG)** state. The CNG is now being used as a better fuel than gasoline for running buses, cars and three-wheelers in metropolitan cities like Delhi, Mumbai, etc., because of its complete combustion and no unburnt carbon is being released into the atmosphere to cause air pollution. Recently a plant for **LNG** has been established in Gujarat. CNG or LNG are very clean fuels which cause very little pollution and also have very high calorific value. Natural gas has octane rating of 130.

6.8 ARTIFICIAL METHODS FOR MANUFACTURE OF PETROL OR GASOLINE

Petrol or gasoline obtained from crude petroleum is not sufficient and can meet only half of world's requirements. It is, therefore, necessary to find alternative methods of obtaining petrol. The deficiency is partly met these days by converting the other less valuable fractions such as heavy oil and kerosene fractions into petrol with the help of the cracking process. Synthetic methods have also been discovered for the manufacture of petrol. The methods generally employed for the artificial production of petrol can be studied under two main heads:

(i) Cracking, (ii) Synthesis.

(i) Cracking : It is a process in which high boiling fractions consisting of higher hydrocarbons are heated strongly to decompose them into lower hydrocarbons with low boiling points. The process of cracking involves the breaking of carbon-carbon and carbon-hydrogen bond resulting in the formation of smaller molecules of various types depending on the conditions used.

For example, when long chain alkanes are heated well above their boiling points (400–800°C) with or without a catalyst, they are broken (or cracked) to yield smaller alkanes, alkenes and hydrogen.

$$\text{Long chain alkanes} \xrightarrow{400\text{–}800^\circ C} \text{Smaller alkanes} + \text{Alkenes} + H_2$$

Thus, by cracking of a single alkane (*e.g.*, decane), a large number of hydrocarbons like heptane, hexane, pentane, butane, propene, butene, pentene, hexene, etc., are produced.

$$\underset{\text{Decane}}{CH_3(CH_2)_8CH_3} \xrightarrow[500^\circ C]{\text{Cracking}} \begin{cases} \underset{\text{Octane}}{CH_3(CH_2)_6CH_3} + \underset{\text{Ethene}}{C_2H_4} \\ \underset{\text{Heptane}}{CH_3(CH_2)_5CH_3} + \underset{\text{Propene}}{C_3H_6} \\ \underset{\text{Hexane}}{CH_3(CH_2)_4CH_3} + \underset{\text{Butene}}{C_4H_8} \\ \underset{\text{Pentane}}{CH_3(CH_2)_3CH_3} + \underset{\text{Pentene}}{C_5H_{10}} \\ \underset{\text{Butane}}{CH_3(CH_2)_2CH_3} + \underset{\text{Hexene}}{C_6H_{12}} \end{cases}$$

Similarly,

$$\underset{\substack{\text{Dodecane} \\ \text{(b.pt. 489 K)}}}{C_{12}H_{26}} \xrightarrow[700^\circ C]{\text{Cracking}} \underset{\substack{\text{Heptane} \\ \text{(b.pt. 371 K)}}}{C_7H_{16}} + \underset{\substack{\text{Pentene} \\ \text{(b.pt. 309 K)}}}{C_5H_{10}}$$

Cracking is carried out in two different ways:

(a) Liquid-phase cracking and

(b) Vapour-phase cracking.

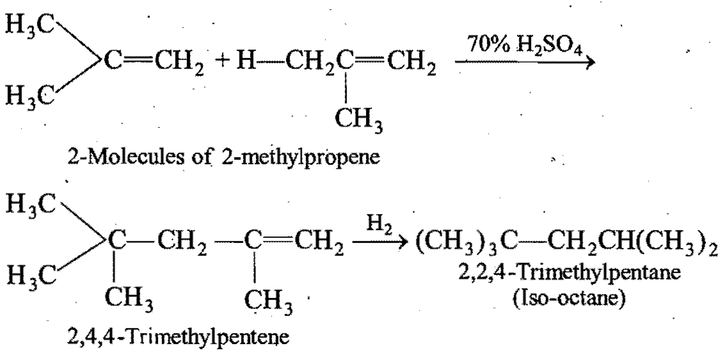
(a) Liquid-phase cracking : In this process, the heavy oil or residual oil is cracked at a high temperature (475–530°C) under high pressure (7 to 70 atmospheric pressure). The high pressure keeps the reaction product in liquid state. The conversion is approximately 70% and the resulting petrol has the octane number in the range 65 to 70.

The cracking can be done in presence of some catalysts like silica, zinc oxide, titanium oxide, ferric oxide and alumina **(catalytic cracking).** The yields of petrol are generally higher when catalyst is used at lower temperature.

(b) Vapour-phase cracking : In this process, kerosene or gas oil is cracked in vapour-phase. The temperature is kept 600–800°C and the pressure is about 3.5 to 10.5 atmospheres. The cracking is facilitated by use of a suitable catalyst. The yields are about 70%.

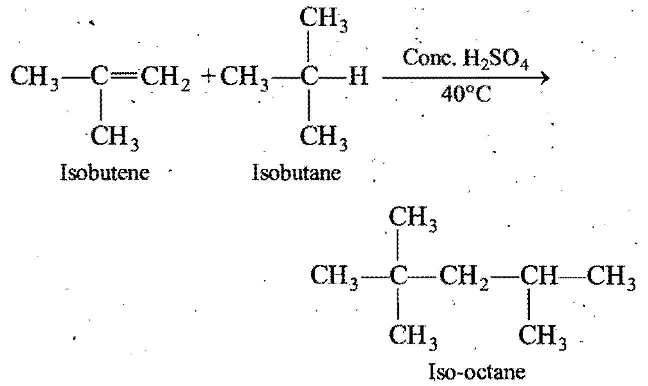
It is observed that petrol obtained by cracking is far superior to petrol obtained by direct distillation of crude petroleum on account of its high octane number (due to presence of large quantities of unsaturated hydrocarbons).

Petrol is also obtained by the **polymerisation** and **alkylation** of simple hydrocarbons obtained during **cracking.** Olefins undergo polymerisation reactions in the presence of catalysts like H_2SO_4 or H_3PO_4. Simple olefins form molecules having 6 to 8 carbon atoms and can be converted into petrol by hydrogenation.

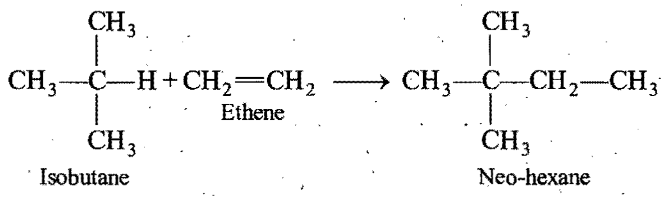


The octane number of polymer gasoline is generally high.

Alkylation occurs under similar conditions. Isobutene reacts with isobutane in presence of conc. H_2SO_4 at about 40°C to form iso-octane.



$$\underset{\text{Isobutene}}{CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2} + \underset{\text{Isobutane}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-H} \xrightarrow[40°C]{\text{Conc. } H_2SO_4} \underset{\text{Iso-octane}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3}$$



$$\underset{\text{Isobutane}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-H} + \underset{\text{Ethene}}{CH_2=CH_2} \longrightarrow \underset{\text{Neo-hexane}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3}$$

(ii) Synthesis : Petrol can be synthesised from coal **(Synthetic petroleum)** by the following two methods:

(a) Bergius process and (b) Fischer-Tropsch process.

(a) Bergius process (Hydrogenation of coal) : This method was invented by **Bergius** in Germany during the first world war. Finely powdered coal and a catalyst (usually ferric oxide, Fe_2O_3 or tin) is made into a paste with heavy oil. The paste is then preheated and pumped to the converter. Here the paste is heated to 450–500°C and hydrogen is passed at about 250 atmospheric pressure. The product of hydrogenation is subjected to fractional distillation.

$$\text{Coal} + H_2 \xrightarrow[\substack{450\text{–}500°C\\250\text{ atm}}]{Fe_2O_3} \text{Mix. of hydrocarbons or crude oil}$$

[synthetic petroleum]

The following fractions are obtained:

(i) Gasoline upto 150°C
(ii) Middle oil between 150–200°C
(iii) Heavy oil 200–300°C
(iv) Residue

Heavy oil and residue are again mixed with coal and the above process is repeated. Middle oil fraction can be separately hydrogenated in the vapour phase in contact with a solid catalyst to form more of gasoline.

The yield of gasoline by this method may be as high as 60%.

(b) Fischer-Tropsch process : In this method, steam is first passed over hot coke to form water gas.

$$\underset{\text{Coke}}{C} + \underset{\text{Steam}}{H_2O} \xrightarrow{1200°C} \underbrace{CO + H_2}_{\text{Water gas}}$$

Water gas is mixed with half its volume of hydrogen and then passed over a catalyst at 200°C under 5–10 atmospheric pressure. The product is synthetic petroleum.

$$xCO + yH_2 \xrightarrow[\text{Heat}]{\text{Co or Ni}} \text{Mixture of hydrocarbons} + H_2O$$

The best catalyst for this process is a mixture of cobalt (100 parts), thoria (5 parts), magnesia (8 parts) and kieselguhr (200 parts).

The artificial petroleum obtained is then fractionally distilled. The various fractions separated are: petrol, kerosene, lubricating oil, diesel oil and paraffin wax. The high boiling fractions are cracked to get more gasoline. The overall yield in this process is slightly higher than Bergius process.

6.9 KNOCKING AND OCTANE NUMBER

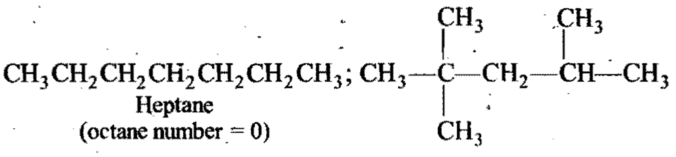
Petrol is used as a fuel in the internal combustion engines of cars, scooters, aeroplanes, etc. A mixture of petrol vapour and air is compressed by a piston within the cylinder of the engine to its one-sixth or one-tenth volume. The compressed mixture is ignited by a spark plug. The fuel burns and energy produced delivers a smooth thrust to the piston. This result in the movement of the piston and the force is transmitted to the wheel of the vehicle. The efficiency of the engine depends on the compression ratio. The increase in compression of the fuel-air mixture beyond a certain point results in irregular burning of the fuel which causes jerks against the piston and gives rise to violent metallic sound. **The metallic sound produced due to irregular burning of the fuel is termed as knocking.** The knocking lowers the efficiency of the engine and results the loss of energy. A fuel which has minimum knocking property is always preferred.

It has been observed that knocking property is related with the nature (composition) of fuel. The straight chain aliphatic hydrocarbons have a higher tendency to knock while branched chain or unsaturated hydrocarbons have less tendency to knock, *i.e.*, the tendency to knock falls off in the following order:

Straight chain alkanes > branched chain alkanes >
olefins > cyclo alkanes > aromatic hydrocarbons

To indicate the quality of gasoline (petrol), a method of gradation has been introduced in 1929 which is termed **octane**

rating or **octane number.** Two compounds we use as standards. Heptane which causes maximum knocking is assigned the octane number 0 (zero) while 2,2,4-trimethylpentane (iso-octane) which causes minimum knocking is assigned the octane number 100.



$$CH_3CH_2CH_2CH_2CH_2CH_2CH_3;\ CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3$$

Heptane (octane number = 0)

2,2,4-Trimethylpentane (octane number = 100)

The octane number of any sample of gasoline is determined by matching its knocking property with the mixture containing iso-octane and heptane in an experimental engine. **The octane number of a given sample may be defined as the percentage by volume of iso-octane present in a mixture of iso-octane and heptane which has the same knocking performance as the fuel itself.** For example, a given sample has the knocking performance equivalent to a mixture containing 60% iso-octane and 40% heptane. The octane number of the gasoline is, therefore, 60.

Antiknock compounds: To reduce the knocking property or to improve the octane number of a fuel certain chemicals are added to it. These are called **antiknock compounds.** One such compound, which is extensively used, is tetraethyl lead (TEL). TEL is used in the form of following mixture:

TEL = 63%, Ethylene bromide = 26%, Ethylene chloride = 9% and a dye = 2%.

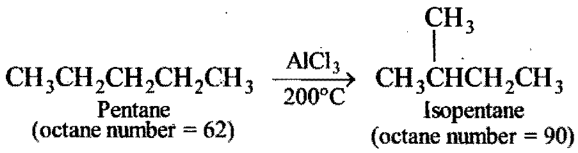
Generally 1 to 3 mL of this mixture is added to one gallon of gasoline. It is believed that tetraethyl lead dissociates to give free ethyl radicals which convert some of the straight-chain hydrocarbons to branched-chain hydrocarbons and thus, improves the octane number. However, there is a disadvantage that the lead is deposited in the engine. To remove the free lead, the ethylene halides are added which combine with lead to form volatile lead halides.

$$Pb + \underset{\text{Ethylene bromide}}{Br-CH_2-CH_2-Br} \longrightarrow \underset{\text{Volatile}}{PbBr_2} + \underset{\text{Ethylene}}{CH_2{=}CH_2}$$

Other Methods for Improving Octane Number of Gasoline

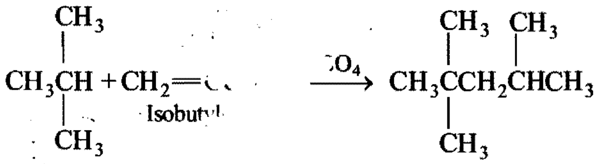
Since, lead compounds are toxic in nature, the lead bromide escaping from the engine pollutes the atmosphere. The modern trend is, therefore, to improve the octane number without using TEL. The octane number of a fuel can be improved by increasing the percentage of branched-chain alkanes, alkenes and aromatic hydrocarbons. The following processes are used for getting no-lead gasoline with better octane number.

(i) Isomerisation (Reforming): By passing gasoline vapours over aluminium chloride ($AlCl_3$) at 200°C.



$$\underset{\substack{\text{Pentane}\\ \text{(octane number = 62)}}}{CH_3CH_2CH_2CH_2CH_3} \xrightarrow[200°C]{AlCl_3} \underset{\substack{\text{Isopentane}\\ \text{(octane number = 90)}}}{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}H}CH_2CH_3}$$

(ii) Alkylation: Isobutylene formed as a by-product during cracking of petroleum, alkylates with isobutane to form iso-octane in presence of concentrated H_2SO_4.

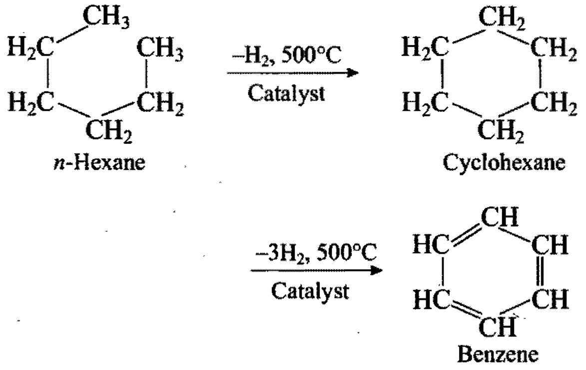


Isobutane

Isobut

Iso-octane
(octane number = 100)

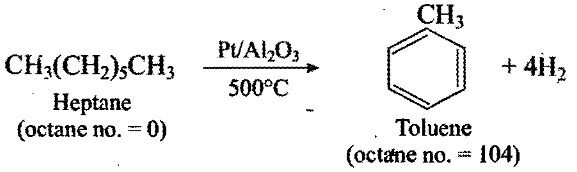
(iii) Aromatization (Platforming): A mixture of benzene, toluene and xylenes known as BTX is obtained when crude naphtha (C_6-C_8 straight chain alkanes) vapours are passed over a catalyst ($Pt + Al_2O_3$) at 500°C. So, the octane number is improved significantly by converting low-octane alkanes into high-octane components.



n-Hexane

Cyclohexane

Benzene



Heptane
(octane no. = 0)

Toluene
(octane no. = 104)

No-lead gasoline sold today is the gasoline obtained by isomerisation and alkylation blended with BTX. Its octane number is 90.

The octane number of petrol can, thus, be improved:

(i) by increasing the proportion of branched-chain or cyclic alkanes,

(ii) by addition of aromatic hydrocarbons (BTX),

(iii) by addition of methanol or ethanol,

(iv) by addition of tetraethyl lead $(C_2H_5)_4Pb$.

6.10 CETANE NUMBER

Cetane number is used for grading the diesel oils. Two compounds have been selected as standards. Hexadecane (cetane) has been assigned cetane number 100 while α-methyl naphthalene is assigned zero cetane number on the basis of ignition property.

The cetane number of a diesel oil is the percentage of cetane (hexadecane) by volume in a mixture of cetane and α-methyl naphthalene which has the same ignition property as the fuel oil in question under similar experimental conditions. Thus, the diesel oil having cetane number 75 would have same ignition property as a mixture of 75% cetane and 25% α-methyl naphthalene.

6.11 FLASH POINT

Volatility of a liquid hydrocarbon determines its explosive nature. Kerosene used for illuminating purposes should not be sufficiently volatile at ordinary temperatures so as to form explosive mixture with air. **The lowest temperature at which an oil gives sufficient vapours to form an explosive mixture with air is referred to as flash point of the oil.**

The flash point or ignition temperature fixed for a particular oil varies from country to country, depends on its climate and controls the percentage of highly volatile hydrocarbons in the oil. The flash point is high for a hot country and low for a cold country. The flash point in India is fixed at 44°C, in France it is fixed at 35°C, and in England at 22.8°C. The flash point of an oil is usually determined by means of "Abel's apparatus".

6.12 PETROCHEMICALS

Petroleum is the biggest and cheapest source of hydrocarbons. These hydrocarbons can be converted into various useful organic compounds. **All such chemicals which are derived from petroleum or natural gas are called petrochemicals.** The modern petrochemical industry produces about half a million useful organic compounds. Petrochemicals provide raw materials for the manufacture of dyes, drugs, plastics, fabrics, insecticides, detergents, food preservatives, disinfectants, etc.

The following list includes some of the chemicals which are obtained from petroleum:

Hydrocarbons	Compounds derived
1. Methane	Methyl chloride, chloroform, methanol, formaldehyde, formic acid, freon, hydrogen for synthesis of ammonia.
2. Ethane	Ethyl chloride, ethyl bromide, acetic acid, acetaldehyde, ethylene, ethyl acetate, nitroethane, acetic anhydride.
3. Ethylene	Ethanol, ethylene oxide, glycol, vinyl chloride, glyoxal, polyethene, styrene, butadiene, acetic acid.
4. Propane	Propanol, propionic acid, isopropyl ether, acetone, nitromethane, nitroethane, nitropropane.
5. Propylene	Glycerol, allyl alcohol, isopropyl alcohol, acrolein, nitroglycerine, dodecylbenzene, cumene, bakelite.
6. Hexane	Benzene, DDT, gammexane.
7. Heptane	Toluene.
8. Cycloalkanes	Benzene, toluene, xylenes, adipic acid.
9. Benzene	Ethylbenzene, styrene, phenol, BHC (insecticide), adipic acid, nylon, cyclohexane, ABS detergents.
10. Toluene	Benzoic acid, TNT, benzaldehyde, saccharin, chloramine-T, benzyl chloride, benzal chloride.

IMPORTANT POINTS TO REMEMBER (SUMMARY)

- Saturated hydrocarbons are called **Paraffins** or **Alkanes.** They have the general formula C_nH_{2n+2}.
- The C—C and C—H bond lengths are equal to 1.54 Å and 1.10 Å respectively. All bond angles are tetrahedral angle (109.5°). The C—C and C—H bond dissociation energies are 83 kcal/mol and 99 kcal/mol respectively.
- They are divided into normal, iso and neo categories.

General methods of preparation

- By hydrogenation of unsaturated hydrocarbons with Ni at 200°C or Raney Ni at room temperature.
- By the reduction of alkyl halides with Zn/HCl or Zn/CH_3COOH or Red P/HI etc.
- By Wurtz reaction:

$$RX + 2Na + XR \xrightarrow{\text{Dry ether}} R—R + 2NaX$$

- By Frankland's reaction:

$$RX + Zn + XR \xrightarrow{\text{Ether}} R—R + ZnX_2$$

- By decarboxylation of carboxylic acids.
- By electrolysis of Na or K salts of fatty acids (Kolbe's electrolytic reaction).
- From Grignard reagents : By double decomposition with compounds containing active hydrogen atom like HOH, $R—OH$, NH_3, $R—NH_2$, R_2NH, $CH_3C{\equiv}CH$, CH_3COOH etc.
- By reduction of alcohols, aldehydes, ketones, carboxylic acids and their derivatives with hot conc. HI and red P in a sealed tube.
- By reduction of aldehydes and ketones ($>C{=}O$) with Zn-Hg and conc. HCl **(Clemmensen's reduction).**

$$>C{=}O + 4H \xrightarrow[\text{Conc. HCl}]{\text{Zn-Hg}} >CH_2$$

- By reduction of aldehydes and ketones with excess of hydrazine on sodium alkoxide on heating **(Wolff-Kishner reduction).**

$$>C{=}O + \underset{\text{Hydrazine}}{H_2N{-}NH_2} \longrightarrow \underset{\text{Hydrazone}}{>C{=}N\cdot NH_2} \xrightarrow[180^\circ C]{C_2H_5ONa} >CH_2$$

- By hydroboration of alkenes:

$$\underset{\text{Alkene}}{RHC{=}CH_2} \xrightarrow{B_2H_6} \underset{\text{Trialkyl borane}}{[RCH_2{-}CH_2{-}]_3B}$$

$$\xrightarrow[H^+]{CH_3COOH} \underset{\text{Alkane}}{RCH_2CH_3}$$

- **By Corey-House synthesis:** $RX + 2Li \xrightarrow{\text{Ether}} R{-}Li + LiX$

$$2R{-}Li + CuI \longrightarrow LiR_2Cu$$

$$\underset{\substack{\text{Lithium dialkyl}\\ \text{cuprate}}}{LiR_2Cu} + R'X \longrightarrow \underset{\text{Alkane}}{R{-}R'} + R{-}Cu + LiX$$

Physical properties

- Physical constants like m.pts., b.pts. and density increase gradually with increase in molecular weights. Straight chain alkanes have higher boiling points than branched chain alkanes having same number of carbon atoms.
  n-alkane > Isoalkane > Neoalkane

Chemical properties

- Both C—C and C—H bonds of alkanes are non-polar and strong sigma bonds cannot break under ordinary conditions; hence, alkanes are quite inert towards common reagents such as acids, alkalies, oxidising and reducing agents. A few important reactions of alkanes are as follows:
- **Halogenation:** Alkanes react with halogens in presence of UV or diffused sunlight at high temperature (250–400°C), the hydrogen atoms of alkane are successively replaced by halogen atoms. This process is known as halogenation **(substitution reaction).** The extent of halogenation depends upon the amount of halogen used. (Reactivity order of halogens is $F_2 > Cl_2 > Br_2 > I_2$)
- Higher alkanes undergo halogenation in controlled conditions and give a mixture of isomeric haloalkanes. The order of reactivity is:
  Tertiary hydrogen > Sec. hydrogen > Primary hydrogen
- Chlorination and bromination proceed in almost identical manner. Reaction with fluorine is very violent but the reaction with iodine is very slow and reversible, so iodination occurs in presence of an oxidising agent.
- Laboratory chlorination of alkane is often done with SO_2Cl_2 instead of Cl_2 and an organic peroxide, *ROOR* is used as an initiator.
- Halogenation occurs by a **free radical chain mechanism.** The important steps are: (i) Initiation (ii) Propagation (iii) Termination.
- **Nitration:** It is a substitution reaction in which a H-atom of alkane is replaced by nitro ($—NO_2$) group. Alkanes can be nitrated with nitric acid in gas phase generally at a temperature 450–500°C. This is known as **vapour phase nitration.**

$$RH + \underset{\text{fuming}}{HO{-}NO_2} \xrightarrow{\Delta} \underset{\text{Nitroalkane}}{R{-}NO_2} + H_2O$$

- Due to the oxidising action of HNO_3, the C—C bonds of higher alkanes also break at high temperature during the reaction and hence, a mixture of lower and corresponding mononitro alkanes are formed.
- Alkanes containing neo-skeleton are easily oxidised with HNO_3 to form carboxylic acids and no nitro compounds.
- Nitration like halogenation also follows **free radical mechanism.**
- **Sulphonation:** The replacement of H-atom by sulphonic acid ($—SO_3H$) group is known as **sulphonation.** Lower alkanes do not undergo sulphonation, but higher alkanes (from hexane onwards) are sulphonated on heating with oleum (conc. H_2SO_4 containing dissolved SO_3) at about 400°C.

$$\underset{\text{Hexane}}{C_6H_{13}{-}H} + HOSO_3H(\text{conc.}) \xrightarrow[400^\circ C]{SO_3} \underset{\substack{\text{Hexane}\\ \text{sulphonic acid}}}{C_6H_{13}{-}SO_3H} + H_2O$$

- Sulphonation also follows **free radical mechanism.**
- **Oxidation:** Alkanes on oxidation give different products under different conditions.
- **Combustion:** Alkanes readily burn in excess of air or oxygen to form CO_2, H_2O and heat. Combustion is an exothermic reaction, hence it is used for the production of heat and energy.
- **Incomplete oxidation:** When alkanes are burned in insufficient supply of oxygen, they give CO and carbon black.
- **Catalytic oxidation:** Lower alkanes undergo restricted oxidation in presence of metallic catalysts at high temperature and pressure to form alcohols, aldehydes and acids, etc.
- **Chemical oxidation:** Alkanes containing tert. hydrogen atoms are oxidised to tert. alcohols by $KMnO_4$.

$$\underset{\text{Isobutane}}{(CH_3)_3CH} \xrightarrow[{[O]}]{KMnO_4} \underset{\text{Tert. butyl alcohol}}{(CH_3)_3C{-}OH}$$

- **Thermal decomposition (or Pyrolysis or Cracking):** The thermal decomposition of organic compounds is known as pyrolysis and the process of breaking C—C bonds or C—H bonds of complex hydrocarbons into simpler molecules by heat is known as **cracking.**
- **Isomerisation:** The process of conversion of one isomer into another is called **isomerisation.** The straight chain alkanes (*n*-alkanes) on treatment with Lewis acid catalysts, *e.g.*, anhydrous $AlCl_3$, conc. HCl, etc., are converted into branched chain alkanes.

$$n\text{-Butane} \xrightarrow[300^\circ C]{\text{Anhyd. } AlCl_3/HCl} \text{Isobutane}$$

- **Aromatisation:** The conversion of aliphatic compounds into aromatic compounds is known as aromatisation.
- **Insertion reaction:** On reaction with diazomethane (CH_2N_2) or ketene ($CH_2{=}C{=}O$), the lower alkanes are

converted into higher homologues due to the introduction of methylene group (—CH_2—).

Petroleum

The **composition** of crude petroleum varies with place of occurrence but essentially it is a mixture of alkanes, cycloalkanes, aromatic hydrocarbons, S, N and oxygen compounds and natural gas, etc.

☐ Modern theory of **origin of petroleum** explains (i) the presence of chlorophyll and haemin (ii) presence of coal deposits near oil fields (iii) presence of N and S compounds along with optically active substances (iv) presence of resins and helium gas.

☐ The crude oil obtained by **mining of petroleum** contains impurities.

☐ The process of dividing crude oil into useful fractions with different boiling ranges [*i.e.*, uncondensed gases (C_1–C_4), crude naphtha (C_5–C_{10}; 30–150°C), kerosene (C_{11}–C_{16}; 150–250°C), heavy oil (C_{16}–C_{18}; 250–400°C), residual oil (C_{17}–C_{40}; above 400°C) and non-volatile residue] and free from undesirable impurities is termed **refining of petroleum.**

☐ Crude naphtha on refractionation yields: (i) Petroleum ether (C_5 – C_6 at 30–70°C), (ii) **Petrol or gasoline** (C_6–C_8 at 70–120°C) and benzene derivatives (C_8–C_{10} at 120–150°C).

☐ **Liquefied petroleum gas (LPG):** It is chiefly a mixture of butane and isobutane (domestic gas) compressed under pressure as liquid and stored in iron cylinders.

☐ **Compressed natural gas (CNG):** The natural gas compressed at very high pressure is called compressed natural gas (CNG). It mainly consists of methane (95%) and other 5% is made up of various gases such as ethane, propane and butane including small amount of other gases.

Artificial Methods for Manufacture of Gasoline

1. Cracking: It is a process in which high boiling fractions consisting of higher hydrocarbons are heated strongly to decompose them into lower hydrocarbons with low boiling points.

$$\text{Long chain alkanes} \xrightarrow{400\text{–}800°C} \text{Smaller alkanes} + \text{Alkenes} + H_2$$

2. Bergius process (Hydrogenation of coal):

$$\text{Coal} + H_2 \xrightarrow[500°C,\ 250\text{ atm}]{Fe_2O_3\text{ catalyst}} \text{Mixture of hydrocarbons or crude oil (Synthetic petroleum)}$$

3. Fischer-Tropsch process (Hydrogenation of water gas):

$$\underset{\text{(Water gas)}}{xCO + yH_2} \xrightarrow[200°C,\ 5\text{–}10\text{ atm}]{\text{Co or Ni}} \text{Mixture of hydrocarbons} + H_2O \text{ (Synthetic petroleum)}$$

☐ **Knocking:** The metallic sound produced due to irregular burning of the fuel is termed as knocking. A fuel with minimum knocking property is always preferred.

☐ The tendency to knock fall off is in the following order:
Straight chain alkanes > branched chain alkanes
> alkenes > cycloalkanes > aromatic hydrocarbons.

☐ **Octane number:** The octane number of a given sample may be defined as the percentage by volume of iso-octane present in a mixture of iso-octane and heptane. Heptane which causes maximum knocking is assigned the octane number zero, while iso-octane (2,2,4-trimethyl pentane) which causes minimum knocking is given the octane number 100.

☐ **Antiknock compounds:** To reduce knocking property or to improve the octane number of a fuel, certain chemicals are added to it. These are called antiknock compounds. Tetraethyl lead **(TEL)** is the best antiknock compound.

☐ **Other methods for improving octane number of gasoline:** The octane number of petrol (gasoline) can be improved by (i) increasing the proportion of branched chain alkanes (by isomerisation or reforming) or alkylation (ii) the addition of aromatic hydrocarbons, BTX (by aromatisation) (iii) addition of TEL $(C_2H_5)_4Pb$ or methanol or ethanol.

☐ **Cetane number:** The cetane number of a diesel oil is the percentage of cetane (hexadecane) by volume in a mixture of cetane and α-methyl naphthalene. It is used for grading the diesel oils. Hexadecane has been assigned cetane number 100 while α-methyl naphthalene is assigned zero cetane number.

☐ **Flash point:** The lowest temperature at which an oil gives sufficient vapours to form an explosive mixture with air is referred to as flash point of the oil. The flash point in India is fixed at 44°C.

☐ **Petrochemicals:** All such chemicals which are derived from petroleum or natural gas are called **petrochemicals.** They provide raw materials for the manufacture of dyes, drugs, plastics, fabrics, insecticides, detergents, food preservatives and disinfectants, etc.

QUESTIONS

❖ Very Short Answer Type

1. Fill in the blanks in the following:
   - (a) The terminal carbon in butane is ...... hybridized.
   - (b) Petroleum is the main source of ....
   - (c) Al_4C_3 evolves ...... when treated with water.
   - (d) $CH_3I + Mg \xrightarrow{Ether} \ldots\ldots \xrightarrow{H_2O} \ldots\ldots$
   - (e) Hydrogenation of unsaturated aliphatic hydrocarbons using nickel as a catalyst is known as ....
   - (f) *n*-Propyl bromide on reaction with sodium in presence of ether gives ...... and the reaction is known as ....
   - (g) Kolbe's electrolysis of ...... produces *n*-hexane at anode.
   - (h) Paraffins mainly undergo ...... reactions.
   - (i) The straight chain isomer of an alkane has a ...... boiling point than the branched chain isomer.
   - (j) Halogenation of alkanes does not occur in ....
   - (k) The halogen which is most reactive in the halogenation of alkanes under the sunlight is ...... (chlorine, bromine, iodine).
   - (l) Sodalime is NaOH and ...... mixture.
   - (m) A sample of gasoline has same knocking properties as a mixture containing 40% *n*-heptane and 60% iso-octane. The octane number of the sample is ....
   - (n) Breaking of higher hydrocarbons into lower hydrocarbons is called ....
   - (o) Gasoline obtained as a result of ...... has a higher octane number than the straight run gasoline.
   - (p) A lead compound known as ...... is used as antiknock in petroleum industry to increase efficiency of fuel consumption.
   - (q) Reduction of alkyl halides with ...... yields alkanes.
   - (r) The gas supplied for cooking is ....
   - (s) Synthetic petrol is obtained by ....
   - (t) Chlorination of propane give rise to ...... monochloro products.
   - (u) When ...... is strongly heated with sodalime C_2H_6 is obtained.
   - (v) $CH_3MgBr + CH_3OH \longrightarrow \ldots\ldots + \ldots\ldots$
   - (w) The shape of methane molecule is ....
   - (x) All alkanes are ...... than water.
   - (y) The conversion of *n*-hexane into benzene in presence of a catalyst Cr_2O_3 at 600°C is termed ....
   - (z) ...... is obtained when methane is oxidised with ozonised oxygen at 450°C.
2. State whether the following statement is **True** or **False:**
   - (a) In alkanes all carbon atoms are sp^3-hybridized.
   - (b) Natural gas consists of lower hydrocarbons.
   - (c) The general formula of alkanes is C_nH_{2n+4}.
   - (d) The alkanes having four or more carbon atoms show only chain isomerism.
   - (e) Sodalime is a mixture of sodium hydroxide and potassium hydroxide.
   - (f) Methane can be obtained by Wurtz reaction.
   - (g) Methane is also called as fire damp or marsh gas.
   - (h) Ethane on nitration at 400°C forms only nitroethane.
   - (i) The decreasing order of boiling points amongst the isomeric pentanes is neo > iso > *n*.
   - (j) Petroleum is called liquid gold.
   - (k) Petrol consists of hydrocarbons from $C_{12}H_{26}$ to $C_{15}H_{32}$.
   - (l) Straight chain hydrocarbons have high octane number values than branched-chain hydrocarbons.
   - (m) TEL increases octane number of gasoline.
   - (n) Wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atoms.
   - (o) Kolbe's electrolysis method is applicable for the preparation of only symmetrical alkanes of the type *R—R*.
   - (p) In Clemmensen reduction, $LiAlH_4$ is used for the reduction of aldehydes and ketones to form alkanes.
   - (q) In alkanes, C—H bond is stronger than C—C bond.
   - (r) Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio of 9 : 1.
   - (s) Fischer-Tropsch method is used for the preparation of synthetic petrol.
   - (t) Neopentane yields three different monochloro derivatives.
   - (u) The three carbon atoms in propane lie in straight line.
   - (v) Alkanes mainly undergo substitution reactions and follow free radical mechanism.
   - (w) For grading diesel oil the term octane number is used.
   - (x) Higher alkanes can be oxidised to fatty acids in presence of manganese stearate.
   - (y) Methane when heated at 1000°C in absence of air, decomposes into carbon black and hydrogen.
   - (z) Ethane is used for making hexachloro ethane which is an artificial camphor.
3. Match the following:

[A] (1) Decarboxylation	(a) Lead tetraethyl
(2) Saturated hydrocarbons	(b) Free radical substitution
(3) Marsh gas	(c) Alkyl halide + Na $\xrightarrow{Ether}$
(4) Antiknock compound	(d) Isomerisation
(5) Wurtz reaction	(e) Petroleum
(6) $CH_4 + Cl_2 \xrightarrow{Sunlight} CH_3Cl$	(f) Paraffins
(7) Conversion of *n*-butane into 2-methylpropane	(g) Methane
(8) Liquid gold	(h) *R*COONa + Sodalime

[B]

(1) Petrol	(a) Methane
(2) Kerosene	(b) Octane number value 100
(3) Aluminium carbide	(c) Mendeleeff
(4) TEL	(d) Cracking
(5) Iso-octane	(e) $C_7 - C_{12}$
(6) Pyrolysis of alkanes	(f) Antiknock compound
(7) Carbide theory	(g) $C_{12} - C_{15}$

4. What happens when:
   - (a) Dry sodium propionate is heated with sodalime?
   - (b) Water is added to aluminium carbide?
   - (c) Ethyl iodide is treated with phosphorus and hydrogen iodide?
   - (d) Electrolysis of an aqueous solution of potassium acetate is done?
   - (e) Ethyl iodide dissolved in dry ether is treated with sodium metal?
   - (f) Methane is treated with iodine in presence of an oxidising agent?
   - (g) *n*-Hexane is treated with Cr_2O_3 supported over alumina at 600°C?
   - (h) Ethane is treated with conc. nitric acid at 450°C?
   - (i) Lithium dimethyl cuprate is treated with ethyl bromide?
5. How will you prepare the following ?
   - (a) *n*-Butane from ethyl bromide.
   - (b) Ethane from acetic acid.
   - (c) Ethane from ethene.
   - (d) Methane from acetic acid.
   - (e) Ethane from methane in two steps.
   - (f) Ethane from ethanol in one step.
   - (g) Methyl chloride from aluminium carbide in two steps.
   - (h) Propane from methane.
6. Complete the following reactions:

(i) $CH_3CH_2Br \xrightarrow[\text{ether}]{Mg} (A) \xrightarrow{C_2H_5OH} (B) + \mathrm{Mg}\left\langle\begin{matrix}OC_2H_5\\ Br\end{matrix}\right.$

(ii) $CH_3Br \xrightarrow[\text{ether}]{Na} (A) \xrightarrow[h\nu]{Br_2} (B) \xrightarrow[\text{ether}]{Na} (C)$

(iii) $CH_3COOH \xrightarrow{NaOH} (A) \xrightarrow[CaO]{NaOH} (B) \xrightarrow[h\nu]{Br_2} (C)$

(iv) $CH_3CH_2CH_2CH_2CH_2CH_2CH_3 \xrightarrow[600°C/15\text{ atm}]{Cr_2O_3/Al_2O_3} (A)$

(v) $CS_2 + H_2S \xrightarrow{Cu} (A) \xrightarrow[200°C/100\text{ atm}]{[O]\text{ Cu tube}} (B)$

(vi) $(CH_3)_2CHBr \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} (A) \xrightarrow{(CH_3)_2CHCH_2Br} (B)$

(vii) $(CH_3)_3CBr \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} (A) \xrightarrow{CH_3CH_2CH_2Br} (B)$

(viii) $CH_3CH_2C(CH_3)_2Br \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} (A) \xrightarrow{CH_3CH_2Br} (B)$

(ix) $(CH_3)_3CH + Br_2 \xrightarrow{h\nu} (A) \xrightarrow[\text{(ii) } D_2O]{\text{(i) Mg/ether}} (B)$

(x) $CH_3CH_2CH_3 + Br_2 \xrightarrow{h\nu} (A) \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} (B) \xrightarrow{^{14}CH_3I} (C)$

(xi)  $+ Br_2 \xrightarrow{h\nu} (A) \xrightarrow[\text{(ii) } D_2O]{\text{(i) Mg/ether}} (B)$

(xii)  $\xrightarrow[500°C]{Cr_2O_3/Al_2O_3} (A) \xrightarrow[(Pt)]{+D_2} (B)$

(xiii) $EtCH{=}CH_2 \xrightarrow{B_2H_6} (A) \xrightarrow[NaOH]{AgNO_3} (B)$

(xiv) $CH_3Br \xrightarrow[\text{ether}]{Mg} (A) \xrightarrow{D_2O} (B) \xrightarrow[\text{one mol.}]{Cl_2, \Delta}$

$(C) \xrightarrow[\text{ether}]{Na} (D)$

7. Answer the following:
   - (a) How many molecules of oxygen would be required for the complete combustion of one molecule of butane?
   - (b) How many chain isomers are possible in C_5H_{12}?
   - (c) What is the octane number of 2,2,4-trimethylpentane?
   - (d) What is the octane number of *n*-hexane?
   - (e) What is the name of the process in which higher alkanes are converted into lower alkanes by heating?
   - (f) Name the two methods used for the synthesis of petrol.
   - (g) What is the flash point fixed in India?
   - (h) What is the name of the process in which normal alkanes are converted into their branched chain isomers in the presence of aluminium chloride and HCl?

❖ Short Answer Type

8. How do you account for the following?
   - (a) Alkanes are inert towards chemical reagents.
   - (b) Chlorination of methane does not occur in dark.
   - (c) Iodination of methane occurs in presence of iodic acid.
   - (d) Why the cracked gasoline is considered to be superior to straight distilled gasoline?
   - (e) The boiling points of branched chain alkanes are lower than their normal isomers.
   - (f) Alkanes containing even number of carbon atoms have higher than expected melting point.
   - (g) Although combustion of alkanes is a strongly exothermic process, it does not occur at moderate temperatures.
   - (h) Tetraethyl lead, $Pb(C_2H_5)_4$, initiates the chlorination of methane in the dark at 150°C.
   - (i) Why does an oil slick form on the surface of the ocean after a spill?
   - (j) A tertiary carbon atom can be oxidised with relative ease.
9. Write short notes on:
   - (a) Sabatier and Senderen reduction
   - (b) Kolbe's electrolytic method
   - (c) Wurtz synthesis
   - (d) Cracking

(e) Theories of petroleum origin
(f) Octane number
(g) Synthetic petrol
(h) Flash point
(i) Antiknock compounds
(j) Cetane number
(k) Clemmensen's reduction
(l) Frankland's reaction

10. Select from each of the following sets the hydrocarbons having lowest and highest boiling point:
(a) *n*-butane, *n*-hexane, *n*-pentane
(b) *n*-pentane, *n*-hexane, 2,3-dimethylbutane
(c) 3,3-dimethylpentane, 2-methylhexane, *n*-heptane

11. (i) Write equations for the preparation of *n*-butane from:
(a) *n*-Butyl bromide, (b) Ethyl bromide,
(c) 1-Butene, (d) 2-Butene
(ii) Which of the following reagents will react with ethane?
(a) Aqueous KOH,
(b) Alkaline $KMnO_4$,
(c) Bromine in presence of light,
(d) Nitric acid at 450°C.
(iii) Write the structural formulae and IUPAC names for all the dibromo derivatives of propane.
(iv) Write the structural formulae and IUPAC names for all the trichloro derivatives of propane.
(v) Starting with bromoethane and bromomethane, prepare propane using the Corey-House synthesis.
(vi) Prepare *n*-hexane from 1-bromopropane using the Corey-House synthesis.
(vii) Prepare 2-deutero propane from iso-propyl bromide.

12. (a) Which is better of (i) and (ii) ?

(i) $CH_3CH_2C(CH_3)_2Br \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} \xrightarrow{CH_3CH_2Br}$

(ii) $CH_3CH_2Br \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} \xrightarrow{CH_3CH_2C(CH_3)_2Br}$

Also identify the product formed.
(b) Sodium salt of which acid will be needed for the preparation of propane?
(c) When sulphuryl chloride (SO_2Cl_2) is used to chlorination of an alkane, an organic peroxide, R_2O_2 is used as initiator. Explain mechanism of chlorination.
(d) Give the condensed formulae for the alkanes (i) C_8H_{18} and (ii) $C_{11}H_{24}$ with the greatest number of methyl groups.
(e) Place the three isomeric pentanes in order of increasing stability at room temperature.
(f) Write the structure of all the alkenes that can be hydrogenated to form 2-methyl pentane.
(g) In the halogenation of alkanes other than methane, there is another chain terminating reaction called *disproportionation.* Write the mechanism of this reaction for $\dot{C}_2H_5$.
(h) Write the structure of an alkane, C_8H_{18} which gives only one monochloro substitution product.

ANSWERS

1. (a) sp^3; (b) alkanes; (c) methane; (d) CH_3MgI, CH_4; (e) Sabatier and Senderen's reaction; (f) *n*-hexane, Wurtz reaction; (g) sodium or potassium salt of butanoic acid; (h) substitution; (i) higher; (j) dark; (k) chlorine; (l) CaO; (m) 60; (n) cracking; (o) cracking; (p) tetra ethyl lead (TEL); (q) nascent hydrogen; (r) LPG (liquefied petroleum gas); (s) Fischer-Tropsch process; (t) two; (u) sodium propionate; (v) CH_4, $Mg(Br)OCH_3$; (w) tetrahedral; (x) lighter; (y) aromatisation; (z) formaldehyde (methanal).

2. (a) True; (b) True; (c) False—general formula is C_nH_{2n+2}; (d) True; (e) False—mixture of NaOH and CaO; (f) False—cannot be obtained by Wurtz reaction; (g) True; (h) False—forms mixture of nitroethane and nitromethane; (i) False—the decreasing order is $n >$ iso $>$ neo; (j) True; (k) False—hydrocarbons from C_7H_{16} to $C_{12}H_{26}$; (l) False—straight chain hydrocarbons have low octane number values than branched-chain hydrocarbons; (m) True; (n) True; (o) True; (p) False—Zn—Hg and HCl is used for reduction; (q) True; (r) False—as the bromination occurs *via* free radical mechanism, the rate of reaction of tertiary hydrogen is much faster as compared to primary hydrogen; (s) True; (t) False—yields only one monochloro derivative; (u) False; (v) True; (w) False—the term cetane number is used; (x) True; (y) True; (z) True.

3. [A] (1– h), (2–f), (3–g), (4–a), (5–c), (6 –b), (7– d), (8– e).
[B] (1–e), (2–g), (3–a), (4 –f), (5 – b), (6 – d), (7– c).

4. (a) $C_2H_5COONa + NaOH \xrightarrow{CaO} C_2H_6 + Na_2CO_3$
(b) $Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$
(c) (i) $3C_2H_5I + 3HI \xrightarrow{150°C} 3C_2H_6 + 3I_2$
(ii) $2P + 3I_2 \longrightarrow 2PI_3$
(d) $2CH_3COOK + 2H_2O \longrightarrow C_2H_6 + 2CO_2 + 2KOH + H_2$
(e) $2C_2H_5I + 2Na \longrightarrow C_4H_{10} + 2NaI$
(f) (i) $CH_4 + I_2 \rightleftharpoons CH_3I + HI$
(ii) $2HI + O \longrightarrow H_2O + I_2$
(g) $C_6H_{14} \xrightarrow[600°C]{Cr_2O_3/Al_2O_3} C_6H_6 + 4H_2$
(h) $C_2H_6 + HNO_3 \xrightarrow{450°C} C_2H_5NO_2 + CH_3NO_2$
(i) $Li(CH_3)_2Cu + C_2H_5Br \longrightarrow C_3H_8 + CH_3Cu + LiBr$

5. (a) $C_2H_5Br + 2Na + BrC_2H_5 \longrightarrow C_2H_5—C_2H_5 + 2NaBr$
(b)
$$\begin{tikzcd} CH_3COOH + KOH \arrow[r] & CH_3COOK + H_2O \arrow[d, "\text{Electrolysis}"] \\ & CH_3—CH_3 \end{tikzcd}$$
(c) $C_2H_4 + H_2 \xrightarrow[300°C]{Ni} C_2H_6$
(d) $CH_3COOH + NaOH \longrightarrow CH_3COONa \xrightarrow[CaO]{NaOH} CH_4$
(e) $CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow[\text{Ether}]{Na} CH_3—CH_3$
(f) $C_2H_5OH \xrightarrow{P/HI} C_2H_6$
(g) $Al_4C_3 \xrightarrow{H_2O} CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl$
(h) $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl \xrightarrow{Na} CH_3—CH_3 \xrightarrow[h\nu]{Cl_2}$

$CH_3CH_2Cl \xrightarrow[Li]{CuI} Li(CH_3CH_2)_2Cu \xrightarrow{CH_3Cl} CH_3CH_2CH_3$

6. (i) (*A*) CH_3CH_2MgBr; (*B*) $CH_3—CH_3$

(ii) (*A*) $CH_3—CH_3$; (*B*) CH_3CH_2Br; (*C*) $CH_3CH_2CH_2CH_3$

(iii) (*A*) CH_3COONa; (*B*) CH_4; (*C*) CH_3Br

(iv) (*A*) $C_6H_5CH_3$ (Toluene)

(v) (*A*) CH_4; (*B*) CH_3OH

(vi) (*A*) $[(CH_3)_2CH]_2LiCu$; (*B*) $(CH_3)_2CHCH_2CH(CH_3)_2$

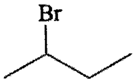
(vii) (*A*) $[(CH_3)_3C]_2LiCu$; (*B*) $(CH_3)_3CCH_2CH_2CH_3$

(viii) (*A*) $[CH_3CH_2C(CH_3)_2]_2LiCu$; (*B*) $CH_3CH_2C(CH_3)_2CH_2CH_3$

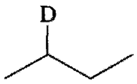
(ix) (*A*) $(CH_3)_3C—Br$; (*B*) $(CH_3)_3CD$

(x) (*A*) $CH_3CH(Br)CH_3$; (*B*) $[(CH_3)_2CH]_2LiCu$; (*C*) $(CH_3)_2CH^{14}CH_3$

(xi) (*A*)

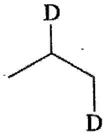


; (*B*)



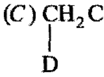
(xii) (*A*)

; (*B*)

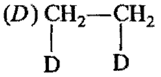


(xiii) (*A*) $(EtCH_2—CH_2—)_3B$; (*B*) $EtCH_2CH_2CH_2CH_2Et$

(xiv) (*A*) CH_3MgBr; (*B*) CH_3D; (*C*)



$\underset{D}{CH_2}Cl$; (*D*)



$\underset{D}{CH_2}—\underset{D}{CH_2}$

7. (a) 13/2 oxygen molecules, (b) three, (c) 100, (d) zero, (e) cracking, (f) (i) Bergius method, (ii) Fischer-Tropsch process, (g) 44°C, (h) isomerisation.

8. (a) Alkanes have no reaction sites due to C—C and C—H non-polar bonds where the chemical reagents can attack.

(b) Chlorination is a free radical substitution. To get chlorine free radicals from Cl_2 molecules energy is required which is not available in dark.

(c) Iodination is a reversible process. To decompose hydrogen iodide, one of the products, an oxidising agent, *i.e.*, iodic acid is required,

$$(5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O).$$

(d) Cracked gasoline possesses branched chain hydrocarbons which have higher octane number. The straight distilled gasoline possesses mainly straight chain hydrocarbons.

(e) The intermolecular forces are weaker in branched chain isomers due to low surface area and therefore, have lower boiling points.

(f) Alkanes with even number of carbon atoms pack in a manner to permit greater intermolecular attraction and therefore, have slightly higher melting points.

(g) The reaction is very slow at room temperature because of a very high energy of activation.

(h) $Pb(C_2H_5)_4$ undergoes thermal homolysis of C—Pb bond at 150°C. The free radical $CH_3\dot{C}H_2$ then generates $\dot{C}l$ which brings chlorination of methane in dark.

(i) Alkanes, the chief constituent of petroleum are insoluble and have a lower density than water.

(j) Alkyl groups being electron releasing groups increase the electron density at tertiary carbon atom which helps easy oxidation.

10. (a) highest b.pt., *n*-hexane; lowest b.pt., *n*-butane.

(b) highest b.pt., *n*-hexane; lowest b.pt., *n*-pentane.

(c) highest b.pt., *n*-heptane; lowest b.pt., 3,3-dimethyl pentane.

11. (i) (a) Mg followed by hydrolysis, (b) Na (Wurtz reaction), (c) H_2/Ni, (d) H_2/Ni.

(ii) (c) and (d).

(iii) $Br_2CHCH_2CH_3$; $CH_3CBr_2CH_3$;
1,1-Dibromopropane ; 2,2-Dibromopropane
$BrCH_2CH_2CH_2Br$; $BrCH_2CHBrCH_3$
1,3-Dibromopropane ; 1,2-Dibromopropane

(iv) $Cl_3CCH_2CH_3$; $Cl_2CHCHClCH_3$;
1,1,1-Trichloropropane ; 1,1,2-Trichloropropane
$Cl_2CHCH_2CH_2Cl$; $ClCH_2CCl_2CH_3$;
1,1,3-Trichloropropane ; 1,2,2-Trichloropropane
$ClCH_2CHClCH_2Cl$
1,2,3-Trichloropropane

(v) $$\underset{\text{Bromoethane}}{CH_3CH_2Br} \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} \underset{\text{Lithium diethylcuprate}}{(CH_3CH_2)_2LiCu} \xrightarrow{CH_3Br} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

(vi) $$CH_3CH_2CH_2Br \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} (CH_3CH_2CH_2)_2LiCu \xrightarrow{CH_3CH_2CH_2Br} CH_3CH_2CH_2CH_2CH_2CH_3$$

(vii) $$(CH_3)_2CH—Br + Mg \xrightarrow{\text{Ether}} (CH_3)_2CH—MgBr \xrightarrow{D_2O} (CH_3)_2CHD$$

12. (a) (i) is better since it uses 1° alkyl halide in second step of reaction.

$$CH_3CH_2C(CH_3)_2Br \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} [CH_3CH_2C(CH_3)_2]_2LiCu \xrightarrow{CH_3CH_2Br} \underset{\text{3,3-Dimethyl pentane}}{CH_3CH_2C(CH_3)_2CH_2CH_3}$$

(b) Butanoic acid

$$\underset{\text{Sodium butanoate}}{CH_3CH_2CH_2COO^-Na^+} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Propane}}{CH_3CH_2CH_3} + Na_2CO_3$$

(c)
$$\left.\begin{array}{ll}\text{Step 1.} & ROOR \longrightarrow 2R\dot{O} \\ \text{Step 2.} & R'H + R\dot{O} \longrightarrow \dot{R}' + ROH\end{array}\right\}\ \text{Initiation}$$

$$\left.\begin{array}{ll}\text{Step 3.} & SO_2Cl_2 + \dot{R}' \longrightarrow \dot{S}O_2Cl + R'Cl \\ \text{Step 4.} & \dot{S}O_2Cl \longrightarrow \dot{C}l + SO_2 \\ \text{Step 5.} & R'H + \dot{C}l \longrightarrow \dot{R}' + HCl\end{array}\right\}\ \text{Propagation}$$

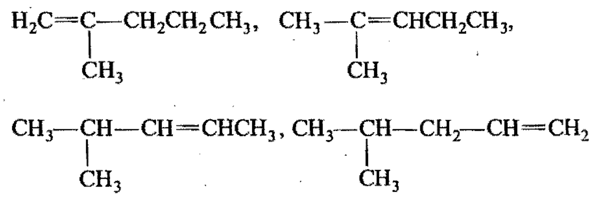
$$\text{Step 6.}\quad \dot{R}' + \dot{C}l \longrightarrow R'Cl \qquad \text{Termination}$$

(d) (i) $(CH_3)_3C—C(CH_3)_3$, (ii) $(CH_3)_3C—C(CH_3)_2—C(CH_3)_3$

(e) The stability generally increases with increase in branched chain. Thus,

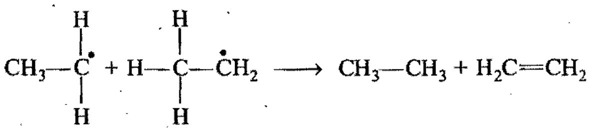
$$CH_3(CH_2)_3CH_3 < (CH_3)_2CHCH_2CH_3 < (CH_3)_4C$$

(f) There are four different positions of double bond; hence, the four different alkenes are:



$$H_2C{=}\underset{CH_3}{C}—CH_2CH_2CH_3,\quad CH_3—\underset{CH_3}{C}{=}CHCH_2CH_3,$$
$$CH_3—\underset{CH_3}{CH}—CH{=}CHCH_3,\quad CH_3—\underset{CH_3}{CH}—CH_2—CH{=}CH_2$$

(g)



$$CH_3—\overset{H}{\underset{H}{\dot{C}}} + H—\overset{H}{\underset{H}{C}}—\dot{C}H_2 \longrightarrow CH_3—CH_3 + H_2C{=}CH_2$$

(h) $$\underset{\text{2,2,3,3-Tetramethylbutane}}{(CH_3)_3C—C(CH_3)_3} \xrightarrow{Cl_2} (CH_3)_3C—C(CH_2)_2CH_2Cl$$

PROBLEMS BASED ON STRUCTURE AND PROPERTIES

1. What volume of methane (NTP) is formed from 16.4 g of sodium acetate by fusion with sodalime?

[Ans. 4.48 L]

[**Hint:** $\underset{\substack{[12+3+12+32+23]\\82\text{ g}}}{CH_3COONa} + NaOH \xrightarrow[\text{heat}]{CaO} \underset{22.4\text{ L}}{CH_4} + Na_2CO_3$]

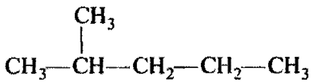
2. If a rocket was fuelled with kerosene and liquid oxygen, what mass of oxygen would be required for every litre of kerosene? (Assume kerosene to have the average composition $C_{14}H_{30}$. The density of kerosene is 0.764 g/mL)

[Ans. 2654.7 g]

[**Hint:** $\underset{198\text{ g}}{C_{14}H_{30}} + \underset{688\text{ g}}{\frac{43}{2}O_2} \longrightarrow 14CO_2 + 15H_2O$]

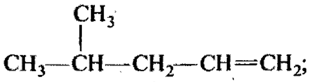
3. Write the structure of all the alkenes that can be hydrogenated to form 2-methylpentane.

[**Hint:** The structure of 2-methylpentane is,



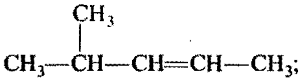
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_2-CH_3$$

There can be four different positions for a double bond; hence, four different alkenes are:



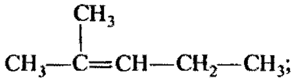
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH=CH_2;$$

(i)



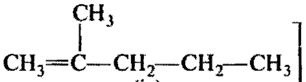
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH=CH-CH_3;$$

(ii)



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-CH_3;$$

(iii)



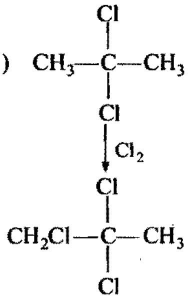
$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-CH_2-CH_3$$

(iv)]

4. In the study of chlorination of propane, four products (*A*, *B*, *C* and *D*) of the formula $C_3H_6Cl_2$ were isolated. Each was further chlorinated to provide trichloro products ($C_3H_5Cl_3$). It was found that *A* provided one trichloro product, *B* gave two and *C* and *D* each gave three. What are the structural formulae of *A*, *B*, *C* and *D*?

[**Hint:** Dichloro isomers,

(*A*)



$$CH_3-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-CH_3 \xrightarrow{Cl_2} CH_2Cl-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-CH_3$$

(One)

(*B*) $ClCH_2CH_2CH_2Cl \xrightarrow{Cl_2}$

1. $Cl_2CHCH_2CH_2Cl$
2. $ClCH_2ClCHCH_2Cl$

(Two)

(*C*) $CH_3CHClCH_2Cl \xrightarrow{Cl_2}$

1. $CH_2ClCHClCH_2Cl$
2. $CH_3CHClCHCl_2$
3. $CH_3CCl_2CH_2Cl$

(Three)

(*D*) $CH_3CH_2CHCl_2 \xrightarrow{Cl_2}$

1. $CH_3CHClCHCl_2$
2. $CH_3CH_2CCl_3$
3. $CH_2ClCH_2CHCl_2$

(Three)]

5. Calculate the heat of combustion of methane at room temperature from the given bond energies:

C—H = 98.7 kcal/mol
O=O = 119.1 kcal/mol
C=O = 192.0 kcal/mol
O—H = 110.6 kcal/mol

[**Hint:** $CH_4 + 2O_2 = CO_2 + 2H_2O \qquad \Delta H = ?$

ΔH = Total bond energies reactants − Total bond energies products

$$= [4\times(C-H) + 2\times(O=O)] - [2\times(C=O) + 4(O-H)]$$
$$= 4\times 98.7 + 2\times 119.1 - 2\times 192.0 - 4\times 110.6$$
$$= -193.4 \text{ kcal/mol}$$]

6. *n*-Butane is produced by monobromination of ethane followed by the Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g *n*-butane; if the bromination takes place with 90% yield and the Wurtz reaction with 85% yield.

[**Hint:** $\underset{30\text{ g}}{C_2H_6} + Br_2 \longrightarrow \underset{109\text{ g}}{C_2H_5Br} + HBr;$

$$\underset{2\times 109\text{ g}}{2C_2H_5Br} + 2Na \longrightarrow \underset{58\text{ g}}{C_4H_{10}} + 2NaBr$$

55 g butane will be produced from

$$= \frac{2\times 109}{58}\times 55 \text{ g ethyl bromide}$$

As the yield is 85%, the actual ethyl bromide required

$$= \frac{2\times 109}{58}\times 55\times\frac{100}{85} = 243.2 \text{ g}$$

243.2 g of ethyl bromide will be produced from

$$\frac{30}{109}\times 243.2 = 66.93 \text{ g ethane}$$

As the yield is 90, the actual ethane required

$$= \frac{100}{90}\times 66.93 = 74.37 \text{ g}$$

Volume of the ethane at NTP $= \frac{74.37}{30}\times 22.4 = 55.5$ L]

7. An alkane, C_7H_{16}, is produced by the reaction of lithium di-(3-pentyl) cuprate with ethyl bromide. What is the structure of alkane?

[**Hint:** This is a Corey-House synthesis.

$$[(CH_3CH_2)_2CH]_2CuLi + CH_3CH_2Br \longrightarrow \underset{\text{(3-Ethylpentane)}}{(CH_3CH_2)_3CH}$$]

8. The alkanes, (a) C_5H_{12} and (b) C_8H_{18}, on treatment with chlorine give only one monochloride. Give the structures of each alkane and its chloride.

[**Hint:** (a) $(CH_3)_4C \longrightarrow (CH_3)_3C-CH_2Cl$;

(b) $(CH_3)_3C-C(CH_3)_3 \longrightarrow (CH_3)_3C-C(CH_3)_2CH_2Cl$]

9. Calculate the ΔH for the two propagation steps in the reaction of methane with chlorine. The bond energies for CH_3—H, CH_3—Cl, H—Cl and Cl—Cl are respectively 105, 85, 103 and 58 kcal/mol.

[**Hint :** **Step 1.** (Breaking of CH_3—H bond) + (forming of H—Cl bond)

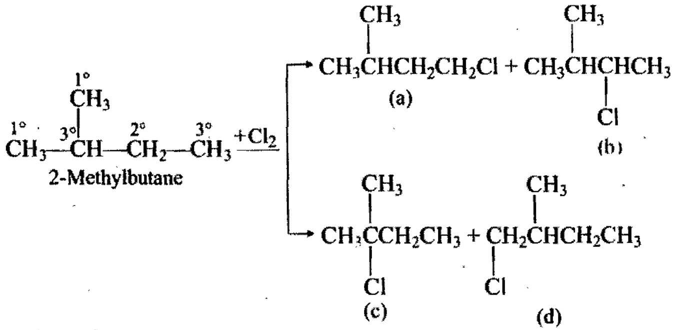
$= 105 + (-103) = +2$ kcal/mol

Step 2. (Breaking of Cl—Cl bond) + (forming of CH_3—Cl bond)

$58 + (-85) = -27$ kcal/mol]

10. The relative reactivity of 1° : 2° : 3° hydrogens to chlorination is 1 : 3.8 : 5 respectively. Calculate the percentage of isomers formed during monochlorination of 2-methylbutane.

[**Hint :**



Relative proportion of the four products can be calculated as:

Isomers	Type (due to reaction of)	Relative amount	% yield
(a) $(CH_3)_2CHCH_2CH_2Cl$	3 equivalent 1° H's	$3 \times 1.0 = 3$	$\frac{3}{21.6} \times 100 = 13.9$
(b) $(CH_3)_2CHCH(Cl)CH_3$	2 equivalent 2° H's	$2 \times 3.8 = 7.6$	$\frac{7.6}{21.6} \times 100 = 35.2$
(c) $(CH_3)_2C(Cl)—CH_2CH_3$	1 equivalent 3° H's	$1 \times 5 = 5.0$	$\frac{5.0}{21.6} \times 100 = 23.1$
(d) $CH_2(Cl)—CH(CH_3)—CH_2CH_3$	6 equivalent 1° H's	$6 \times 1.0 = 6.0$	$\frac{6.0}{21.6} \times 100 = 27.8$]

11. The relative reactivity of 1° : 2° : 3° hydrogen to bromination is 1 : 82 : 1600. Calculate relative amount of each product on monobromination of iso-butane.

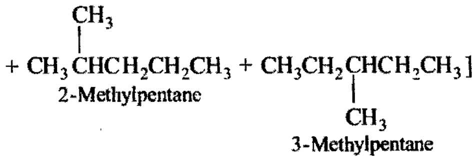
[Ans. 1-bromo 2-methylpropane 0.6%, 2-bromo-2-methylpropane 99.4%]

[**Hint :** Do like **Q. No. 10**]

12. (a) What are the different products obtained on insertion of *n*-pentane using diazomethane?

[**Hint :** $CH_2N_2 \xrightarrow{h\nu} :CH_2 + N_2$

$CH_3—(CH_2)_3—CH_3 + CH_2N_2 \longrightarrow CH_3—(CH_2)_4—CH_3$ *n*-Hexane

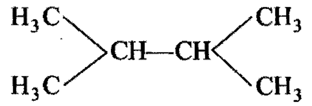


$+ CH_3CH(CH_3)CH_2CH_2CH_3 + CH_3CH_2CH(CH_3)CH_2CH_3$]

2-Methylpentane, 3-Methylpentane

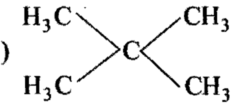
(b) Which of the following alkanes will give single insertion product?

(i)

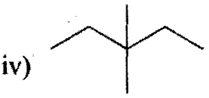


(ii) $CH_3—CH_2—CH_3$

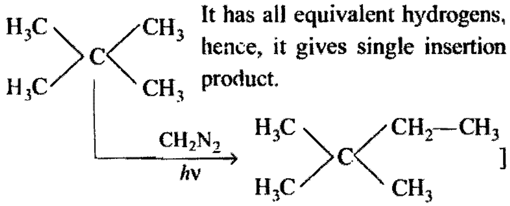
(iii)



(iv)



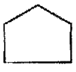
[**Hint :** (iii)



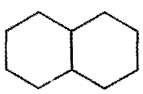
It has all equivalent hydrogens, hence, it gives single insertion product.]

13. Give the major products of monobromination of following compounds.

(i)

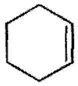


(ii)



(iii)

(iv)

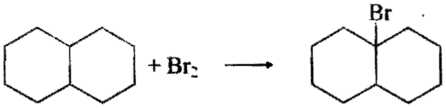


[**Hint:**

(i)

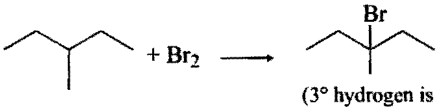
(all carbons are identical)

(ii)



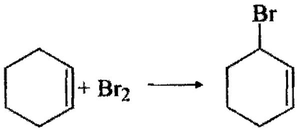
(3° hydrogen is more reactive)

(iii)



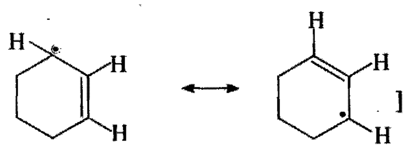
(3° hydrogen is more reactive)

(iv)



(Allylic hydrogen is more reactive)

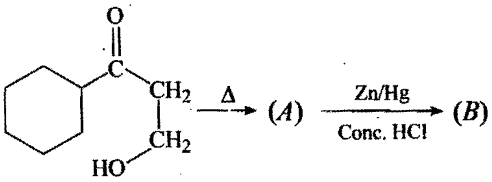
[**Hint:** Allylic free radical is resonance stabilized.



]

14. Complete the following reactions:

(i)

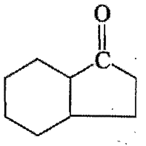


(ii) $(CH_3)_2CHBr \xrightarrow[(2)\ CuI]{(1)\ Li} (A) \xrightarrow{(CH_3)_2CHCH_2Br} (B)$

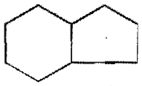
(iii) (A) alkene $\xrightarrow[300°C]{H_2/Ni} (B)$

$(CH_3)_3CBr \xrightarrow[(2)\ CuI]{(1)\ Li} (C) \xrightarrow{(CH_3)_2CHBr} (B)$.

[**Hint :** (i) (A)

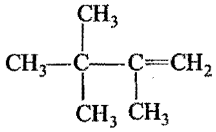


; (B)



(ii) (A) $[(CH_3)_2CH]_2LiCu$
(B) $(CH_3)_2CHCH_2CH(CH_3)_2$

(iii) (A)



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{C}=CH_2$

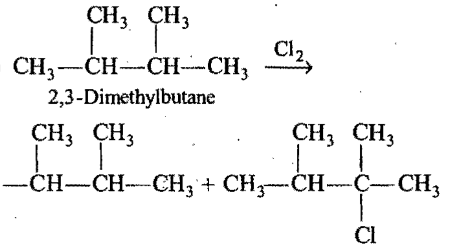
(B) $(CH_3)_3C\,CH(CH_3)_2$
(C) $[(CH_3)_3C]\,LiCu$].

15. (a) An alkane, C_6H_{14} gives two monochloro derivative. Give its structure.

(b) C_6H_{12} (A) has chiral centre. When it is hydrogenated, gives C_6H_{14} (B) in which there is no chiral centre. Identify (A) and (B).

(c) $C_5H_{11}Cl$ gives 2, 2, 5, 5-tetramethylhexane as main product on Wurtz reaction. Give the structure of $C_5H_{11}Cl$.

[**Hint:** (a)

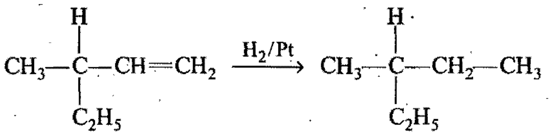


$CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3 \xrightarrow{Cl_2}$

2,3-Dimethylbutane

$ClCH_2-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3 + CH_3-\overset{CH_3}{CH}-\overset{CH_3}{\underset{Cl}{C}}-CH_3$

(b) (A)

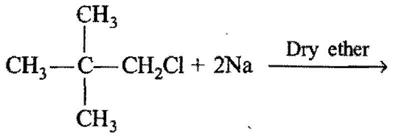


$CH_3-\overset{H}{\underset{C_2H_5}{C}}-CH=CH_2 \xrightarrow{H_2/Pt} CH_3-\overset{H}{\underset{C_2H_5}{C}}-CH_2-CH_3$

Chiral molecule (3-Methyl-1-pentene)

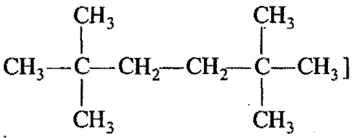
Achiral molecule

(c)



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Cl + 2Na \xrightarrow{\text{Dry ether}}$

1-Chloro-2,2-dimethylpropane

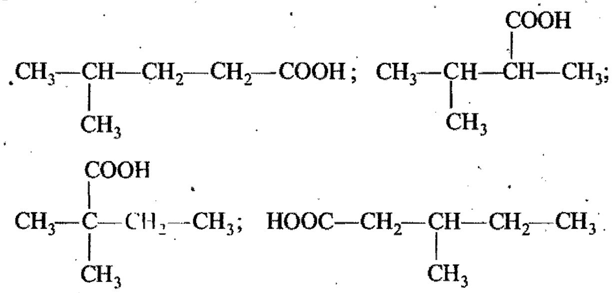


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$]

2,2,5,5-Tetramethylhexane

16. How many monocarboxylic acids are possible which on decarboxylation form iso-pentane?

[**Hint:**



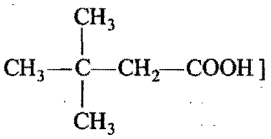
$CH_3-\underset{CH_3}{CH}-CH_2-CH_2-COOH$; $CH_3-\underset{CH_3}{CH}-\overset{COOH}{CH}-CH_3$;

$CH_3-\overset{COOH}{\underset{CH_3}{C}}-CH_2-CH_3$; $HOOC-CH_2-\underset{CH_3}{CH}-CH_2-CH_3$

Four isomeric monocarboxylic acids are possible.]

17. How many monocarboxylic acids are possible, which on decarboxylation give neopentane?

[**Hint:** Only one carboxylic acid is possible.



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-COOH$]

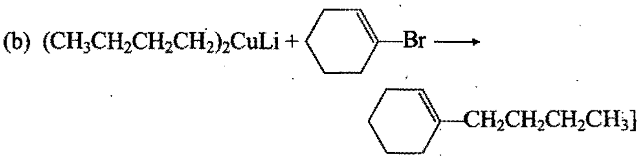
18. Suggest a combination of organic halide and cuprate reagent appropriate for the preparation of each of the following compounds:

(a) 2-Methylbutane (b) 1-Butylcyclohexene

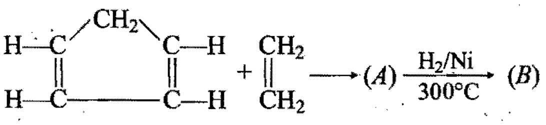
[**Hint:**

(a) $CH_3I + LiCu[CH_2CH(CH_3)_2]_2 \longrightarrow CH_3CH_2CH(CH_3)_2$
2-Methylbutane

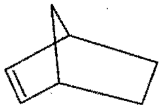
(b)



19. Complete the following reaction:

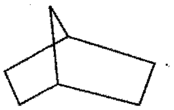


[**Hint:** (A)



Bicyclo (2,2,1)-2-heptene

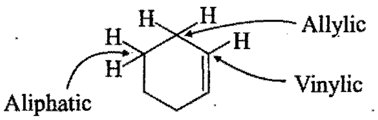
(B)



Bicyclo (2,2,1)-heptane]

20. Indicate the reactivity of vinylic, allylic and aliphatic hydrogen in cyclohexene.

[**Hint:**



Reactivity sequence :

	Allylic	>	Aliphatic	>	Vinylic]
B.E.	87 kcal/mol		95 kcal/mol		108 kcal/mol]

OBJECTIVE QUESTIONS

SET I : This set contains questions with single correct answer.

1. The name fire-damp is given to:
(a) methane ☐ (b) ethane ☐
(c) propane ☐ (d) butane ☐

2. Marsh gas mainly contains:
(a) C_2H_2 ☐ (b) CH_4 ☐
(c) H_2S ☐ (d) CO ☐

3. Both methane and ethane may be obtained by a suitable one step reaction from: **[BHU 2004; UGET (Med.) 2007]**
(a) CH_3I ☐ (b) CH_3CH_2I ☐
(c) CH_3OH ☐ (d) C_2H_5OH ☐

4. Formation of alkane by action of zinc and alkyl halide is called:
(a) Wurtz reaction ☐ (b) Frankland reaction ☐
(c) Kolbe's reaction ☐ (d) Clemmensen reaction ☐

5. The highest boiling point is expected for:
(a) iso-octane ☐
(b) *n*-octane ☐
(c) 2,2,3,3-tetramethylbutane ☐
(d) *n*-butane ☐

6. When water vapours are passed over aluminium carbide, we get:
(a) acetaldehyde ☐ (b) ethylene ☐
(c) methane ☐ (d) methyl alcohol ☐

7. When electrolysis of potassium acetate is carried out, we get:
(a) methane ☐ (b) ethylene ☐
(c) ethane ☐ (d) acetylene ☐

8. When Grignard reagent (CH_3MgBr) is treated with water, we get:
(a) ethane ☐ (b) ethyl alcohol ☐
(c) methyl alcohol ☐ (d) methane ☐

9. Action of heat on a mixture of sodium propionate and sodalime produces:
(a) methane ☐ (b) ethane ☐
(c) propane ☐ (d) ethylene ☐

10. Ethane can be prepared by:
(a) heating sodalime with sodium acetate ☐
(b) electrolysis of sodium succinate ☐
(c) electrolysis of sodium acetate ☐
(d) all of these ☐

11. Wurtz reaction is used to prepare:
(a) methane only ☐ (b) symmetrical alkanes ☐
(c) unsymmetrical alkanes ☐ (d) all of these ☐

12. For the conversion of CH_3OH into methane, the reagent used is:
(a) sodium ☐ (b) P and HI ☐
(c) hydrogen ☐ (d) sodium hydroxide ☐

13. The products formed when the mixture of methane and steam is passed over finely divided nickel at 1000°C are:
(a) CO_2 and H_2 ☐ (b) CO and H_2 ☐
(c) CH_3OH and H_2 ☐ (d) none of these ☐

14. Carbon black is obtained when methane is:
(a) heated in absence of air ☐
(b) heated in presence of nitrogen ☐
(c) heated in presence of ammonia ☐
(d) heated with steam ☐

15. What is the volume of oxygen required for the complete combustion of 4 litre of ethane?
(a) 4 litre ☐ (b) 8 litre ☐
(c) 12 litre ☐ (d) 14 litre ☐

16. Kerosene is a mixture of:
(a) aromatic hydrocarbons ☐
(b) aliphatic hydrocarbons ☐
(c) saturated hydrocarbons ☐
(d) alicyclic hydrocarbons ☐

17. Which of the following substances is used as antiknock compound?
(a) TEL ☐ (b) Lead tetrachloride ☐
(c) Lead acetate ☐ (d) C_2H_5PbCl ☐

18. Most of hydrocarbons from petroleum are obtained by:
(a) fractional distillation ☐
(b) fractional crystallisation ☐
(c) vaporisation ☐
(d) isomerisation ☐

19. The knocking will be minimum when the mixture of fuel is:
(a) straight chained ☐ (b) iso-carbonation ☐
(c) neo-carbonation ☐ (d) none of these ☐

20. Petroleum is a mixture of:
(a) alkanes ☐ (b) cycloalkanes ☐
(c) aromatic hydrocarbons ☐ (d) all of these ☐

21. Iso-octane is added to petrol:
(a) to precipitate inorganic material ☐
(b) to prevent freezing of petrol ☐
(c) to increase the boiling point ☐
(d) as an antiknocking agent ☐

22. The fraction obtained between temperatures 150 –300°C during fractional distillation of crude petroleum is:
(a) paraffin wax ☐ (b) heavy oil ☐
(c) kerosene ☐ (d) naphtha ☐

23. Hydrogenation of coal is done for the production of synthetic petrol in:
(a) Sabatier process ☐ (b) Bergius process ☐
(c) cracking process ☐ (d) none of these ☐

24. The number of chain isomers of alkane containing six carbon atoms is:
(a) 3 ☐ (b) 4 ☐
(c) 5 ☐ (d) 6 ☐

25. The compressed gas available in cooking gas cylinders is a mixture of:

(a) $C_6H_6 + C_6H_5CH_3$ ☐ (b) $C_2H_4 + C_2H_2$ ☐
(c) $C_2H_4 + CH_4$ ☐ (d) $C_4H_{10} + C_3H_8$ ☐

26. By Wurtz reaction, a mixture of methyl iodide and ethyl iodide gives:
(a) propane ☐
(b) ethane ☐
(c) butane ☐
(d) a mixture of the above three ☐

27. Select the correct statement about alkanes:
(a) they are polar in nature ☐
(b) they are soluble in water ☐
(c) they are non-combustible ☐
(d) their dipole moment is zero ☐

28. Reaction of ROH with $R'MgX$ produces:
[JEE (WB) 2009]
(a) RH ☐ (b) $R'H$ ☐
(c) $R—R$ ☐ (d) $R'—R'$ ☐

29. It is necessary to use ...... in the iodination of alkane.
(a) alcohol ☐ (b) oxidising agent ☐
(c) benzene ☐ (d) reducing agent ☐

30. The reaction conditions leading to best yields of C_2H_5Cl are:
(a) $C_2H_6\text{ (excess)} + Cl_2 \xrightarrow{\text{UV light}}$ ☐
(b) $C_2H_6 + Cl_2 \xrightarrow[\text{room temp.}]{\text{Dark}}$ ☐
(c) $C_2H_6 + Cl_2\text{(excess)} \xrightarrow{\text{UV light}}$ ☐
(d) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$ ☐

31. A mixture of CS_2 and H_2S on passing over heated copper gives:
(a) methane ☐ (b) ethane ☐
(c) complex mixture ☐ (d) propane ☐

32. For the preparation of alkanes, concentrated solution of sodium or potassium salt of saturated acid is subjected to:
(a) hydrolysis ☐ (b) oxidation ☐
(c) hydrogenation ☐ (d) electrolysis ☐

33. The gas supplied in cylinders for cooking is:
(a) marsh gas ☐
(b) LPG ☐
(c) mixture of CH_4 and C_2H_6 ☐
(d) mixture of ethane and propane ☐

34. The thermal decomposition of alkanes is known as:
(a) cracking ☐ (b) isomerisation ☐
(c) dehydration ☐ (d) reforming ☐

35. Which of the following is not prepared by Kolbe's electrolytic process?
(a) C_3H_8 ☐ (b) C_2H_6 ☐
(c) C_4H_{10} ☐ (d) C_6H_{14} ☐

36. When *n*-hexane is passed over Cr_2O_3/Al_2O_3 at 600°C, ... is formed.
(a) hexane ☐ (b) hexyne ☐
(c) benzene ☐ (d) none of these ☐

37. Which of the following compounds has been given an octane number of 100?
(a) *n*-Hexane ☐ (b) Iso-octane ☐
(c) Neo-pentane ☐ (d) Neo-octane ☐

38. The number of different substitution products possible when bromine and ethane are allowed to react, is:
(a) 6 ☐ (b) 8 ☐
(c) 7 ☐ (d) 9 ☐
[**Hint :** One mono-substituted, two di-substituted, two tri-substituted, two tetra-substituted, one penta-substituted and one hexa-substituted.]

39. The reagents and conditions to convert methyl iodide to methane are:
(a) action of dry Ag_2O ☐
(b) KCN followed by refluxing with dil. HCl ☐
(c) aqueous NaOH followed by boiling Al_2O_3 at 640 K ☐
(d) Mg in dry ether followed by boiling with water ☐

40. A gaseous hydrocarbon 'X' on reaction with bromine in light forms a mixture of two monobromo alkanes and HBr. The hydrocarbon 'X' is:
(a) C_2H_6 ☐ (b) C_3H_6 ☐
(c) C_3H_8 ☐ (d) C_4H_{10} ☐

41. Which of the following is not linked with methane?
(a) Marsh gas ☐ (b) Natural gas ☐
(c) Producer gas ☐ (d) Coal gas ☐

42. The reaction,

$$H_2C{=}CH_2 + H_2 \xrightarrow[250-300°C]{Ni} CH_3—CH_3$$

is called :
(a) Wurtz's reaction ☐
(b) Kolbe's synthesis ☐
(c) Sabatier and Senderen's reaction ☐
(d) Carbylamine reaction ☐

43. Paraffin wax is:
(a) ester ☐
(b) alcohol ☐
(c) unsaturated hydrocarbons ☐
(d) saturated hydrocarbons ☐

44. Octane number of gasoline can be increased by addition of BTX. BTX stands for:
(a) butane, tetraethyl lead and xylene ☐
(b) butane, tetramethyl lead and xylene ☐
(c) benzene, toluene and xylene ☐
(d) benzene, tetraethyl lead and xylene ☐

45. The flash point in India is fixed at:
(a) 44°C ☐ (b) 35°C ☐
(c) 22.8°C ☐ (d) 30°C ☐

46. Photochemical chlorination of alkane is initiated by a process of:
(a) pyrolysis ☐ (b) substitution ☐
(c) homolysis ☐ (d) peroxidation ☐

47. Zinc-copper couple that can be used as a reducing agent is obtained by:
(a) mixing zinc dust and copper gauze ☐
(b) zinc coated with copper ☐

(c) copper coated with zinc ☐
(d) zinc and copper wires welded together ☐

48. 2.84 g of methyl iodide was completely converted into methyl magnesium iodide and the product was decomposed by excess of ethanol. The volume of the gaseous hydrocarbon produced at NTP will be:
(a) 22.4 litre ☐ (b) 22400 mL ☐
(c) 0.448 litre ☐ (d) 0.224 litre ☐

49. Decarboxylation of isobutyric acid gives *n*-alkane but reduction of isobutyric acid with phosphorus and hydrogen iodide gives:
(a) *n*-propane ☐ (b) iso-butane ☐
(c) *n*-butane ☐ (d) none of these ☐

50. Correct IUPAC name of alkane obtained in the reaction of 2-chloropropane + sodium and dry ether is:
(a) 2,3-dimethylbutane ☐ (b) 2-isopropylpropane ☐
(c) *n*-hexane ☐ (d) none of these ☐

51. The IUPAC name of neo-pentane is: **[AIEEE 2009]**
(a) 2-methyl butane ☐ (b) 2,2-dimethyl butane ☐
(c) 2-methyl propane ☐ (d) 2,2-dimethyl propane ☐

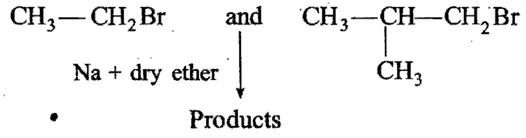
52. In the complete combustion of C_nH_{2n+2}, the number of oxygen moles required is:
(a) $\frac{n}{2O_2}$ ☐ (b) $\left(\frac{n+1}{2}\right)O_2$ ☐
(c) $\left(\frac{3n+1}{2}\right)O_2$ ☐ (d) $\left(\frac{n+2}{2}\right)O_2$ ☐

53. Which of the following isomers of the pentane gives four monochloropentane on chlorination?
(a) *n*-Pentane ☐
(b) iso-Pentane ☐
(c) neo-Pentane ☐
(d) 2,2-Dimethylpropane ☐

54. Number of di-substituted isomers of the product of the reaction, $CH_3CH_2CH_3 + Br_2$, would be:
(a) 2 ☐ (b) 1 ☐
(c) 3 ☐ (d) 4 ☐

55. Aqueous solution of sodium acetate and sodium propionate on electrolysis yields:
(a) ethane ☐ (b) butane ☐
(c) propane ☐ (d) all of these ☐

56. What is the maximum number of carbon atoms in the expected products of the Wurtz reaction?



$$CH_3—CH_2Br \text{ and } CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2Br \xrightarrow{\text{Na + dry ether}} \text{Products}$$

(a) 8 ☐ (b) 6 ☐
(c) 4 ☐ (d) 2 ☐

57. The reactivity of hydrogen atoms attached to carbon atom in an alkane has the order:
(a) tertiary > primary > secondary ☐
(b) secondary > primary > tertiary ☐
(c) tertiary > secondary > primary ☐
(d) primary > secondary > tertiary ☐

58. Grignard reagent gives alkane with:
(a) H_2O ☐ (b) C_2H_5OH ☐
(c) $C_2H_5NH_2$ ☐ (d) all of these ☐

59. The octane number of a fuel containing 90% of *n*-heptane and 10% of 2,2,4-trimethylpentane is:
(a) 10 ☐ (b) 90 ☐
(c) 100 ☐ (d) 50 ☐

60. Kolbe's synthesis of sodium salt of butanoic acid gives:
(a) *n*-hexane ☐ (b) iso-butane ☐
(c) *n*-butane ☐ (d) propane ☐

61. The function of sodalime (a mixture of solid NaOH and solid CaO) in the decarboxylation reaction is:
(a) to increase the rate of reaction ☐
(b) to decrease the rate of reaction ☐
(c) to change the rate of reaction ☐
(d) none is correct ☐

62. Which of the following is the correct sequence of steps in the halogenation of an alkane?
(a) Propagation, initiation, termination ☐
(b) Initiation, termination, propagation ☐
(c) Initiation, propagation, termination ☐
(d) Propagation, termination, initiation ☐

63. Reaction of alkanes with halogen is explosive in case of:
(a) Cl_2 ☐ (b) F_2 ☐
(c) Br_2 ☐ (d) I_2 ☐

64. Fischer-Tropsch process is used in the manufacture of:
(a) ethane ☐ (b) benzene ☐
(c) synthetic petrol ☐ (d) LPG ☐

65. A hydrocarbon with formula C_8H_{18} gives one monochloro derivative. The hydrocarbon is:
(a) *n*-octane ☐
(b) 2-methylheptane ☐
(c) 2,2,4-trimethylpentane ☐
(d) 2,2,3,3-tetramethylbutane ☐

66. Which of the following alkanes can be synthesised in good yield by the Wurtz reaction?
(a) $(CH_3)_2CH—CH_2—CH(CH_3)_2$ ☐
(b) $(CH_3)_2CH—CH_2CH_2—CH(CH_3)_2$ ☐
(c) $CH_3CH_2—C(CH_3)_2—CH_2CH_3$ ☐
(d) $(CH_3)_3C—CH_2—CH_2—CH_3$ ☐

67. The order of appearance of the following with increasing temperature during the refining of crude oil is:
(a) kerosene, gasoline, diesel ☐
(b) diesel, gasoline, kerosene ☐
(c) gasoline, kerosene, diesel ☐
(d) gasoline, diesel, kerosene ☐

68. Which of the following fractions of petroleum has the lowest boiling point?
(a) Gasoline ☐ (b) Kerosene ☐
(c) Diesel oil ☐ (d) Heavy oil ☐

69. Isobutyl magnesium bromide with dry ether and absolute alcohol gives:
(a) $(CH_3)_2CH—CH_2OH$ and CH_3CH_2MgBr ☐

(b) $(CH_3)_2CH—CH_2CH_2CH_3$ and Mg(OH)Br ☐
(c) $(CH_3)_2CH_2, H_2C{=}CH_2$ and Mg(OH)Br ☐
(d) $(CH_3)_3CH$ and CH_3CH_2OMgBr ☐

70. Natural gas is primarily composed of:
(a) methane ☐ (b) *n*-butane ☐
(c) *n*-octane ☐ (d) a mixture of octanes ☐

71. The most important method to prepare lower hydrocarbon is:
(a) cracking ☐
(b) Sabatier-Senderen's reaction ☐
(c) heating salts of fatty acids with sodalime ☐
(d) direct synthesis ☐

72. Butane can be converted into 2-methylpropane, if heated with:
(a) Al_2Cl_6 ☐ (b) Cr_2O_3 ☐
(c) CrO_2Cl_2 ☐ (d) Na/ether ☐

73. Percentage of hydrogen is maximum in:
(a) C_2H_2 ☐ (b) C_2H_4 ☐
(c) C_2H_6 ☐ (d) CH_4 ☐

74. Domestic cooking gas consists of mostly:
(a) methane and ethane ☐
(b) liquefied butane and iso-butane ☐
(c) ethylene and carbon monoxide ☐
(d) hydrogen and acetylene ☐

75. Paraffin dissolves in:
(a) distilled water ☐ (b) methanol ☐
(c) benzene ☐ (d) salt water ☐

76. Liquid hydrocarbons is converted into a mixture of gaseous hydrocarbon by: **[CBSE (PMT) Prelims 2010]**
(a) cracking ☐ (b) hydrolysis ☐
(c) oxidation ☐ (d) distillation ☐

77. The complete combustion of CH_4 gives: **[BHU 2004]**
(a) $CO + H_2$ ☐ (b) $CO + N_2$ ☐
(c) $CO + N_2O$ ☐ (d) $CO_2 + H_2O$ ☐

78. How many types of carbon atoms are present in 2,2,3-trimethylpentane?
(a) One ☐ (b) Two ☐
(c) Three ☐ (d) Four ☐

79. Which one of the following is called Raney's nickel?
(a) Nickel in a fine state of division ☐
(b) Nickel-iron alloy ☐
(c) Nickel-aluminium alloy ☐
(d) Nickel-chromium alloy ☐

80. Finely divided platinum and palladium commonly known as platinum and palladium black, may be prepared by reducing their soluble salts with:
(a) H_2O ☐ (b) C_2H_5OH ☐
(c) HCHO ☐ (d) C_6H_6 ☐

81. Aluminium amalgam used as a reducing agent, is obtained by:
(a) dipping aluminium foil in mercuric chloride solution ☐
(b) mixing aluminium powder with mercury ☐
(c) mixing aluminium nitrate with mercuric oxide ☐
(d) adding mercury to aluminium chloride solution ☐

82. Adam's catalyst is:
(a) platinum metal ☐ (b) palladium ☐
(c) nickel metal ☐ (d) PtO_2 ☐

83. A gas believed to be the cause of explosion in coal mines is:
(a) CH_4 ☐ (b) C_2H_6 ☐
(c) C_3H_8 ☐ (d) C_4H_{10} ☐

84. When propanal is heated with Zn–Hg and conc. HCl, which is formed?
(a) C_3H_4 ☐ (b) C_3H_6 ☐
(c) C_3H_8 ☐ (d) C_3H_7Cl ☐

85. Catalytic reduction of water gas gives:
(a) acetylene ☐ (b) ethylene ☐
(c) ethane ☐ (d) methane ☐

86. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is:
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 1 ☐

87. $(CH_3)_3C—MgCl$ on reaction with D_2O produces:
(a) $(CH_3)_3CD$ ☐ (b) $(CH_3)_3OD$ ☐
(c) $(CD_3)_3CD$ ☐ (d) $(CD_3)_3OD$ ☐

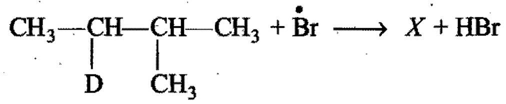
88. The most stable conformation of *n*-butane is:
(a) skew boat ☐ (b) gauche ☐
(c) staggered anti ☐ (d) eclipsed ☐

89. Which of the following reactions is expected to readily give a hydrocarbon product in good yield?
(a) $(CH_3)_3C—Cl \xrightarrow{C_2H_5OH}$ ☐
(b) $RCOOK \xrightarrow{\text{Electrolysis}}$ ☐
(c) $CH_3—CH_3 \xrightarrow[h\nu]{Cl_2}$ ☐
(d) $RCOOAg \xrightarrow{Br_2}$ ☐

90. Octane number is zero for: **[KCET 2002]**
(a) iso-heptane ☐ (b) *n*-heptane ☐
(c) iso-octane ☐ (d) *n*-octane ☐

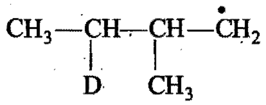
91. Main constituent (s) of LPG is/are: **[AFMC 2009]**
(a) methane ☐ (b) H_2, CH_4, isobutane ☐
(c) iso-butane, propane ☐ (d) none of these ☐

92. Consider the following reaction,

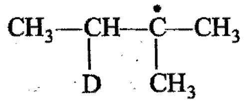


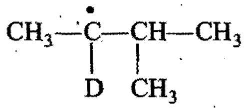
$$CH_3—\underset{D}{CH}—\underset{CH_3}{CH}—CH_3 + \dot{B}r \longrightarrow X + HBr$$

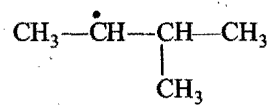
Identify the structure of major product X :
[IIT (S) 2002]

(a) 

$CH_3—\underset{D}{CH}—\underset{CH_3}{CH}—\dot{C}H_2$ ☐

(b) 
$CH_3-\underset{D}{\underset{|}{CH}}-\overset{\bullet}{\underset{CH_3}{\underset{|}{C}}}-CH_3$ ☐

(c) 
$CH_3-\overset{\bullet}{\underset{D}{\underset{|}{C}}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$ ☐

(d) 
$CH_3-\overset{\bullet}{CH}-\underset{CH_3}{\underset{|}{CH}}-CH_3$ ☐

93. Which hydrocarbon is mainly present in gobar gas? **[AFMC 2003]**

(a) Butane ☐ (b) Propane ☐
(c) Methane ☐ (d) Ethane ☐

94. On mixing certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloro alkane. The alkane could be: **[AIEEE 2003; JEE (WB) 2010]**

(a) propane ☐ (b) pentane ☐
(c) iso-pentane ☐ (d) neo-pentane ☐

95. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon? **[AIEEE 2004]**

(a) Ethyl acetate ☐ (b) Acetic acid ☐
(c) Acetamide ☐ (d) Butan-2-one ☐

96. A petroleum fraction having boiling range 70–200°C and containing 6–10 carbon atoms per molecule is called: **[UPSEAT 2004]**

(a) natural gas ☐ (b) gas oil ☐
(c) gasoline ☐ (d) kerosene ☐

97. The compound having only primary hydrogen atoms is: **[AIIMS 2004]**

(a) butane ☐ (b) iso-butene ☐
(c) cyclohexane ☐ (d) 2,3-dimethylbutene ☐

98. Octane number can be changed by: **[AFMC 2004]**

(a) isomerisation ☐ (b) alkylation ☐
(c) cyclisation ☐ (d) all of these ☐

99. Which of the following yields both alkane and alkene? **[AFMC 2004]**

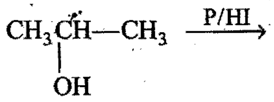
(a) Kolbe's reaction ☐ (b) Williamson's synthesis ☐
(c) Wurtz reaction ☐ (d) Sandmeyer's reaction ☐

100. 2-Methyl butane on reacting with bromine in the presence of sunlight gives mainly: **[AIEEE 2005]**

(a) 1-bromo-2-methylbutane ☐
(b) 2-bromo-2-methylbutane ☐
(c) 2-bromo-3-methylbutane ☐
(d) 1-bromo-3-methylbutane ☐

101. Which of the following reactions will not give propane? **[DPMT 2005]**

(a) $CH_3CH_2CH_2Cl \xrightarrow[H_2O]{Mg/ether}$ ☐

(b) 
$CH_3\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{P/HI}$ ☐

(c) $CH_3HC{=}CH_2 \xrightarrow[CH_3COOH]{B_2H_6}$ ☐

(d) $CH_3COCl \xrightarrow[H_2O]{CH_3MgX}$ ☐

102. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is: **[AIEEE 2005]**

(a) *n*-hexane ☐ (b) 2,3-dimethyl butane ☐
(c) 2,2-dimethyl butane ☐ (d) 2-methyl pentane ☐

103. X is heated with sodalime and gives ethane. X is: **[AFMC 2005]**

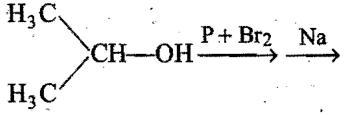
(a) ethanoic acid ☐ (b) methanoic acid ☐
(c) propanoic acid ☐ (d) either (a) or (c) ☐

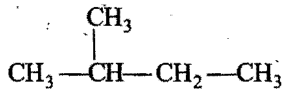
104. In order to get propane gas, which of the following should be subjected to sodalime decarboxylation? **[BVP 2006]**

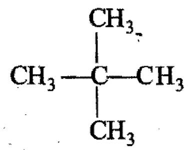
(a) Sodium formate ☐
(b) Mixture of sodium acetate and sodium ethanoate ☐
(c) Sodium butyrate ☐
(d) Sodium propionate ☐

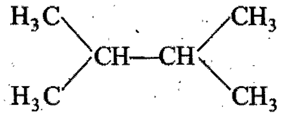
105. Methyl bromide is converted into ethane by heating it in ether medium with: **[CET (Karnataka) 2006; CET Engg. (Pb.) 2007]**

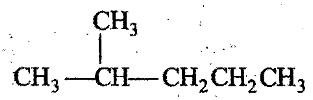
(a) Al ☐ (b) Zn ☐
(c) Na ☐ (d) Cu ☐

106. 
X; X is: **[DCE 2006]**

(a) 
$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$ ☐

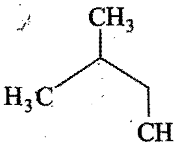
(b) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$ ☐

(c) 
☐

(d) 
$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2CH_2CH_3$ ☐

107. Petroleum is obtained from water gas, name of the reaction involved is: **[DCE 2006]**

(a) Fischer-Tropsch ☐ (b) Bergius ☐
(c) Dow's ☐ (d) Kjeldahl's ☐

108. 
$\xrightarrow{Cl_2,\, h\nu}$ N (isomeric products),

$C_5H_{11}Cl \xrightarrow[\text{distillation}]{\text{Fractional}}$ M (isomeric products)

Give the number of N and M: **[IIT 2006]**

(a) 6, 6 ☐ (b) 6, 4 ☐
(c) 4, 4 ☐ (d) 3, 3 ☐

109. When CH_3COOH reacts with CH_3MgX, then: **[BCECE (Med.) 2006]**
(a) CH_3COX is formed ☐
(b) hydrocarbon is formed ☐
(c) acetone is formed ☐
(d) alcohol is formed ☐

110. Which of the following liberates methane on treatment with water? **[CMC (Med.) Vellore 2007]**
(a) Silicon carbide ☐ (b) Calcium carbide ☐
(c) Beryllium carbide ☐ (d) Magnesium carbide ☐

111. The geometry of methane molecule is: **[MGIMS (Med.) 2007]**
(a) tetrahedral ☐ (b) pyramidal ☐
(c) octahedral ☐ (d) square planar ☐

112. Alkyl halides react with dialkyl copper reagents to give: **[UPSEE (Engg.) 2007]**
(a) alkenyl halides ☐ (b) alkanes ☐
(c) alkyl copper halides ☐ (d) alkenes ☐

113. Which of the following isomeric heptanes can yield seven different monochlorinated products upon free radical chlorination? **[PMT (Kerala) 2010]**
(a) 2,3-Dimethylpentane ☐ (b) 2,2-Dimethylpentane ☐
(c) 3-Methylhexane ☐ (d) 2-Methylhexane ☐
(e) 2,4-Dimethylpentane ☐

114. Which of the following has highest knocking property? **[AFMC 2007]**
(a) Aromatic hydrocarbons ☐
(b) Olefins ☐
(c) Branched chain paraffins ☐
(d) Straight chain paraffins ☐

115. Octane number can be changed by: **[AMU (Med.) 2007]**
(a) isomerisation ☐ (b) alkylation ☐
(c) cyclisation ☐ (d) all of these ☐

116. Which of the following has lowest octane number? **[CMC (Med.) Vellore 2007]**
(a) *n*-Hexadecane ☐ (b) iso-Octane ☐
(c) *n*-Hexane ☐ (d) *n*-Heptane ☐

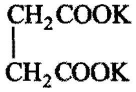
117. The treatment of CH_3MgX with $CH_3—C{\equiv}C—H$ produces: **[AIEEE 2008]**
(a) CH_4 ☐ (b) $CH_3HC{=}CH_2$ ☐
(c) $CH_3—C{\equiv}C—CH_3$ ☐ (d) $CH_3HC{=}CHCH_3$ ☐

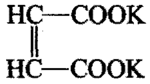
118. $CH_3CH_3 + HNO_3 \xrightarrow{675K} ?$ **[VITEEE 2008]**
(a) $CH_3CH_2NO_2$ ☐
(b) $CH_3CH_2NO_2 + CH_3NO_2$ ☐
(c) $2CH_3NO_2$ ☐
(d) $H_2C{=}CH_2$ ☐

SET II: This set contains questions with two or more correct answers.

119. Which of the following carbides can be used to prepare methane by its action with water? **[BHU (Mains) 2007]**
(a) Aluminium carbide ☐ (b) Beryllium carbide ☐
(c) Calcium carbide ☐ (d) Silicon carbide ☐

120. Methane can be prepared by:
(a) alkyl magnesium bromide ☐
(b) Wurtz reaction ☐
(c) decarboxylation ☐
(d) Friedel-Crafts reaction ☐

121. Kolbe's electrolytic method can be applied on:
(a) CH_3COONa ☐ (b)

$\begin{array}{l} CH_2COOK \\ | \\ CH_2COOK \end{array}$ ☐

(c)

$\begin{array}{l} HC—COOK \\ \| \\ HC—COOK \end{array}$ ☐ (d) C_6H_5COONa ☐

122. Both methane and ethane may be obtained by one step reaction from:
(a) CH_3I ☐ (b) CH_3COOK ☐
(c) $H_2C{=}CH_2$ ☐ (d) CH_3MgBr ☐

123. Grignard reagent gives alkane with:
(a) C_2H_5OH ☐ (b) HOH ☐
(c) NH_3 ☐ (d) $C_2H_5NH_2$ ☐

124. $CH_3CH_2CH_3 \xrightarrow{400\text{-}600°C} X + Y$
X and *Y* are: **[UPSEE (Engg.) 2008]**
(a) H_2 and methane ☐ (b) H_2 and ethylene ☐
(c) H_2 and propylene ☐ (d) methane and ethylene ☐

125. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms two monochloro derivatives. The alkane could be: **[BHU (Mains) 2008]**
(a) propane ☐ (b) pentane ☐
(c) iso-butane ☐ (d) neo-pentane ☐

ASSERTION-REASON TYPE QUESTIONS

Following questions consist of an **Assertion (A)** and **Reason (R).** Use the following keys to select the correct answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation of the (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation of the (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) Corey-House reaction can be used to prepare both symmetrical and asymmetrical alkane.
(R) Lithium metal is involved in it.

2. (A) The octane number of branched chain hydrocarbon is higher than that of unbranched chain hydrocarbon.
(R) The branched chain hydrocarbons are more volatile as compared to unbranched chain hydrocarbons.

3. (A) The boiling point of *n*-alkanes increases with increase in number of carbon atoms.
(R) van der Waals' force of attraction increases with increase in number of carbon and molecular mass.

4. (A) In cracking of alkanes C—C bond is broken but not C—H bond.
(R) Bond energy of C—C bond is less than C—H bond.

5. (A) Melting point of neo-pentane is greater than that of *n*-pentane but the boiling point of *n*-pentane is more than that of neo-pentane.
(R) Melting point depends upon packing in crystal lattice whereas boiling point depends upon surface area of the molecule.

6. (A) Fuel in aeroplane has a high percentage of highly branched chain alkanes.
(R) Octane number of branched alkanes is less than that of straight chain or normal alkanes.

7. (A) Propene and cyclopropane both give addition reactions only.
(R) Propene and cyclopropane are ring chain isomer.

ANSWERS

OBJECTIVE QUESTIONS

1. (a)	**2.** (b)	**3.** (a)	**4.** (b)	**5.** (b)	**6.** (c)	**7.** (c)	**8.** (d)	**9.** (b)	**10.** (c)
11. (b)	**12.** (b)	**13.** (b)	**14.** (a)	**15.** (d)	**16.** (b)	**17.** (a)	**18.** (a)	**19.** (c)	**20.** (d)
21. (d)	**22.** (c)	**23.** (b)	**24.** (c)	**25.** (d)	**26.** (d)	**27.** (d)	**28.** (b)	**29.** (b)	**30.** (a)
31. (a)	**32.** (d)	**33.** (b)	**34.** (a)	**35.** (a)	**36.** (c)	**37.** (b)	**38.** (d)	**39.** (d)	**40.** (c)
41. (c)	**42.** (c)	**43.** (d)	**44.** (c)	**45.** (a)	**46.** (c)	**47.** (b)	**48.** (c)	**49.** (b)	**50.** (a)
51. (d)	**52.** (c)	**53.** (b)	**54.** (d)	**55.** (d)	**56.** (a)	**57.** (c)	**58.** (d)	**59.** (a)	**60.** (a)
61. (b)	**62.** (c)	**63.** (b)	**64.** (c)	**65.** (d)	**66.** (b)	**67.** (c)	**68.** (a)	**69.** (d)	**70.** (a)
71. (c)	**72.** (a)	**73.** (d)	**74.** (b)	**75.** (c)	**76.** (a)	**77.** (d)	**78.** (d)	**79.** (a)	**80.** (c)
81. (a)	**82.** (d)	**83.** (a)	**84.** (c)	**85.** (d)	**86.** (a)	**87.** (a)	**88.** (c)	**89.** (b)	**90.** (b)
91. (c)	**92.** (b)	**93.** (c)	**94.** (d)	**95.** (d)	**96.** (c)	**97.** (b)	**98.** (d)	**99.** (a)	**100.** (b)
101. (d)	**102.** (b)	**103.** (c)	**104.** (c)	**105.** (c)	**106.** (c)	**107.** (a)	**108.** (b)	**109.** (b)	**110.** (c)
111. (a)	**112.** (b)	**113.** (c)	**114.** (d)	**115.** (d)	**116.** (a)	**117.** (a)	**118.** (b)	**119.** (a,b)	**120.** (a,c)
121. (a,b,c)	**122.** (a,b)	**123.** (a,b,c,d)	**124.** (c,d)	**125.** (a,c)					

ASSERTION-REASON TYPE QUESTIONS

1. (b)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (a)	**6.** (c)	**7.** (b)

BRAIN STORMING PROBLEMS

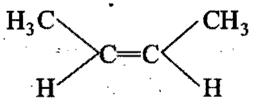
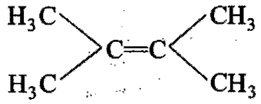
1. Methane can be prepared by:
(a) Wittig reaction ☐ (b) Wurtz method ☐
(c) Kolbe's method ☐ (d) Decarboxylation ☐
(e) Corey-House method

2. Match List I with List II and select the correct answer from the given codes:

List I Reaction	List II Metals used
A. Wurtz reaction	1. Ni
B. Sabatier Senderen's reaction	2. Zn
C. Frankland reaction	3. Li
D. Corey-House synthesis	4. Na

Codes :

	A	B	C	D
(a)	1	2	3	4
(b)	4	1	2	3
(c)	3	2	4	1
(d)	2	4	2	3

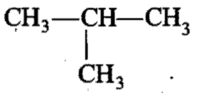
3. Which of the following compounds will give the maximum yield of alkane on hydrogenation?
(a) $H_2C{=}CH_2$ ☐
(b) $CH_3-CH{=}CH_2$ ☐
(c)  ☐
(d)  ☐

4. If a mixture of methane, ammonia and oxygen is passed over Pt-gauge at 700°C then the product will be:
(a) HCOOH ☐ (b) HCN ☐
(c) CH_3NH_2 ☐ (d) all of these ☐

5. Which of the following alkanes is affected by $AlCl_3$?
(a) CH_4 ☐ (b) C_2H_6 ☐
(c) C_3H_8 ☐ (d) C_4H_{10} (*n*-butane) ☐

6. Which of the following cannot be considered as a mechanistic step in chain reaction of methane with Cl_2?
(a) $Cl_2 \longrightarrow Cl^*$ ☐
(b) $CH_4 + Cl^* \longrightarrow CH_3Cl + H^*$ ☐
(c) $Cl^* + CH_4 \longrightarrow \overset{*}{C}H_3 + HCl$ ☐
(d) $Cl^* + \overset{*}{C}H_3 \longrightarrow CH_3Cl^*$ ☐

7. The nitration of which of the following alkanes will give the maximum number of products?
(a) Propane ☐ (b) Neo-pentane ☐
(c) Ethane ☐ (d) Methane ☐

8. Which of the following cannot be prepared by the Wurtz reaction?
(a) CH_3-CH_3 ☐ (b)  $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$ ☐
(c) $(CH_3)_2CHCH_3$ ☐ (d) $CH_3CH_2CH_2CH_3$ ☐

9. Which among the following reagents convert alkyl halide into alkane?
(a) Bu_3SnH ☐ (b) Na/dry ether ☐
(c) R_2CuLi ☐ (d) All of these ☐

10. Which among the following genera (plants) is the future source of hydrocarbons?
(a) Cassia ☐ (b) Accasia ☐
(c) Euphorbia ☐ (d) Thia ☐

11. Select the correct statements among the following:
(a) methane is present in the atmosphere of Jupiter ☐
(b) in Fischer-Tropsch process, alkane is synthesised by liquefaction of coal ☐
(c) methane on pyrolysis give carbon black ☐
(d) pyrolysis of alkanes is also called as isomerisation ☐

12. Antiknocking agent used for unleaded gasoline is:
(a) BXT ☐ (b) TBA ☐
(c) MTBE ☐ (d) all of these ☐

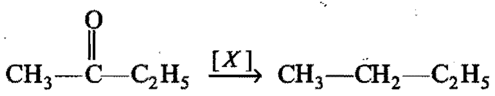
13. By which of the following reagents, butanoic acid can be converted into butane?
(a) Red P/HI ☐ (b) NaOH/CaO ☐
(c) CH_3MgBr ☐ (d) All of these ☐

14. Which among the following is known as Gilman reagent?
(a) R_2CuLi ☐ (b) LiI ☐
(c) CuI ☐ (d) Li ☐

15. Which among the following carbides on hydrolysis give alkane?
(a) Al_4C_3 ☐ (b) CaC_2 ☐
(c) Be_2C ☐ (d) SiC ☐

16. Methane cannot be synthesised by which of the following methods?
(a) Wurtz reaction ☐
(b) Kolbe's reaction ☐
(c) Corey-House synthesis ☐
(d) All of the above ☐

17. In the given reaction,



$$CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5 \xrightarrow{[X]} CH_3-CH_2-C_2H_5$$

X will be:
(a) $LiAlH_4$ ☐ (b) $NaBH_4$ ☐
(c) Bu_3SnH ☐ (d) NH_2-NH_2/OH^- ☐

18. What will be the least molecular mass of an alkane which is optically active?
(a) 70 ☐ (b) 80 ☐
(c) 90 ☐ (d) 100 ☐

19. The products obtained in the reaction,

$$C_6H_5CH_2—CH_3 \xrightarrow[273\ K]{Cl_2,\ h\nu}$$

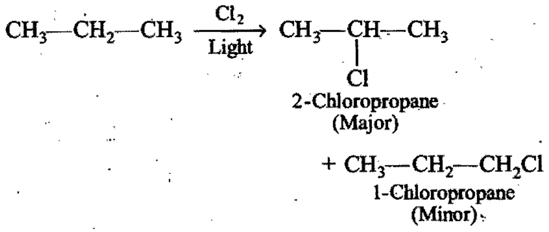
is/are:

(a) $C_6H_5CHCl—CH_3$ ☐ (b) $C_6H_5CH_2—CH_2Cl$ ☐
(c) $C_6H_5CCl_2—CH_3$ ☐ (d) $C_6H_5CHClCH_2Cl$ ☐

20. Chlorination of propane is carried out in the presence of sunlight. The % yield of major and minor alkyl halides will be:

(a) 92%, 8% ☐ (b) 70%, 30% ☐
(c) 80%, 20% ☐ (d) 86%, 14% ☐

[**Hint :**



$$CH_3—CH_2—CH_3 \xrightarrow[\text{Light}]{Cl_2} CH_3—\underset{\underset{Cl}{|}}{CH}—CH_3 \quad \text{2-Chloropropane (Major)} \quad + CH_3—CH_2—CH_2Cl \quad \text{1-Chloropropane (Minor)}$$

Ratio of products can be calculated as,

$$\frac{\text{1-Chloropropane}}{\text{2-Chloropropane}} = \frac{\text{Number of 2° hydrogen}}{\text{Number of 1° hydrogen}} \times \frac{\text{Reactivity of 1° hydrogen}}{\text{Reactivity of 2° hydrogen}}$$

$$= \frac{2}{6} \times \frac{1}{3.8} = \frac{1}{11.4}$$

$$\text{\% of 2-Chloropropane} = \frac{11.4}{12.4} \times 100 = 92\%$$

% of 1-Chloropropane = 100 − 92 = 8%]

21. The highest boiling point is expected for:

(a) iso-octane ☐
(b) *n*-octane ☐
(c) 2,2,3,3-tetramethyl butane ☐
(d) *n*-pentane ☐

22. Tetraethyl lead (TEL) in petrol was used as antiknocking agent, which creates lead pollution. In order to avoid lead pollution, the substitute of TEL is used in unleaded-petrol. The substitute is denoted as:

(a) AK–33–X ☐ (b) BK–33–X ☐
(c) CK–33–X ☐ (d) DK–33–X ☐

[**Hint :** AK–33–X; Its chemical name is cyclopentadienyl manganese tricarbonyl.]

23. If an alkane has number of carbon atoms equal to *n*, then the number of moles of oxygen required for its complete combustion is:

(a) $\frac{3n+1}{2}$ ☐ (b) $2n$ ☐
(c) $\frac{n}{2}$ ☐ (d) $(2n+1)$ ☐

[**Hint :** $C_nH_{2n+2} + \frac{(3n+1)}{2}O_2 \longrightarrow nCO_2 + \frac{(2n+2)}{2}H_2O$]

24. Which of the following is the condition for best yield of C_2H_5Cl?

(a) $C_2H_6\ (\text{excess}) + Cl_2 \xrightarrow{\text{UV light}}$ ☐
(b) $C_2H_6 + SOCl_2 \xrightarrow[\text{room temp.}]{\text{dark}}$ ☐
(c) $C_2H_6 + Cl_2\ (\text{excess}) \longrightarrow$ ☐
(d) $C_2H_6 + PCl_5 \xrightarrow{\text{UV light}}$ ☐

25. An alkane with even number of carbon only, can result in:

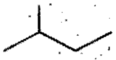
(a) Sabatier Senderens reaction ☐
(b) Wurtz reaction ☐
(c) Kolbe's electrolytic reaction ☐
(d) Grignard reaction ☐

26. *n*-Hexane can be converted to benzene by the treatment with:

(a) alk. $KMnO_4$ ☐ (b) alc. KOH ☐
(c) Cr_2O_3 at 770 K ☐ (d) $LiAlH_4$ ☐

27. Following are the isomers of molecular formula for C_5H_{12}:

I



II

III

Decreasing order of their boiling points is:

(a) I < II < III ☐ (b) I > II > III ☐
(c) II > I > III ☐ (d) III > I > II ☐

28. An unknown carboxylic acid salt on Kolbe's electrolysis form cyclobutane; the carboxylic acid can be:

(a) adipic acid ☐ (b) hexanoic acid ☐
(c) succinic acid ☐ (d) fumaric acid ☐

29. A compound has molecular mass 42. It should be:

(a) propane ☐ (b) cyclopropane ☐
(c) propene ☐ (d) butane ☐

30. Petrol is a mixture hydrocarbons from C_6 to C_8. The quality of petrol is determined in terms of octane number. The higher the octane number, better is the quality of fuel. The correct order of octane number is:

(a) cycloalkanes < alkenes < alkanes < aromatic hydrocarbons
(b) alkenes < alkanes < aromatic hydrocarbons < cycloalkanes
(c) alkanes < aromatic hydrocarbons < cycloalkanes < alkenes
(d) alkanes < alkenes < cycloalkanes < aromatic hydrocarbons

ANSWERS : BRAIN STORMING PROBLEMS

1. (d)	2. (b)	3. (a)	4. (b)	5. (d)	6. (b)	7. (a)	8. (b,c)	9. (d)	10. (c)
11. (a,b,c)	12. (d)	13. (a)	14. (a)	15. (a)	16. (d)	17. (d)	18. (d)	19. (a,c)	20. (a)
21. (b)	22. (a)	23. (a)	24. (a)	25. (c)	26. (c)	27. (b)	28. (a)	29. (b,c)	30. (d)

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Adolf von Baeyer suggested that, since carbon prefers to have tetrahedral geometry with bond angles of approximately 109°, ring sizes other than five and six may be too strained to exist. Baeyer based his hypothesis on the simple geometrical notion that a three-membered ring (cyclopropane) should be an equilateral triangle with bond angles to 60°, a four membered ring (cyclobutane) should be a square with bond angles of 90° and so on. According to Baeyer's analysis, cyclopropane, with a bond angle compression of $109° - 60° = 49°$, should have a large amount of angle strain and must therefore be highly reactive. Cyclohexane becomes puckered to releave its strain. The angular deviation of cycloalkane is (–11°). Greater is the angular deviation more is the torsional strain.

Answer the following questions:

1. Which of the following is most reactive cycloalkane?
   (a) Cyclopropane
   (b) Cyclobutane
   (c) Cyclopentane
   (d) Cyclohexane
2. Which among the following is most strained cycloalkane?
   (a) Cyclopropane
   (b) Cyclobutane
   (c) Cyclopentane
   (d) Cyclohexane
3. The tendancy of cyclopropane (I), cyclobutane (II) and cyclopentane (III) to form addition compounds is in the order:
   (a) $I > II > III$
   (b) $I = II > III$
   (c) $I > II = III$
   (d) $I = III > II$
4. Which among the following has greatest bond angle?
   (a) Cyclopropane
   (b) Cyclobutane
   (c) Cyclopentane
   (d) Cyclohexane
5. Which of the following cycloalkanes has zero strain energy?
   (a) Cyclobutane
   (b) Cyclopentane
   (c) Cyclohexane
   (d) Cyclopropane

Passage 2

Wurtz reaction involves the condensation of two molecules of alkyl halides in the presence of sodium and dry ether.

$$R—X + 2Na + X—R \xrightarrow{\text{Dry ether}} R—R + 2NaX$$

In this reaction small amount of alkene is also formed as byproduct.

$$CH_3CH_2Br + CH_3CH_2Br \xrightarrow{\text{Na /Dry ether}}$$
$$CH_3—CH_2—CH_2—CH_3 + \underbrace{H_2C{=}CH_2 + CH_3—CH_3}_{\text{Byproducts}}$$

Tertiary alkyl halides do not give Wurtz reaction. Frankland reaction is similar but has certain advantages over Wurtz reaction. It is useful in the synthesis of symmetrical alkanes. Frankland reaction is shown by primary, secondary as well as tertiary alkyl halide.

Answer the following questions.

1. Which of the following alkanes is not obtained from Wurtz reaction?
   (a) Methane
   (b) Ethane
   (c) Propane
   (d) Butane
2. Disproportionation takes place in:
   (a) Wurtz reaction
   (b) Frankland reaction
   (c) both of these
   (d) none of these
3. Which among the following compounds will give Wurtz reaction?
   (a) $CH_2{=}CH—Br$
   (b) $C_6H_5—Br$
   (c) $H_2C{=}CH—CH_2—Br$
   (d) None of these
4. A mixture of ethyl iodide and methyl iodide is subjected to the Wurtz reaction. The products formed are:
   (a) ethane
   (b) butane
   (c) propane
   (d) 2-methyl propane
5. Which of the following compounds cannot be prepared by Wurtz reaction?
   (a) Ethane
   (b) Iso-butane
   (c) *n*-Butane
   (d) Neo-pentane

Passage 3

Gasoline infact is a poor fuel for internal combustion engine. When such fuels are used in an engine, combustion can be initiated before the spark plug fires. This produces 'Knocking' or 'Pinging' in the running engine. The quality of fuel is indicated by its **octane number.** Straight chain hydrocarbons have low octane number. A scale was set up to evaluate this important knock property of gasoline. Iso-octane, an excellent fuel with a highly branched structure, was arbitrarily given a rating (octane number = 100), *n*-Heptane being a poor fuel was given the octane number of zero.

The octane number of gasoline can also be increased by the addition of other compounds besides the tetraethyl lead (TEL) which is a pollutant. The compounds used in gasoline to improve its quality or octane number are:

BTX : Benzene Toluene Xylene
TBA : Tertiary Butyl Alcohol
MTBE : Methyl Tertiary Butyl Alcohol

Quality of diesel fuel is measured in terms of cetane number. Cetane compound is already given 100 cetane number whereas α-methyl naphthalene is given the cetane number zero.

Answer the following questions:

1. What is the IUPAC name of the compound having octane number equal to 100?
   (a) *n*-Heptane
   (b) 2,2,4-Trimethyl pentane
   (c) 2,2,3-Trimethyl heptane
   (d) 2,2,4,4-Tetramethyl butane
2. Select the correct statements among the following:
   (a) cetane number is assigned for diesel fuel
   (b) cetane number is assigned for kerosine oil
   (c) greater is the cetane number, more efficient is the fuel
   (d) cetane number and octane number are same

3. Hexadecane is commonly called:
(a) octane
(b) cetane
(c) gasohol
(d) natalite

4. Octane number of regular gasoline is 87. It has same knocking property as:
(a) a mixture containing 87% iso-octane and 13% heptane
(b) a mixture containing 13% iso-octane and 87% heptane
(c) 87 g iso-octane dissolved in 1 litre alcohol
(d) 13 g iso-octane dissolved in 1 litre water

5. Select the correct statement about the efficiency of gasoline:
(a) branched alkanes are better fuel than straight chain alkane
(b) lesser is the octane number, greater is the efficiency of fuel
(c) high quality fuel has greater knocking property
(d) all of these

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	**1.** (a)	**2.** (a)	**3.** (a)	**4.** (d)	**5.** (c)
Passage 2	**1.** (a)	**2.** (a)	**3.** (c)	**4.** (a,b,c)	**5.** (b,d)
Passage 3	**1.** (b)	**2.** (a,c)	**3.** (b)	**4.** (a)	**5.** (a)

7

UNSATURATED HYDROCARBONS

[Alkenes (Olefins) and Alkynes (Acetylenes)]

7.1 INTRODUCTION

The open chain hydrocarbons which contain lesser number of hydrogen atoms than the corresponding alkanes containing same number of carbon atoms are called **unsaturated hydrocarbons.** The members which contain two hydrogen atoms less than the corresponding saturated hydrocarbons are known as **olefins*** and are represented by the general formula C_nH_{2n}. These are characterised by the presence of a double bond between two adjacent carbon atoms, $>C{=}C<$, in the molecule. In IUPAC system, the olefins are termed as **alkenes.****

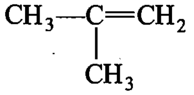
The unsaturated hydrocarbons which are characterised by the presence of a triple bond between two adjacent carbon atoms, $-C{\equiv}C-$, in the molecule and contain four hydrogen atoms less than the corresponding saturated hydrocarbons are termed **alkynes.** These are represented by a general formula C_nH_{2n-2}.

Alkenes seldom occur free in nature. Lower alkenes occur in coal gas in minute quantities. Ethylene is present in natural gas. However, alkenes are produced in large amounts by cracking of petroleum.

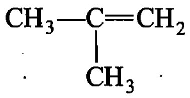
7.2 NOMENCLATURE OF ALKENES

There are three ways of naming the alkenes or olefins.

(i) The common system : The common names of first three members are derived from the corresponding alkanes by changing the ending -ane to -ylene. Greek letters are used to distinguish isomers as to indicate the position of double bond. α, β, γ, etc., are written to indicate the carbon atoms having double bond.

$H_2C{=}CH_2$	(Ethane – ane + ylene)	Ethylene
$CH_3{-}CH{=}CH_2$	(Propane – ane + ylene)	Propylene
$CH_3{-}CH_2{-}CH{=}\overset{\alpha}{C}H_2$	(Butane – ane + ylene)	α-Butylene
$CH_3{-}CH{=}\overset{\beta}{C}H{-}CH_3$	(Butane – ane + ylene)	β-Butylene
 $CH_3{-}\underset{\displaystyle CH_3}{\underset{\vert}{C}}{=}CH_2$	(Isobutane – ane + ylene)	Iso-butylene
$CH_3CH_2CH_2CH{=}\overset{\alpha}{C}H_2$		α-Amylene
$CH_3CH_2CH{=}\overset{\beta}{C}H{-}CH_3$		β-Amylene

(ii) As derivatives of ethylene : Olefins are named as substituted derivatives of ethylene. The names are derived by adding the name of alkyl groups replacing the hydrogen atom/atoms of the ethylene to the parent name ethylene. The dialkyl derivatives are of two types, symmetrical or unsymmetrical, depending upon whether the alkyl groups are attached to the same carbon atom or to different carbon atoms.

$CH_3{-}CH{=}CH_2$	Methyl ethylene
$CH_3{-}CH{=}CH{-}CH_3$	Sym-dimethyl ethylene
 $CH_3{-}\underset{\displaystyle CH_3}{\underset{\vert}{C}}{=}CH_2$	Unsym-dimethyl ethylene

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* The term olefin has its origin from an old Dutch name of ethylene 'Olefiant gas' (oil forming gas) which refers to the oily nature of the product (ethylene chloride) formed by the combination of ethylene and chlorine.

Alkenes containing two carbon-carbon double bonds are called **dienes or **alkadienes.**

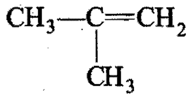
(iii) IUPAC system : The name is obtained by dropping the suffix -ane from the name of the corresponding alkane and adding the suffix -ene.

Alkane – ane + ene = Alkene

The position of the double bond is indicated by the number of the first carbon atom (lowest numbered) involved in the double bond. Alkyl groups are numbered, named and placed as prefixes in alphabetic order. When there are two or three double bonds in the molecule, the ending -ane of the corresponding alkane is replaced by -adiene or -atriene.

$H_2C{=}CH_2$ Ethene ; $CH_3CH{=}CH_2$ Propene

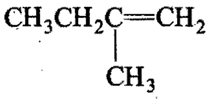
$CH_3CH_2CH{=}CH_2$ But-1-ene ; $CH_3CH{=}CHCH_3$ But-2-ene



$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$

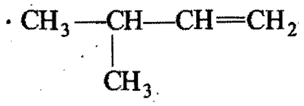
2-Methylprop-1-ene ; $CH_3CH_2CH_2CH{=}CH_2$ Pent-1-ene

$CH_3CH_2CH{=}CHCH_3$ Pent-2-ene ;



$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$

2-Methylbut-1-ene



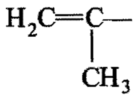
$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH_2$

3-Methylbut-1-ene ; $H_2C{=}CH{-}CH{=}CH_2$ Buta-1,3-diene

Alkenyl groups : The monovalent groups obtained by the removal of one hydrogen atom from alkenes are called alkenyl groups.

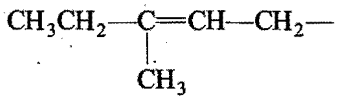
$H_2C{=}CH{-}$ Ethenyl (Vinyl) ; $H_2C{=}CH{-}CH_2{-}$ 2-Propenyl (Allyl)

$CH_3{-}CH{=}CH{-}$ 1-Propenyl ; $CH_3{-}CH{=}CH{-}CH_2{-}$ 2-Butenyl (Crotyl)



$H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}$

Isopropenyl
(1-Methylvinyl)

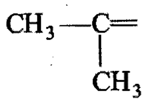


$CH_3CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2{-}$

3-Methylpent-2-enyl

Alkylidene groups :

$H_3C{-}CH{=}$ Ethylidene ; $CH_3{-}CH_2{-}CH{=}$ Propylidene ;



$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}$

Isopropylidene

7.3 ISOMERISM IN ALKENES

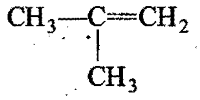
Alkenes can show the following types of isomerism. Ethene and propene do not show structural isomerism.

(a) Position isomerism : This is due to the position of double bond in the same molecular formula. Butene has two position isomers.

$CH_3CH_2CH{=}CH_2$ But-1-ene ; $CH_3CH{=}CHCH_3$ But-2-ene

(b) Chain isomerism : This is due to the difference in the nature of carbon skeleton:

$CH_3CH_2CH{=}CH_2$ But-1-ene ;

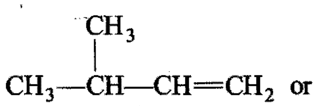


$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$

2-Methylpropene

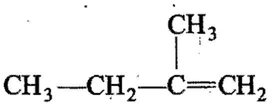
Chain isomers

$CH_3CH_2CH_2CH{=}CH_2$ Pent-1-ene ;



$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{CH}}{-}CH{=}CH_2$

3-Methylbut-1-ene or

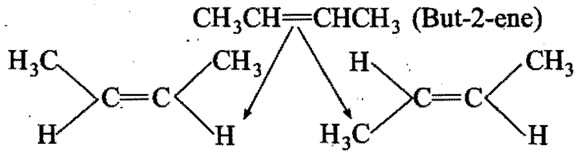


$CH_3{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$

2-Methylbut-1-ene

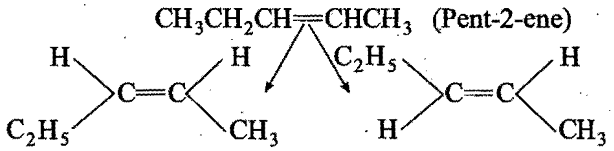
Chain isomers

(c) Geometrical isomerism : Due to restricted rotation about the double bond, the alkenes (with the exception of ethene and propene) show geometrical isomerism. But-2-ene shows geometrical isomerism.



Cis-form *Trans*-form

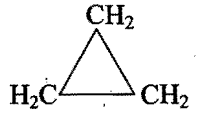
Pent-2-ene also shows geometrical isomerism.



Cis-form *Trans*-form

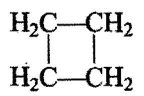
Besides the above three types, alkenes show ring-chain isomerism with cycloalkanes.

$CH_3CH{=}CH_2$ Propene ;



Cyclopropane

$CH_3CH_2CH{=}CH_2$ But-1-ene ;

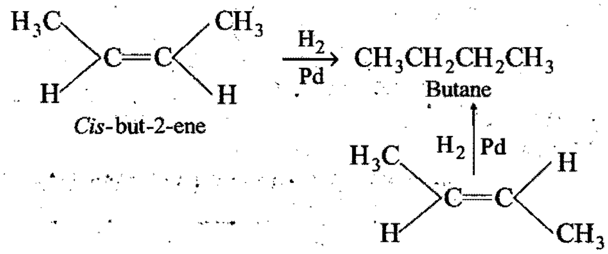


Cyclobutane

7.4 STABILITY OF ALKENES (HEATS OF HYDROGENATION)

The relative stability of alkenes can be determined by comparing their **enthalpies of hydrogenation,** (*i.e.,* the heat evolved when one molecule of alkene reacts with hydrogen).

So; heats of hydrogenation have been used to assess the relative stabilities of alkenes in much the same way as was described for heats of combustion as catalytic hydrogenation of but-1-ene, *cis*-but-2-ene or *trans*-but-2-ene yields the same product, butane in presence of catalyst such as Pd or Pt.



Cis-but-2-ene

Trans-but-2-ene

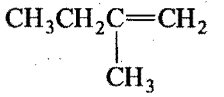
It has been observed that enthalpy of hydrogenation of *cis*-isomer is 120.0 kJ/mol and that of *trans*-isomer is 115.0 kJ/mol. Thus, the measured heats of hydrogenation reveal that *trans*-but-2-ene is 5 kJ/mol (1.2 kcal/mol) lower in energy than *cis*-but-2-ene and that *cis*-but-2-ene is 7 kJ/mol (1.7 kcal/mol) lower in energy than but-1-ene. In otherwords, the *trans*-isomer is 5 kJ/mol more stable than the *cis*-isomer.

The energy differences between the isomeric butenes as measured by their heats of hydrogenation are, within experimental error, equal to the differences in their heats of combustion.

Heats of hydrogenation can be used to estimate the stability of double bonds as structural units, even in alkenes, that are not isomers and also depends upon the position of double bonds. For example,

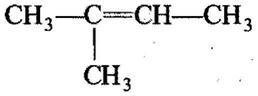
$CH_3CH_2CH_2CH{=}CH_2$

Pent-1-ene
(Monosubstituted)
$\Delta H = -126$ kJ/mol



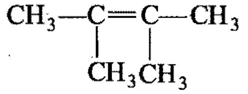
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$

2-Methylbut-1-ene
(Disubstituted)
$\Delta H = -119.5$ kJ/mol



$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_3$

2-Methylbut-2-ene
(Trisubstituted)
$\Delta H = -112.5$ kJ/mol



$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3$

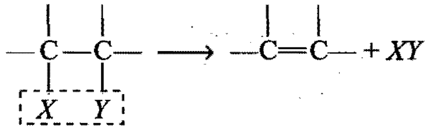
2,3-Dimethyl
but-2-ene
(Tetrasubstituted)
$\Delta H = -111.5$ kJ/mol

The **more substituted alkenes,** (*i.e.*, greater the number of alkyl groups attached to the double bond) **are more stable.** Thus, the order of stability of alkenes is:

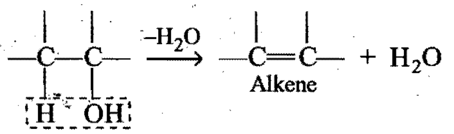
$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > RCH{=}CHR > RCH{=}CH_2 > H_2C{=}CH_2$$

7.5 GENERAL METHODS OF PREPARATION OF ALKENES

Alkenes containing upto five carbon atoms can be obtained in pure form from the petroleum. More complicated alkenes and also the simpler ones can be prepared by the application of any one of the general methods. Most of the methods involve elimination of atoms or groups from two adjacent carbon atoms from the molecules having only single bonds.



1. By dehydration of alcohols: An alcohol is converted into an alkene by dehydration, *i.e.*, elimination of a molecule of water.



Alkene

Alcohol

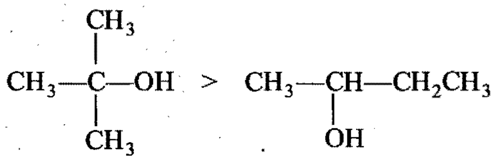
The dehydration of alcohols is generally carried out in either of two ways:

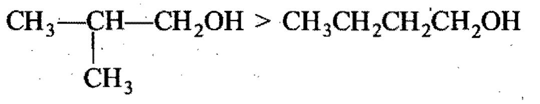
(a) heating the alcohol with acid catalyst like concentrated sulphuric acid or phosphoric acid H_3PO_4 or *p*-toluene sulphonic acid or P_2O_5 to temperatures as high as 200°C. or

(b) passing the vapours of alcohol over alumina (Al_2O_3) at 350 – 400°C, (Al_2O_3 serves as a **Lewis acid**).

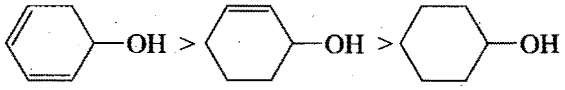
The ease of dehydration follows the following order:

Tertiary (3°) > Secondary (2°) > Primary (1°)





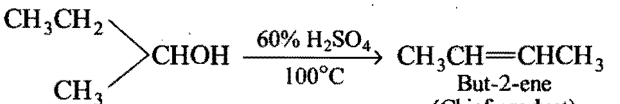
$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CH_2OH > CH_3CH_2CH_2CH_2OH$



(This sequence of reactivity is due to conjugate stabilization in the ring.)

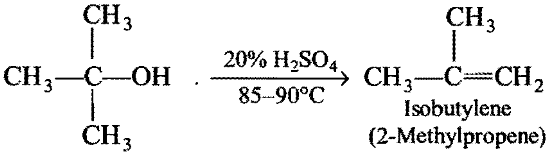
$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[170°C]{95\%\ H_2SO_4} \underset{\text{Ethylene}}{H_2C{=}CH_2}$$

$$\underset{\substack{\text{Butan-1-ol}\\(n\text{-Butyl alcohol) 1°}}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[140°C]{75\%\ H_2SO_4} \underset{\substack{\text{But-2-ene}\\\text{(Unexpected chief product)}}}{CH_3CH{=}CHCH_3}$$



Butan-2-ol
(*Sec.* butyl alcohol) 2°

But-2-ene
(Chief product)

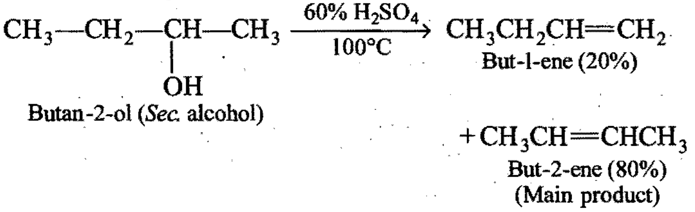


2-Methylpropan-2-ol
(*Tert.* butyl alcohol) 3°

Isobutylene
(2-Methylpropene)

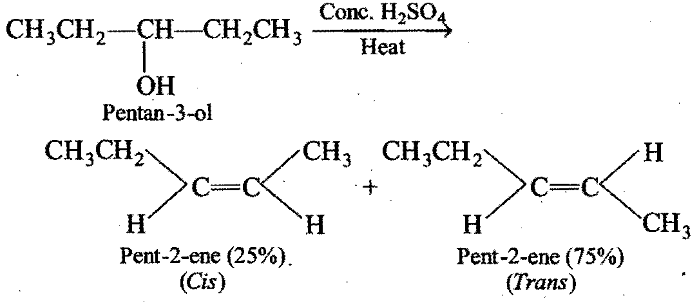
In the dehydration of secondary and tertiary alcohols, when there is a possibility of formation of two isomers, the hydrogen atom is preferentially eliminated from the adjacent carbon atom with the fewer number of hydrogen atoms.

This is **Saytzeff's rule.**



$$\underset{\text{Butan-2-ol (Sec. alcohol)}}{CH_3—CH_2—\underset{|}{\underset{OH}{CH}}—CH_3} \xrightarrow[100°C]{60\% \ H_2SO_4} \underset{\text{But-1-ene (20\%)}}{CH_3CH_2CH{=}CH_2} + \underset{\text{But-2-ene (80\%) (Main product)}}{CH_3CH{=}CHCH_3}$$

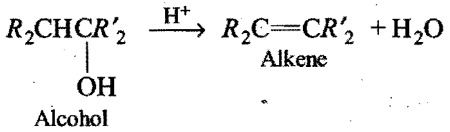
Dehydration of alcohols are **stereoselective** reactions in which a single starting compound can yield two or more stereoisomeric products and proceeds in the direction that produces the most highly substituted alkene and the more stable one is formed in greater amounts. A carbocation intermediate is involved and sometimes rearrangements take place during elimination. For example, butan-2-ol gives but-2-ene (80%) and more stable *trans*-stereoisomer predominates. Pentan-3-ol gives 75% *trans*-pent-2-ene and 25% *cis*-pent-2-ene and so on.



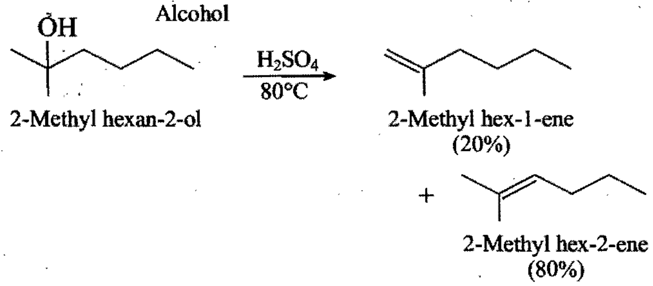
Pentan-3-ol

Pent-2-ene (25%) (*Cis*)

Pent-2-ene (75%) (*Trans*)



$$\underset{\text{Alcohol}}{R_2CH\underset{|}{\underset{OH}{C}}R'_2} \xrightarrow{H^+} \underset{\text{Alkene}}{R_2C{=}CR'_2} + H_2O$$



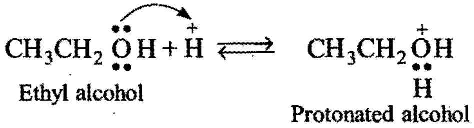
2-Methyl hexan-2-ol

2-Methyl hex-1-ene (20%)

2-Methyl hex-2-ene (80%)

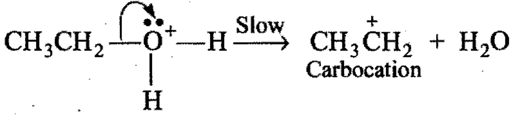
Mechanism : The mechanism of acid catalysed dehydration involves the formation of carbocation as an intermediate. The reaction is believed to occur in three steps:

1st step : Due to the presence of two lone pairs of electrons on oxygen, alcohols act as **weak bases.** Therefore, they react with strong mineral acids (H_2SO_4 or HCl etc.) to form a protonated alcohol (oxonium ion).



$$\underset{\text{Ethyl alcohol}}{CH_3CH_2\ddot{\underset{\bullet\bullet}{O}}H} + \overset{+}{H} \rightleftharpoons \underset{\text{Protonated alcohol}}{CH_3CH_2\overset{+}{\underset{\underset{H}{\bullet\bullet}}{O}}H}$$

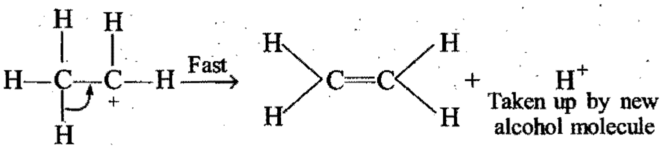
2nd step : The presence of positive charge on highly electronegative oxygen atom weakens the C—O bond. As a result, the protonated ethanol breaks with the elimination of a water molecule to form ethyl carbocation.



$$CH_3CH_2—\underset{\underset{H}{|}}{\overset{\bullet\bullet}{O^+}}—H \xrightarrow{Slow} \underset{\text{Carbocation}}{CH_3\overset{+}{C}H_2} + H_2O$$

This step is slow and hence is the rate-determining step of the reaction.

3rd step : Finally the carbocation being unstable and a reactive chemical species, readily loses a hydrogen ion to yield an alkene.



As alkene is more volatile than alcohol, it is easily driven out from the reaction mixture and thus the reaction is completed inspite of the reversible nature.

[The formation of ethylene from ethyl alcohol can also be explained in the following manner.]

1st step : When ethyl alcohol is reacted with H_2SO_4 at 170°C, it forms ethyl hydrogen sulphate.

$$C_2H_5OH + H—HSO_4 \longrightarrow C_2H_5HSO_4 + H_2O$$

2nd step : Ethyl hydrogen sulphate decomposes to form alkene.

$$C_2H_5HSO_4 \longrightarrow C_2H_4 + H_2SO_4$$

A controlling factor in the dehydration is the formation of carbocation. The alcohol is dehydrated more easily which forms a carbocation more easily. **The more stable the carbocation, the more easily it is formed.** Thus, the ease of dehydration follows the same sequence as the ease of formation of carbocations, *i.e.*, the stability of the carbocations.

Tertiary (3°) > Secondary (2°) > Primary (1°)

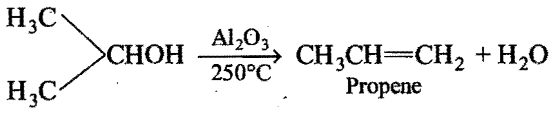
(The detailed mechanism is given in chapter 5).

The same sequence is observed when vapours of alcohols are passed over alumina for dehydration. Some other dehydrating agents are P_2O_5, BF_3, conc. H_3PO_4, dry HCl, $CaCl_2$ and $KHSO_4$, etc.

$$\text{Primary alcohol} \xrightarrow[350°C]{Al_2O_3} \text{Alkene} + H_2O$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[350°C]{Al_2O_3} \underset{\text{Ethylene}}{H_2C{=}CH_2} + H_2O$$

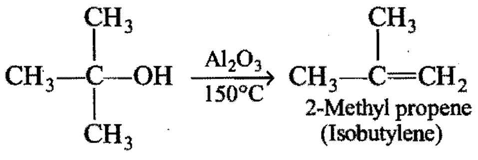
$$\text{Secondary alcohol} \xrightarrow[250°C]{Al_2O_3} \text{Alkene} + H_2O$$



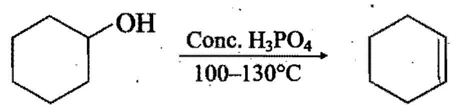
Isopropyl alcohol

Propene

$$\text{Tertiary alcohol} \xrightarrow[150°C]{Al_2O_3} \text{Alkene} + H_2O$$



$$\underset{\textit{Tert.}\text{ butyl alcohol}}{CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—OH} \xrightarrow[150°C]{Al_2O_3} \underset{\text{2-Methyl propene (Isobutylene)}}{CH_3—\overset{\overset{CH_3}{|}}{C}{=}CH_2}$$

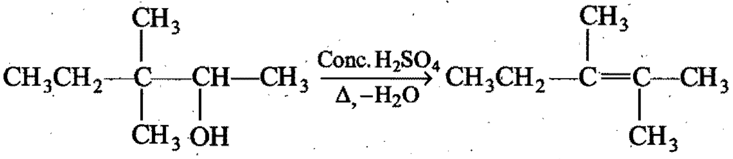


Cyclohexanol Cyclohexene

In the case of secondary and tertiary alcohols, the **Saytzeff's rule** is followed when dehydration is done with the help of alumina.

Retropinacol rearrangement (Wagner rearrangement) : It is the rearrangement in open chain compounds in which shifting of $C_6H_5^-$ (Ph^-); CH_3^- and H^- takes place to form more stable carbocation and hence more stable products. Shifting of these groups takes place in following sequence:

$$C_6H_5^-\ (Ph^-) > CH_3^- > H^-$$

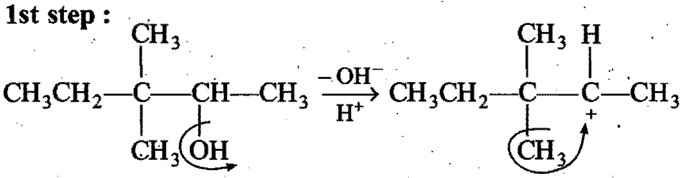


$$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3 \xrightarrow[\Delta,-H_2O]{Conc.\ H_2SO_4} CH_3CH_2-\overset{CH_3}{C}=\underset{CH_3}{C}-CH_3$$

3,3-Dimethyl pentan-2-ol 2,3-Dimethyl pent-2-ene

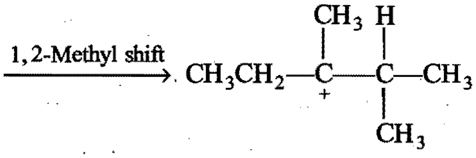
Mechanism:

1st step :



$$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3 \xrightarrow[H^+]{-OH^-} CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\underset{+}{\overset{H}{C}}-CH_3$$

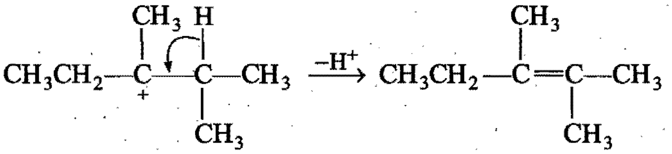
2° Carbocation (Less stable)



$$\xrightarrow{1,2\text{-Methyl shift}} CH_3CH_2-\underset{+}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3$$

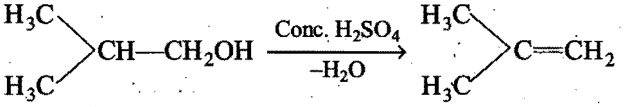
3° Carbocation (More stable)

2nd step :



$$CH_3CH_2-\underset{+}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3 \xrightarrow{-H^+} CH_3CH_2-\overset{CH_3}{C}=\underset{CH_3}{C}-CH_3$$

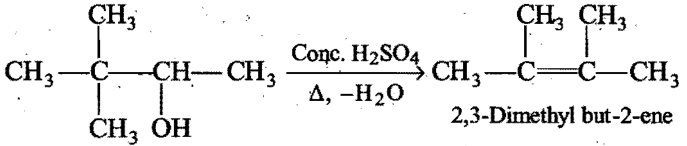
Other examples are :



2-Methyl propan-1-ol 2-Methyl propene (No methyl shift)

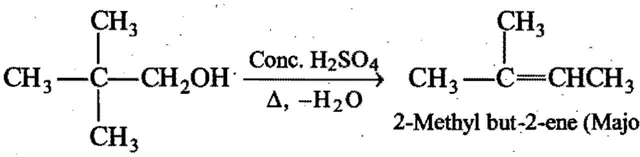
$$\xrightarrow[-H_2O]{Conc.\ H_2SO_4} H_2C=CH-CH_2-CH_3$$

But-1-ene (Involving methyl shift)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3 \xrightarrow[\Delta,\ -H_2O]{Conc.\ H_2SO_4} CH_3-\overset{CH_3}{C}=\overset{CH_3}{C}-CH_3$$

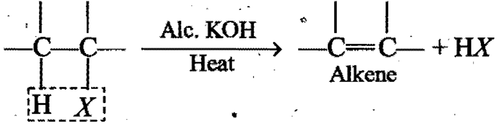
3,3-Dimethyl butan-2-ol 2,3-Dimethyl but-2-ene



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH \xrightarrow[\Delta,\ -H_2O]{Conc.\ H_2SO_4} CH_3-\overset{CH_3}{C}=CHCH_3$$

2,2-Dimethyl propan-1-ol 2-Methyl but-2-ene (Major)

2. By dehydrohalogenation of alkyl halides : Dehydrohalogenation involves removal of the halogen atom together with a hydrogen atom from a carbon adjacent to the one bearing the halogen. Alcoholic KOH is used for dehydrohalogenation.



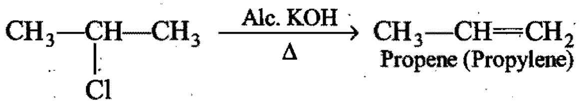
$$-\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}- \xrightarrow[Heat]{Alc.\ KOH} -\overset{|}{C}=\overset{|}{C}- + HX$$

Alkyl halide Alkene

The alkene is prepared by heating together the alkyl halide and a solution of potassium hydroxide in alcohol at higher temperature. For example:

$$CH_3CH_2CH_2Cl \xrightarrow[\Delta]{Alc.\ KOH} CH_3CH=CH_2 + KCl + H_2O$$

n-Propyl chloride Propene

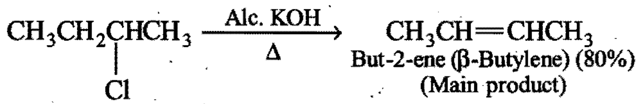


$$CH_3-\underset{Cl}{CH}-CH_3 \xrightarrow[\Delta]{Alc.\ KOH} CH_3-CH=CH_2$$

Isopropyl chloride Propene (Propylene)

$$CH_3CH_2CH_2CH_2Cl \xrightarrow[\Delta]{Alc.\ KOH} CH_3CH_2CH=CH_2$$

n-Butyl chloride But-1-ene (α-Butylene)



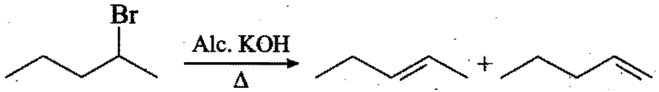
$$CH_3CH_2\underset{Cl}{C}HCH_3 \xrightarrow[\Delta]{Alc.\ KOH} CH_3CH=CHCH_3$$

(2-Chlorobutane) *Sec.* butyl chloride

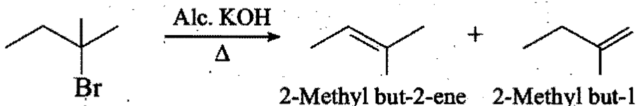
But-2-ene (β-Butylene) (80%) (Main product)

$$+ CH_3CH_2CH=CH_2$$

But-1-ene (20%)

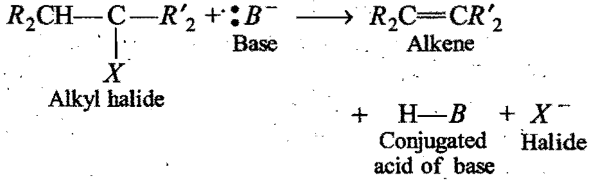


2-Bromopentane Pent-2-ene (Major) Pent-1-ene (Minor)



2-Bromo-2-methyl butane 2-Methyl but-2-ene (70%) 2-Methyl but-1-ene (30%)

So, in strong bases ($pK_a = -16$) hydroxide ions (OH^-) cause a proton and a halide to be lost from adjacent carbons of an alkyl halide to yield an alkene.



$$R_2CH-\underset{X}{C}-R'_2 + :B^- \longrightarrow R_2C=CR'_2 + H-B + X^-$$

Alkyl halide Base Alkene Conjugated acid of base Halide

This is an example of elimination (E_2) reaction as it follows the second order kinetics.

According to the **Saytzeff's rule**, when two alkenes may be formed; the alkene which is most substituted one predominates.

The formation of less substituted alkene in an elimination reaction is called as a **Hofmann elimination** and that of more substituted alkene as a **Zaitsev elimination.** Regioselectivity is in accordance with the Zaitsev rule.

The ease of dehydrohalogenation in alkyl halide is in the order:

Tertiary > Secondary > Primary

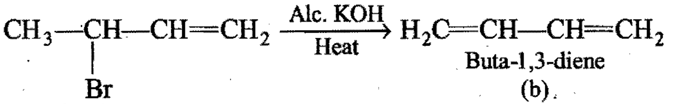
The ease of dehydrohalogenation for different halogens is in the order:

Iodide > Bromide > Chloride

The yields are very good in the case of tertiary and secondary alkyl halides but only fair or low in the case of primary alkyl halides. **Saytzeff's rule** is followed in these reactions. This is in accordance with the stability of alkenes, a more substituted alkene is more stable than less substituted alkene owing to higher number of resonating forms.

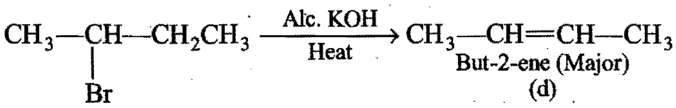
This method is preferred because of less complications in comparison to dehydration of alcohols which is accompanied by a hydride shift leading to the formation of an intermediate more stable carbocation.

Further greater the conjugation, greater the stability (due to resonance) hence easier the dehydrohalogenation.



$$CH_3-\underset{\underset{Br}{|}}{CH}-CH=CH_2 \xrightarrow[\text{Heat}]{\text{Alc. KOH}} H_2C=CH-CH=CH_2$$

3-Bromobut-1-ene (a) Buta-1,3-diene (b).

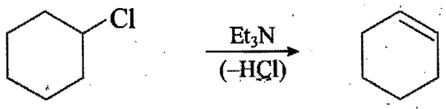


$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2CH_3 \xrightarrow[\text{Heat}]{\text{Alc. KOH}} CH_3-CH=CH-CH_3$$

2-Bromobutane (c) But-2-ene (Major) (d)

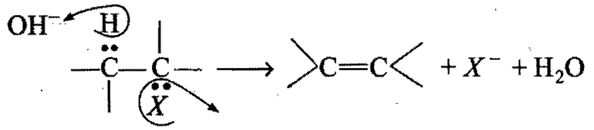
Since the product (b) is more stable than (d) hence, dehydrohalogenation of (a) is easier than that of (c).

Stronger bases like $NaNH_2$ or C_2H_5ONa in ethanol or triethyl amine, $(C_2H_5)_3N$, can also be used in place of alcoholic KOH for dehydrohalogenation (Et_3N is a bulky base and poor nucleophile, minimising S_N2 reaction).



Chlorocyclohexane Cyclohexene

Mechanism : The function of hydroxide ion is to pull the hydrogen ion away from carbon atom; simultaneously the halide ion separates and the double bond forms.



$$CH_3CH_2Br + C_2H_5O^- \longrightarrow H_2C=CH_2 + C_2H_5OH + Br^-$$

Ethoxide ion Ethene

The reaction does not take place in stepwise manner but involves a concerted mechanism. It is an example of E_2 reaction and represents a bimolecular β-elimination reaction.

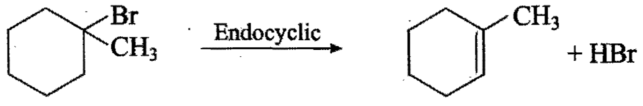
The energy required for the cleavage of C—H and C—X bonds is provided by,

(i) formation of bond between H^+ and OH^- ions,

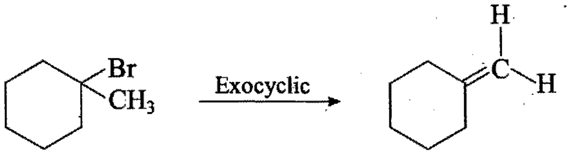
(ii) formation of π-bond and

(iii) solvation of halide ion in alcohol. All these release a considerable amount of energy.

Let us consider elimination of HBr from 1-bromo-1-methyl cyclohexane. There are two possibilities of dehydrohalogenation.



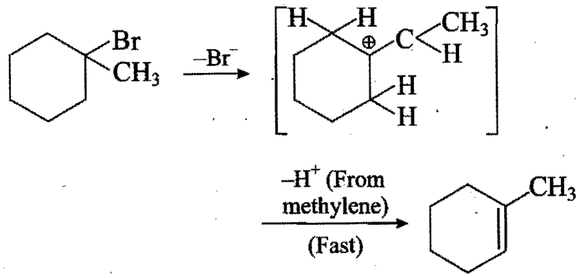
1-Bromo-1-methyl-cyclohexane 1-Methylcyclo-hexene (94%)



Methylenecyclo-hexane (6%)

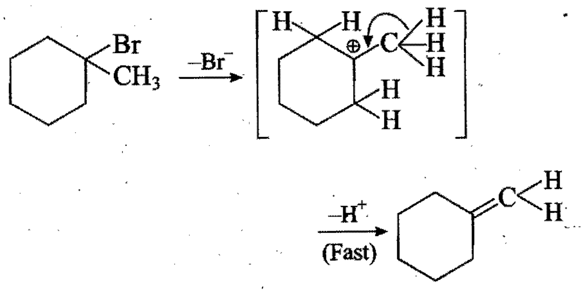
Mechanism

(i)



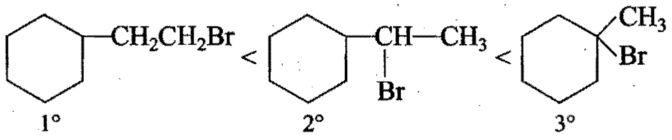
Formation of this product is according to **Saytzeff's rule.**

(ii)

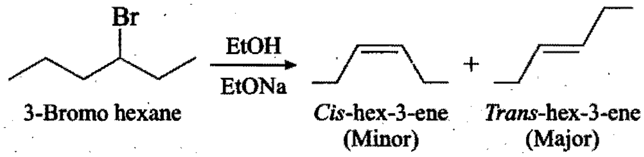


The formation of less substituted alkene in an elimination reaction is called as **Hofmann elimination.**

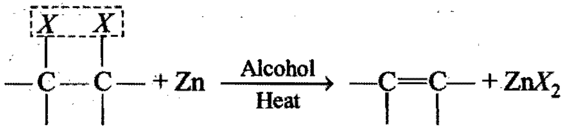
The increasing order of dehydrohalogenation is:



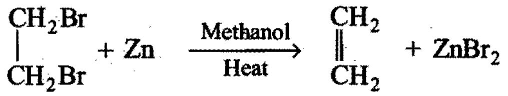
In addition to being regioselective, dehydrohalogenation of alkyl halide is stereoselective and favours the formation of more stable isomer.



3. Dehalogenation of vicinal dihalides (Two halogen atoms are attached to adjacent carbon atoms) : When vicinal dihalide is heated with Zn/Cu couple in methanolic solution, pure alkene is formed.

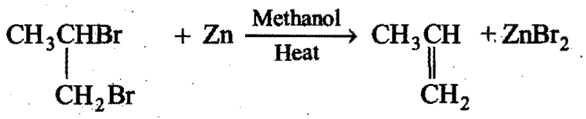


$$-\overset{X}{\underset{|}{C}}-\overset{X}{\underset{|}{C}}- + Zn \xrightarrow[\text{Heat}]{\text{Alcohol}} -\underset{|}{C}=\underset{|}{C}- + ZnX_2$$



$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + Zn \xrightarrow[\text{Heat}]{\text{Methanol}} \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + ZnBr_2$$

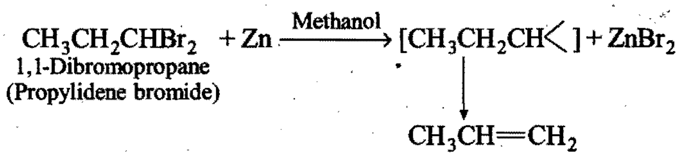
1,2-Dibromoethane (Ethylene bromide) Ethylene



$$\begin{matrix} CH_3CHBr \\ | \\ CH_2Br \end{matrix} + Zn \xrightarrow[\text{Heat}]{\text{Methanol}} \begin{matrix} CH_3CH \\ \| \\ CH_2 \end{matrix} + ZnBr_2$$

1,2-Dibromopropane (Propylene bromide) Propylene

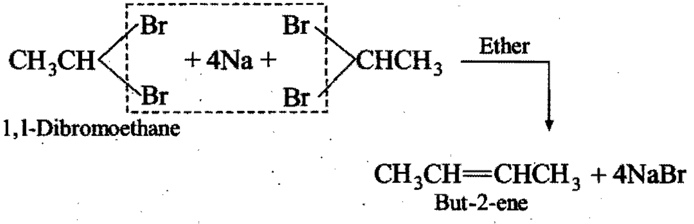
Gem-dihalides have also been used in the preparation of alkenes.



$$CH_3CH_2CHBr_2 + Zn \xrightarrow{\text{Methanol}} [CH_3CH_2CH\lessdot] + ZnBr_2 \;\downarrow\; CH_3CH=CH_2$$

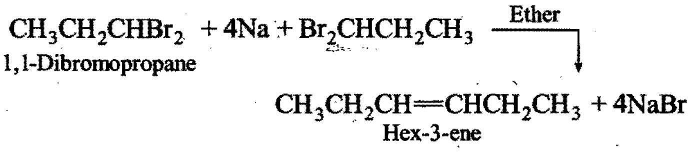
1,1-Dibromopropane (Propylidene bromide) Propylene

If sodium metal is used in place of zinc (like Wurtz reaction), then higher alkenes can be obtained.



$$CH_3CH\langle^{Br}_{Br} + 4Na + {}^{Br}_{Br}\rangle CHCH_3 \xrightarrow{\text{Ether}} CH_3CH=CHCH_3 + 4NaBr$$

1,1-Dibromoethane But-2-ene



$$CH_3CH_2CHBr_2 + 4Na + Br_2CHCH_2CH_3 \xrightarrow{\text{Ether}} CH_3CH_2CH=CHCH_2CH_3 + 4NaBr$$

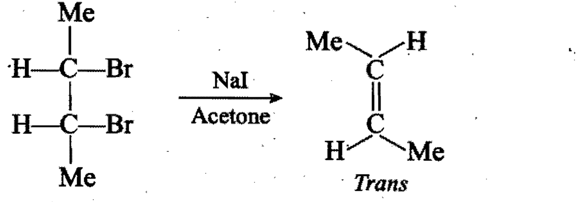
1,1-Dibromopropane Hex-3-ene

In place of Zn dust, NaI in acetone can also be used by E_2 mechanism.

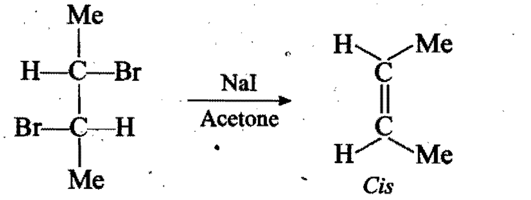
$$BrCH_2-CH_2Br \xrightarrow[\text{Acetone}]{\text{NaI}} H_2C=CH_2 + NaBr + IBr$$

1,2-Dibromoethane Ethylene

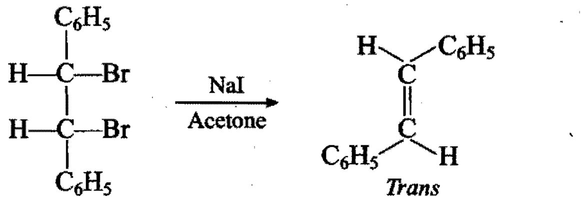
Stereo selectivity: Elimination of halogen from dihalides give dominant *trans*-product.



Trans

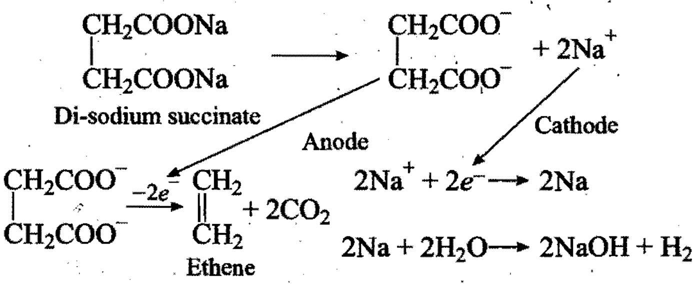


Cis



Trans

4. Electrolysis of salts of dicarboxylic acids : When sodium or potassium salt of saturated dicarboxylic acids of succinic acid type are subjected to electrolysis in aqueous solution, alkenes are formed.



The method is an extension of **Kolbe's method** for the preparation of alkanes.

5. Controlled partial hydrogenation (reduction) of alkynes : Alkynes react with hydrogen when passed over heated catalyst (**Lindlar's catalyst**)—Palladium poisoned with $CaCO_3$ or $BaSO_4$ and partially poisoned by addition of $PbCO_3$, S or quinoline to form predominantly *cis*-alkenes (as high as 98%).

$$R-C\equiv C-H + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar's}} R-CH=CH_2$$

Alkyne Alkene

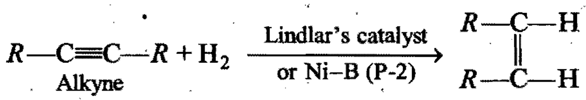
$$CH_3-C\equiv C-H + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar's}} CH_3-CH=CH_2$$

Propyne Propene

$$HC\equiv CH + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar's}} H_2C=CH_2$$

Acetylene Ethylene (Ethene)

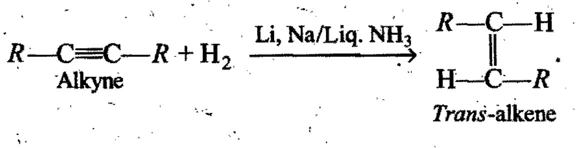
(a) Hydrogenation of alkynes with Lindlar's catalyst or a nickel boride called **P–2** catalyst yields only *cis*-alkene.



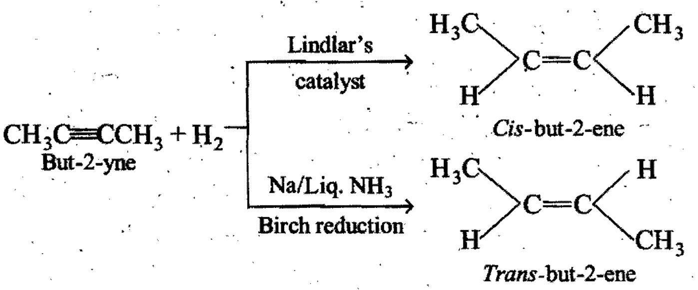
$$R-C\equiv C-R + H_2 \xrightarrow[\text{or Ni–B (P-2)}]{\text{Lindlar's catalyst}} \begin{matrix} R-C-H \\ \| \\ R-C-H \end{matrix}$$

Alkyne *Cis*-alkene

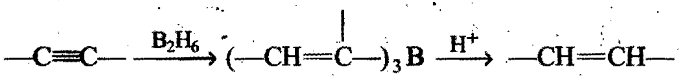
(b) But reduction of alkynes with lithium or sodium in liquid NH_3 **(Birch reduction)** yields predominantly *trans*-alkene.



So,



(c) Hydroboronation of alkynes (with B_2H_6) followed by protolysis (with H^+) gives almost pure *cis*-alkene.



$$-C\equiv C- \xrightarrow{B_2H_6} (-CH=\overset{|}{C}-)_3B \xrightarrow{H^+} -CH=CH-$$

6. Pyrolysis or cracking : Higher alkanes when heated at high temperature (500–700°C) decompose to produce a lower alkane and an alkene (C—C fission).

$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow{\text{Cracking}} \underset{\text{Propene}}{CH_3CH=CH_2} + \underset{\text{Methane}}{CH_4}$$

or

$$H_2C=CH_2 + CH_3-CH_3$$

$$\underset{n\text{-Hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3} \xrightarrow{\text{Cracking}} \underset{\text{Propene}}{CH_3CH=CH_2} + \underset{\text{Propane}}{CH_3CH_2CH_3}$$

The presence of catalyst (like oxides of Cr, vanadium and Mo), however, accelerates the C—H linkage fission.

$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[\text{(Catalyst)}]{\text{Cracking}} \underset{\text{Propene}}{CH_3CH=CH_2} + H_2$$

7. Pyrolysis of quaternary ammonium compounds : Many alkenes are conveniently prepared by heating quaternary ammonium compounds.

$$\underset{\text{Tetraethylammonium hydroxide}}{(C_2H_5)_4\overset{+}{N}\overset{-}{O}H} \xrightarrow{\text{Heat}} \underset{\text{Triethylamine (tert. amine)}}{(C_2H_5)_3N} + \underset{\text{Ethene}}{C_2H_4} + H_2O$$

$$(C_2H_5)_4\overset{+}{N}\overset{-}{X} \xrightarrow{\text{Heat}} (C_2H_5)_3N + C_2H_4 + HX$$

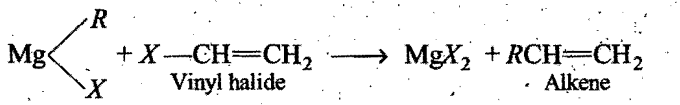
It is called **Hofmann elimination** with the formation of an amine having smaller alkyl groups on the π-bonded carbon. This reaction is E_2 elimination with an amine as leaving group.

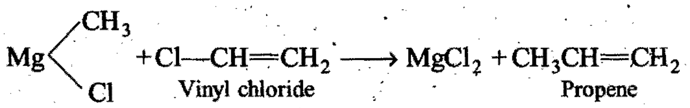
8. Action of copper alkyl on vinyl chlorides : Alkyl derivatives of ethylene can be conveniently prepared by the action of copper alkyls on vinyl chloride.

$$\underset{\text{Vinyl chloride}}{H_2C=CHCl} \xrightarrow{CuR_2} H_2C=CHR$$

$$H_2C=CHCl \xrightarrow{(CH_3)_2Cu} \underset{\text{Propene}}{H_2C=CH-CH_3}$$

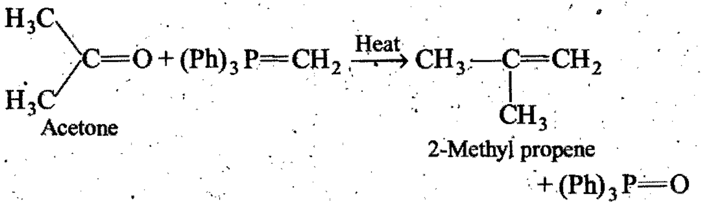
9. By Grignard reagents : Alkenes can be obtained by reacting Grignard reagent with vinyl chloride.



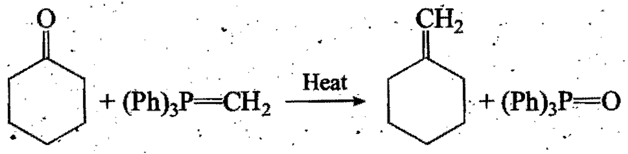


10. By Wittig reaction: Conversion of aldehydes and ketones to alkenes with the help of alkylidene (methylene) triphenyl phosphorus (Wittig reagent) is known as Wittig reaction, *e.g.*,

$$\underset{\text{Acetaldehyde}}{CH_3CH=O} + (C_6H_5)_3P=CH_2 \xrightarrow{\text{Heat}} \underset{\text{Propene}}{CH_3CH=CH_2} + \underset{\text{Triphenyl phosphine oxide}}{(C_6H_5)_3P=O}$$

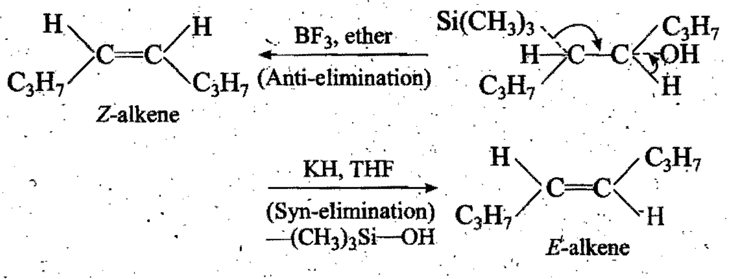


$$\underset{\text{Benzaldehyde}}{C_6H_5CH=O} + (Ph)_3P=CH_2 \xrightarrow{\text{Heat}} \underset{\text{Styrene}}{C_6H_5CH=CH_2} + (Ph)_3P=O$$

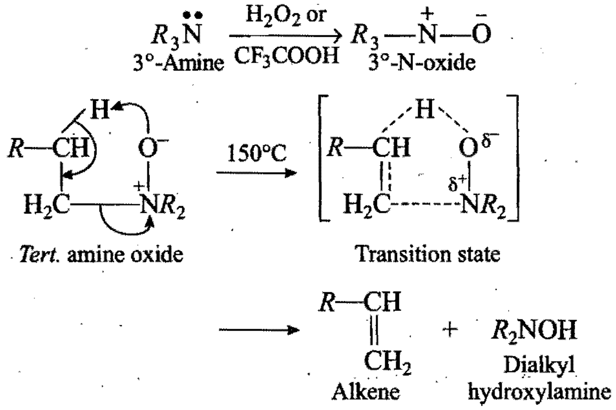


Now, carbonyl compound is added directly to ether solution of Wittig reagent.

11. Peterson reaction: β-Hydroxy alkyl silane gives elimination reaction in presence of acid as well as base. It is stereoselective of *E*- and *Z*- isomers of alkene.



12. Cope reaction or cope elimination: When a 3°-amine oxide containing at least one β-hydrogen is heated at 150°C, it decomposes to form an alkene and a derivative of hydroxylamine (Thermal elimination).



$$\underset{\text{3°-Amine}}{R_3\ddot{N}} \xrightarrow[CF_3COOH]{H_2O_2 \text{ or}} \underset{\text{3°-N-oxide}}{R_3-\overset{+}{N}-\overset{-}{O}}$$

$$\xrightarrow{} \underset{\text{Alkene}}{R-CH=CH_2} + \underset{\text{Dialkyl hydroxylamine}}{R_2NOH}$$

This reaction may also be carried out in dimethyl sulphoxide or THF at room temperature.

7.6 GENERAL CHARACTERISTICS

Physical properties : (i) The first three members are gases, the next fourteen members are liquids while alkenes with more than 17 carbon atoms in the molecule are solids at room temperature.

(ii) Except ethene, all are odourless. Ethene has pleasant odour. All are colourless.

(iii) Like alkanes, alkenes are insoluble in water but dissolve freely in organic solvents.

(iv) The boiling points, melting points and specific gravities show a gradual increase with the increase of molecular mass in the homologous series. They are less volatile than alkanes, *i.e.*, their boiling and melting points are higher than corresponding alkanes. *Cis*-isomer has a higher boiling point than *trans*-isomer due to higher polarity.

For example, *cis*-but-2-ene has boiling point 277 K and *trans*-but-2-ene has boiling point 274 K.

However, *trans*-alkenes have higher melting points than their corresponding *cis*-isomers. For example, *cis*-but-2-ene (m.pt. = 134 K) and *trans*-but-2-ene (m.pt. = 167 K). This is due to the fact that the *trans*-alkene molecules are symmetrical and therefore, they can pack more closely in the crystal lattice than the *cis*-alkene molecules. So, larger amount of energy is required to break the crystal lattice of *trans*-alkene than the corresponding lattice of *cis*-alkene, *i.e.*, *trans*-isomers are more stable than the *cis*-isomers.

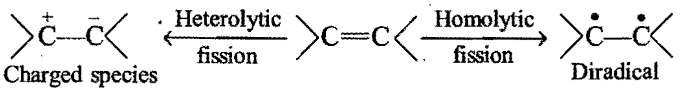
(v) They are weakly polar. The values of dipole moment for alkenes are pretty close in the range of 0.35 to 0.40 D. However, *trans*-isomers have zero dipole moment and are non-polar.

(vi) The double bond in alkenes consists one sigma and one pi-bond.

Carbon-carbon double bond (C=C) is shorter than the carbon-carbon single bond.

The total bond dissociation energy of double bond (146 kcal) is greater than carbon-carbon single bond dissociation energy (83 kcal). Hence, the double bond is stronger than carbon-carbon single bond.

Chemical properties : The most important reactions of alkenes are the addition reactions. Alkenes are reactive due to the presence of double bond. The double bond consists of a strong σ-bond and a weaker π-bond. The π-electrons are loosely held and are, therefore, easily polarisable. In addition reactions, the π-bond is broken and two new σ-bonds are formed. The fission of the bond may be heterolytic or homolytic as shown below.



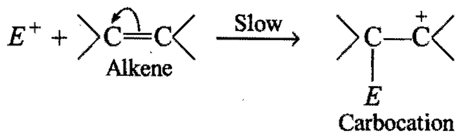
In polar solvents, addition proceeds by ionic mechanism (*i.e.*, at low temperature), whereas in the presence of light or non-polar solvents, the addition occurs by free radical mechanism (*i.e.*, at high temperature).

Ionic mechanism involves three steps:

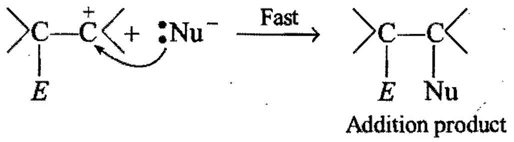
1st step : The reagent E—Nu ionises to give an electrophile and nucleophile.

$$E-Nu \longrightarrow E^+ + :Nu^-$$

2nd step : The electrophile attacks the carbon-carbon double bond and forms a covalent bond with one of the carbon atoms by utilising the π-electrons. The other carbon atom acquires positive charge, *i. e.*, formation of carbocation occurs.



3rd step : The nucleophile now attacks the carbocation to form an addition product.



As the addition reaction is initiated by an electrophile, the reaction is termed as electrophilic addition.

The addition of electrophilic reagents relieves the strain of $>C=C<$ (bond angle 120°) by changing it to $>C-C<$ (bond angle 109.5°). The reactivity order for alkenes has been given on the basis of heat of hydrogenation as,

$$H_2C=CH_2 > R-CH=CH_2 > R_2C=CH_2 \approx R-CH=CHR > R_2C=CHR > R_2C=CR_2$$

The reactivity of alkenes is, however, also related to the following factors:

(i) Steric effect, (ii) Hyperconjugation and (iii) Heat of combustion.

Alkenes (except ethene) also contain alkyl groups. Alkyl part is very stable. Like alkanes, this part can show substitution reactions with difficulty.

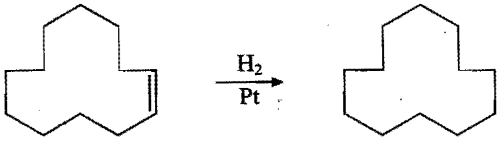
1. Addition reactions: The important addition reactions of alkenes are described below:

(a) Addition of hydrogen (Hydrogenation): Alkenes combine with hydrogen under pressure and in presence of a catalyst (Ni, Pt, Pd or Rh) to form corresponding alkanes **(Sabatier-Senderen's reaction).**

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + H_2 \xrightarrow{\text{Catalyst}} \underset{\text{Ethane}}{CH_3{-}CH_3} + \text{Heat}$$

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + H_2 \xrightarrow{\text{Catalyst}} \underset{\text{Propane}}{CH_3CH_2CH_3} + \text{Heat}$$

$$\underset{\text{Alkene}}{R_2C{=}CR_2} + H_2 \xrightarrow[\text{Pd or Rh}]{\text{Ni, Pt,}} \underset{\text{Alkane}}{R_2CH{-}CHR_2}$$



Cis-cyclododecene Cyclododecane (100%)

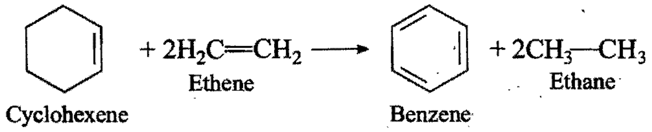
When nickel is used as a catalyst, the reaction is carried out at 200–300°C and in presence of Pt or Pd, the hydrogenation can occur even at room temperature. Hydrogenation follows free radical mechanism.

Hydrogenation is exothermic. The heat of hydrogenation of every alkene is fairly close to an approximate value of 30 kcal/mol. The heat of hydrogenation of an alkene is an index of its stability. **The lower the heat of hydrogenation of an alkene, the more stable it is.** *Trans*-but-2-ene (27.6 kcal/mol) is more stable than *cis*-but-2-ene (28.6 kcal/mol) and but-1-ene (30.3 kcal/mol).

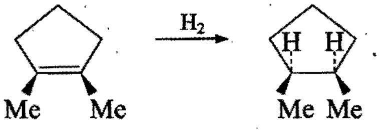
A terminal double bond may be reduced by sodium in liquid ammonia in the presence of an alcohol (MeOH or EtOH). This is called **Birch reduction.**

$$RCH{=}CH_2 + 2H \xrightarrow[\text{EtOH}]{\text{Na/Liq. NH}_3} RCH_2CH_3$$

Cyclohexene can also reduce olefinic bond, and itself is oxidised to benzene.



The double bond is also reduced in excellent yield by $NaBH_4{-}PtCl_2$.



[Meso or syn addition product]

The rate of hydrogenation of olefinic bonds at room temperature is $-CH{=}CH_2 > -CH{=}CH-$ or a ring double bond.

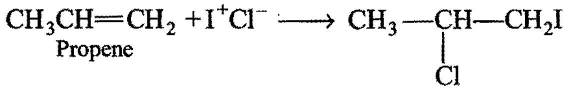
(b) Addition of halogens: Halogens (chlorine and bromine only) add at ordinary temperatures to alkenes in presence of an inert solvent, (*e.g.*, CCl_4) to form vicinal dihalides. Br_2 water is decolourised by unsaturated hydrocarbons (hence the **test of unsaturation**).

$$\underset{\substack{\text{(Brown}\\\text{colour)}}}{Br_2} + \underset{\text{Ethylene}}{H_2C{=}CH_2} \xrightarrow[\text{(Inert solvent)}]{CCl_4} \underset{\substack{\text{Ethylene bromide}\\\text{(Colourless)}}}{CH_2Br{-}CH_2Br}$$

$$\underset{\substack{\text{(Brown}\\\text{colour)}}}{Br_2} + \underset{\text{Propylene}}{CH_3CH{=}CH_2} \xrightarrow[\text{solvent}]{\text{Inert}} \underset{\substack{\text{Propylene bromide}\\\text{(Colourless)}}}{CH_3CHBrCH_2Br}$$

The reaction with fluorine is explosive whereas iodine reacts very slowly. When alkene is bubbled through alcoholic solution of iodine (I_2 solution in CCl_4), a mixed halide is formed.

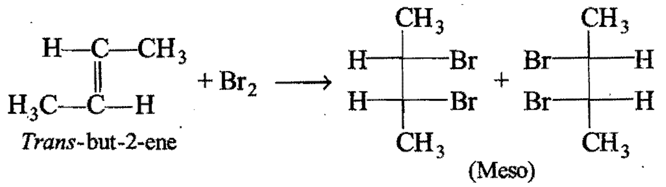
$$H_2C{=}CH_2 + I^+Cl^- \longrightarrow CH_2I{-}CH_2Cl$$



$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + I^+Cl^- \longrightarrow CH_3{-}\underset{\substack{|\\Cl}}{CH}{-}CH_2I$$

2-Chloro-1-iodopropane

With *trans*-but-2-ene, the product of Br_2 addition is optically inactive due to the formation of symmetric meso compounds.



In general, for symmetrical alkenes and symmetrical reagents, the addition takes place as:

cis-alkene + syn-addition ⟶ meso
trans-alkene + syn-addition ⟶ racemic
cis-alkene + anti-addition ⟶ racemic
trans-alkene + anti-addition ⟶ meso

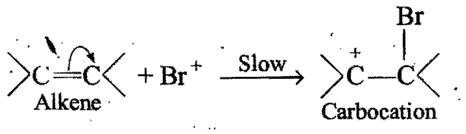
This reaction provides a useful **test for unsaturation,** the brown colour of the bromine being rapidly discharged as the colourless dibromo derivative is formed. The reaction is stereospecific, anti-addition is observed. A **stereospecific reaction** is that where stereoisomeric starting substrate produce products which are stereoisomers of each other.

Mechanism

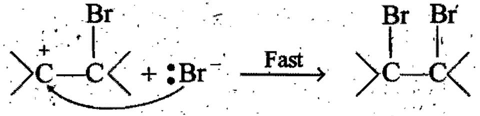
1st step: The Br_2 molecule ionises on interaction with π-bond.

$$Br_2 \longrightarrow \underset{\substack{\text{Bromonium ion}\\\text{(Electrophile)}}}{Br^+} + \underset{\substack{\text{Bromide ion}\\\text{(Nucleophile)}}}{:Br^-}$$

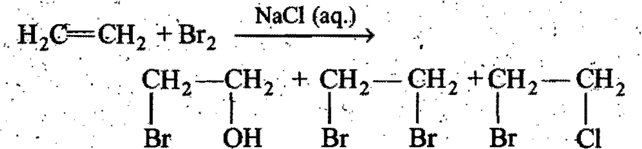
2nd step: Bromonium ion attacks the double bond to form a carbocation.



3rd step : Nucleophile (Br^-) attacks the carbocation to form addition product.

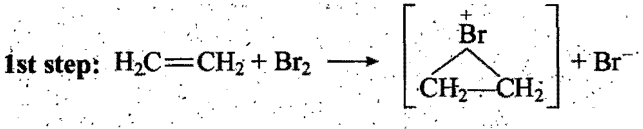


Mechanism was proved by following addition reaction.

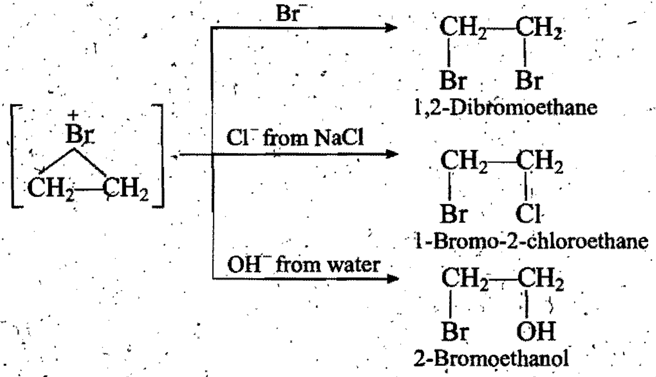


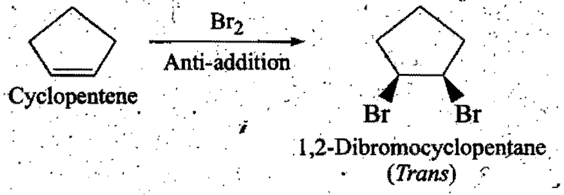
$$H_2C{=}CH_2 + Br_2 \xrightarrow{\text{NaCl (aq.)}} \underset{|\quad\ \ |}{CH_2{-}CH_2}_{\ Br\quad OH} + \underset{|\quad\ \ |}{CH_2{-}CH_2}_{\ Br\quad Br} + \underset{|\quad\ \ |}{CH_2{-}CH_2}_{\ Br\quad Cl}$$

Mechanism

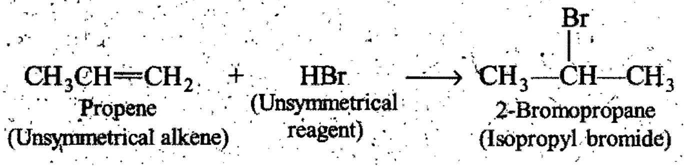


2nd step :



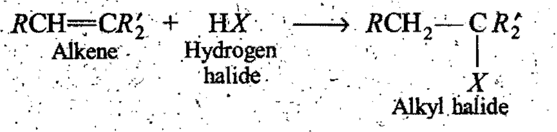


(c) Addition of halogen acids : Alkenes react with halogen acids (HCl, HBr or HI) to form alkyl halides.



$$\underset{\substack{\text{Propene}\\\text{(Unsymmetrical alkene)}}}{CH_3CH{=}CH_2} + \underset{\substack{\text{(Unsymmetrical}\\\text{reagent)}}}{HBr} \longrightarrow \underset{\substack{\text{2-Bromopropane}\\\text{(Isopropyl bromide)}}}{CH_3{-}\overset{\overset{Br}{|}}{C}H{-}CH_3}$$

A proton and a halogen add to the double bond of an alkene to form an alkyl halide in accordance with Markownikoff's rule under normal condition.



$$\underset{\text{Alkene}}{RCH{=}CR'_2} + \underset{\substack{\text{Hydrogen}\\\text{halide}}}{HX} \longrightarrow \underset{\text{Alkyl halide}}{RCH_2{-}\underset{\underset{X}{|}}{C}R'_2}$$

Unsymmetrical alkenes give two different products with unsymmetrical reagents. These products are constitutional isomers. The one product which predominates in the reaction is called a **regioselective reaction.**

Thus, ionic addition of unsymmetrical reagents to unsymmetrical alkenes is regioselective reaction.

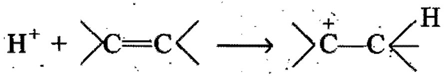
- The order of reactivity of the hydrogen halides is:

$$HI > HBr > HCl > HF$$

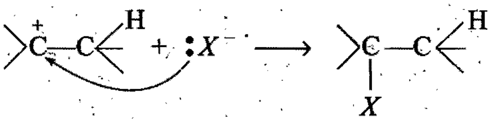
Mechanism

1st step : H*X* ionises, $HX \rightleftharpoons H^+ + :X^-$

2nd step : Electrophile (H^+) attacks the double bond to form carbocation.



3rd step : Nucleophile attacks the carbocation to form the alkyl halide.



Markownikoff's Rule : The negative part of the unsymmetrical reagent adds to less hydrogenated (more substituted) carbon atom of the double bond. The modern version of the rule is that electrophilic addition to a carbon-carbon double bond involves the rearrangement (1,2-hydride or 1,2-methyl shift) leading to the intermediate formation of a more stable carbocation (carbonium ion). The order of stability is:

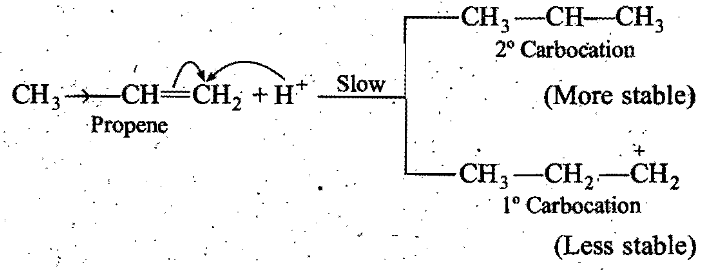
$$3° > 2° > 1° > \overset{+}{C}H_3$$

For example, an addition of HBr to propene is an **ionic electrophilic addition reaction,** in which the electrophile in the step 1 is H^+.

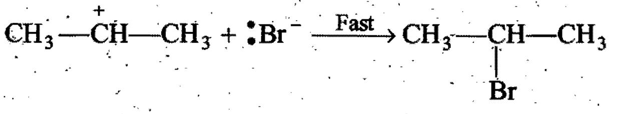
Mechanism:

Step 1: $HBr \longrightarrow \underset{\text{Attacking electrophile}}{H^+} + :Br^-$

Step 2: The proton (H^+) attacks the π-bond to give a stable carbocation.



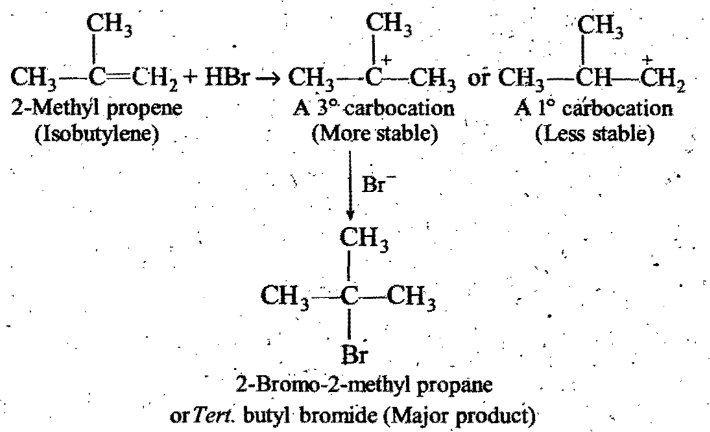
Step 3: The nucleophile bromide ion attacks the more stable 2° carbocation to give 2-bromopropane (major product).



$$CH_3{-}\overset{+}{C}H{-}CH_3 + :Br^- \xrightarrow{\text{Fast}} CH_3{-}\underset{\underset{Br}{|}}{C}H{-}CH_3$$

2-Bromopropane

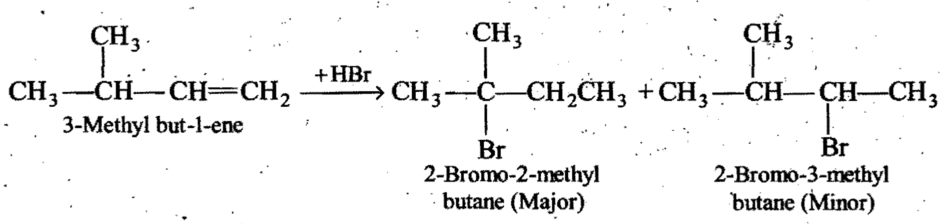
In another example, an addition of HBr to isobutylene forms *tert.* butyl bromide (2-bromo-2-methyl propane) as major product. It is a completely regioselective reaction, as one of the possible product (1-bromo-2-methylpropane) is not formed at all.



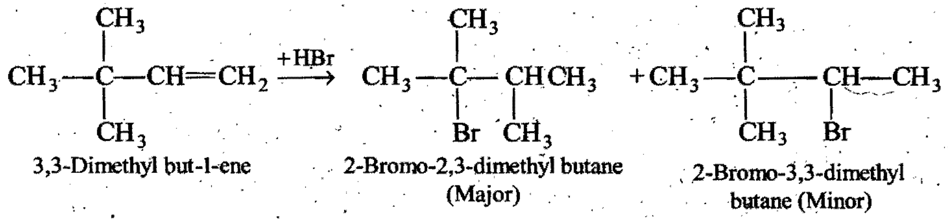
$$\underset{\substack{\text{2-Methyl propene}\\ \text{(Isobutylene)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2} + HBr \rightarrow \underset{\substack{\text{A 3° carbocation}\\ \text{(More stable)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\overset{+}{C}}-CH_3} \text{ or } \underset{\substack{\text{A 1° carbocation}\\ \text{(Less stable)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{+}{C}H_2}$$

$$\xrightarrow{Br^-} \underset{\substack{\text{2-Bromo-2-methyl propane}\\ \text{or } Tert. \text{ butyl bromide (Major product)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3}$$

Other examples are:

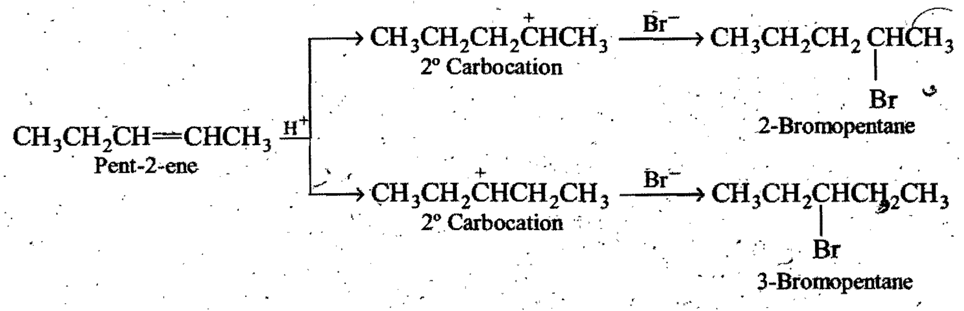


$$\underset{\text{3-Methyl but-1-ene}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH=CH_2} \xrightarrow{+HBr} \underset{\substack{\text{2-Bromo-2-methyl}\\ \text{butane (Major)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_2CH_3} + \underset{\substack{\text{2-Bromo-3-methyl}\\ \text{butane (Minor)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3}$$



$$\underset{\text{3,3-Dimethyl but-1-ene}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH=CH_2} \xrightarrow{+HBr} \underset{\substack{\text{2-Bromo-2,3-dimethyl butane}\\ \text{(Major)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_3} + \underset{\substack{\text{2-Bromo-3,3-dimethyl}\\ \text{butane (Minor)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3}$$

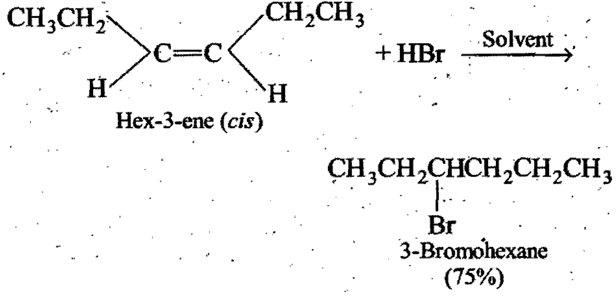
The addition of HX to 2-pentene is not regioselective as both alkyl halides (2-Bromopentane and 3-Bromopentane) are formed in comparable amounts.



$$\underset{\text{Pent-2-ene}}{CH_3CH_2CH=CHCH_3} \xrightarrow{H^+} \underset{\text{2° Carbocation}}{CH_3CH_2CH_2\overset{+}{C}HCH_3} \xrightarrow{Br^-} \underset{\text{2-Bromopentane}}{CH_3CH_2CH_2\underset{\underset{\displaystyle Br}{|}}{CH}CH_3}$$

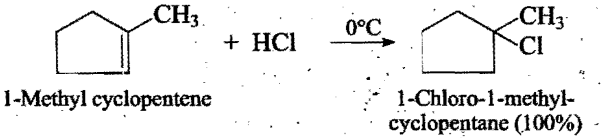
$$\underset{\text{Pent-2-ene}}{CH_3CH_2CH=CHCH_3} \xrightarrow{H^+} \underset{\text{2° Carbocation}}{CH_3CH_2\overset{+}{C}HCH_2CH_3} \xrightarrow{Br^-} \underset{\text{3-Bromopentane}}{CH_3CH_2\underset{\underset{\displaystyle Br}{|}}{CH}CH_2CH_3}$$

Addition occurs rapidly in a variety of solvents, including chloroform, benzene, acetic acid and dichloromethane, etc.



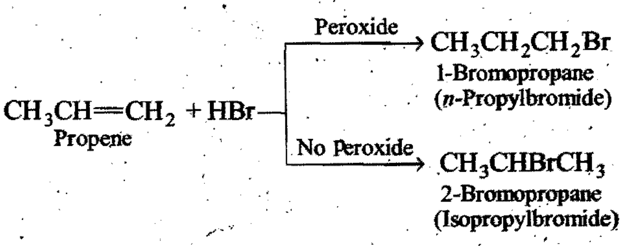
Hex-3-ene (*cis*) + HBr $\xrightarrow{\text{Solvent}}$

$$\underset{\substack{\text{3-Bromohexane}\\ \text{(75\%)}}}{CH_3CH_2\underset{\underset{\displaystyle Br}{|}}{CH}CH_2CH_2CH_3}$$



1-Methyl cyclopentene + HCl $\xrightarrow{0°C}$ 1-Chloro-1-methyl-cyclopentane (100%)

Peroxide effect : Kharasch observed that the addition of HBr to unsymmetrical alkenes in the presence of organic peroxides [$(C_6H_5COO)_2$, Benzoyl peroxide] follows an opposite course to that suggested by Markownikoff. This is termed anti-Markownikoff or peroxide effect.



$$\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\substack{\text{1-Bromopropane}\\ (n\text{-Propylbromide})}}{CH_3CH_2CH_2Br}$$

$$\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow{\text{No Peroxide}} \underset{\substack{\text{2-Bromopropane}\\ \text{(Isopropylbromide)}}}{CH_3CHBrCH_3}$$

In presence of benzoyl peroxide, the reaction is **free radical electrophilic addition reaction,** in which the electrophile here is $Br^{\bullet}$ free radical which is obtained by the action of benzoyl peroxide on HBr.

Mechanism:

Step 1: Peroxide undergoes fission to give free radicals **(initiation).**

$$\underset{\text{Benzoyl peroxide}}{C_6H_5CO—O—O—COC_6H_5} \xrightarrow[\text{(Homolytic fission)}]{\text{Heat}} \underset{\substack{\text{Benzoyl radical}\\ \text{(Unstable)}}}{2C_6H_5CO\dot{O}} \longrightarrow \underset{\text{Phenyl free radical}}{[2\dot{C}_6H_5 + 2CO_2]}$$

Step 2: HBr combines with free radical to form bromine-free radical.

$$\dot{C}_6H_5 + H—Br \longrightarrow C_6H_6 + \dot{B}r$$

Step 3: $\dot{B}r$ attacks the double bond of alkene to form a more stable free radical **(Propagation).**

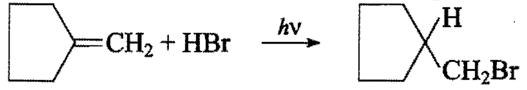
$$CH_3—CH{=}CH_2 + \dot{B}r \xrightarrow{\text{Slow}} \underset{\substack{\text{2° Free radical}\\ \text{(More stable)}}}{CH_3—\dot{C}H—CH_2Br}$$

Step 4: More stable free radical attacks the HBr **(termination).**

$$CH_3\dot{C}H—CH_2Br + H—Br \xrightarrow{\text{Fast}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} + \dot{B}r$$

Step 5: $\dot{B}r + \dot{B}r \longrightarrow Br_2$

Free radical chain reaction can also be initiated photochemically either with or without adding peroxides.



Methylene cyclopentane   Bromomethyl cyclopentane (60%)

Note : Peroxide effect is effective only in the case of HBr and not effective in the case of HCl and HI. This is due to the following reasons:

1. H—Cl bond (103 kcal/mol) is stronger than H—Br bond (87 kcal/mol). H—Cl is not decomposed by peroxide-free radical.
2. Iodine-free radical formed as H—I bond is weaker but iodine-free radicals readily combine with each other to form iodine molecules rather than to attack the double bond.
3. In H—Br both the chain propagation steps 3 and 4 are exothermic while in HCl step 3 is exothermic and step 4 is endothermic. In HI, step 3 is endothermic.

The abnormal addition of HBr in presence of peroxide can be prevented by the addition of an inhibitor such as diphenyl amine or catechol, etc.

Anti-Markownikoff addition is observed if the alkene bears a powerful electron withdrawing group (*–I* group) attached directly to the doubly bonded carbon.

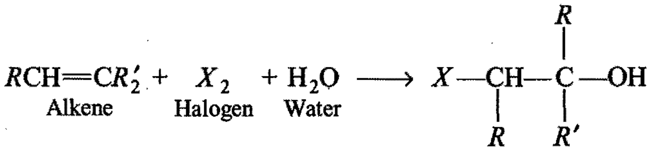
$$H_2C{=}CH—CF_3 \xrightarrow{+HBr} BrCH_2—CH_2CF_3$$

$$H_2C{=}CH—N(CH_3)_3 \xrightarrow{+HBr} BrCH_2—CH_2N(CH_3)_3$$

(d) Addition of hypohalous acids : Alkenes form halohydrins with hypohalous acids, (*i.e.*, chlorine or bromine in aqueous solution). In place of HOCl or HOBr, chlorine or bromine in presence of water can be used.

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + \overset{-}{H}\overset{+}{O}Cl \xrightarrow{Cl_2,\, H_2O} \underset{\substack{\text{Ethylene chlorohydrin}\\ \text{(2-Chloroethanol)}}}{CH_2OH—CH_2Cl}$$

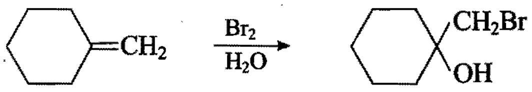
$$\underset{\text{Propylene}}{CH_3—CH{=}CH_2} + \overset{-}{H}\overset{+}{O}Cl \xrightarrow{Cl_2,\, H_2O} \underset{\substack{\text{Propylene chlorohydrin}\\ \text{(1-Chloropropan-2-ol)}}}{CH_3CHOH—CH_2Cl}$$



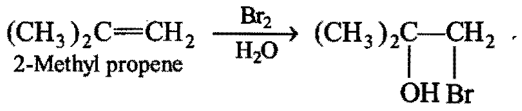
$$\underset{\text{Alkene}}{RCH{=}CR'_2} + \underset{\text{Halogen}}{X_2} + \underset{\text{Water}}{H_2O} \longrightarrow X—\underset{R}{CH}—\overset{R}{\underset{R'}{C}}—OH$$

Vicinal halohydrin

+ HX
Hydrogen halide



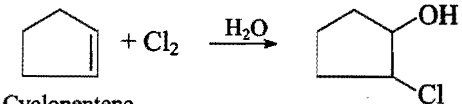
Methylene cyclohexane   1-Bromomethyl cyclohexanol (90%)



$$\underset{\text{2-Methyl propene}}{(CH_3)_2C{=}CH_2} \xrightarrow[H_2O]{Br_2} (CH_3)_2\underset{OH}{C}—\underset{Br}{CH_2}$$

1-Bromo-2-methyl-propan-2-ol (77%)

Oxygen is more electronegative than bromine (or chlorine or iodine) and so the HO—Br bond is polarized.



Cyclopentene   2-Chlorocyclo-pentanol (*Trans*)

In these halohydrin formation reactions, a halonium ion is formed as an intermediate which is attacked by water in aqueous solution.

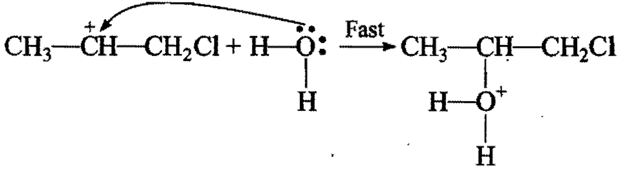
The order of reactivity of different X_2/H_2O (HO—*X*) is:

$$Cl_2/H_2O(HOCl) > Br_2/H_2O(HOBr) > I_2/H_2O(I—OH)$$

Mechanism: The addition of halogens in presence of water occurs through the intermediate formation of halonium ion as shown below:

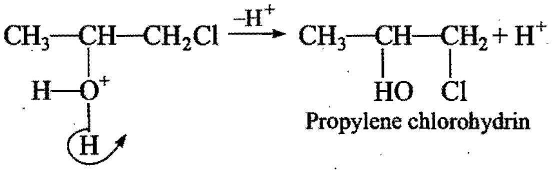
1st step: $\underset{\text{Propylene}}{CH_3CH{=}CH_2} + \overset{\delta^+}{Cl}—\overset{\delta^-}{Cl} \xrightarrow{\text{Slow}} CH_3\overset{+}{C}H—CH_2Cl + Cl^-$

2nd step:



$$CH_3—\overset{+}{C}H—CH_2Cl + H—\underset{H}{\ddot{O}}: \xrightarrow{\text{Fast}} CH_3—\underset{H—\underset{H}{O^+}}{CH}—CH_2Cl$$

3rd step:

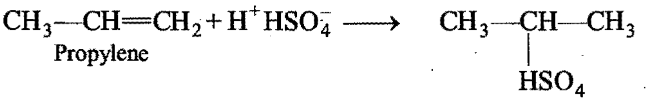


$$CH_3-\underset{\underset{\underset{H}{|}}{H-O^+}}{\underset{|}{CH}}-CH_2Cl \xrightarrow{-H^+} CH_3-\underset{HO}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}+H^+$$

Propylene chlorohydrin

(e) Addition of sulphuric acid: Cold and concentrated sulphuric acid or fuming sulphuric acid readily adds upto alkenes to form alkyl hydrogen sulphate. In the case of unsymmetrical alkenes, Markownikoff's rule is followed:

$$\underset{\text{Ethylene}}{H_2C=CH_2} + H^+HSO_4^- \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2HSO_4}$$



$$\underset{\text{Propylene}}{CH_3-CH=CH_2} + H^+HSO_4^- \longrightarrow CH_3-\underset{HSO_4}{\underset{|}{CH}}-CH_3$$

Isopropyl hydrogen sulphate

Ethyl hydrogen sulphate on heating at 160 –170°C yields ethylene again. Hence, **this reaction is used in the separation of ethylene or alkene from a gaseous mixture of alkanes and alkenes.**

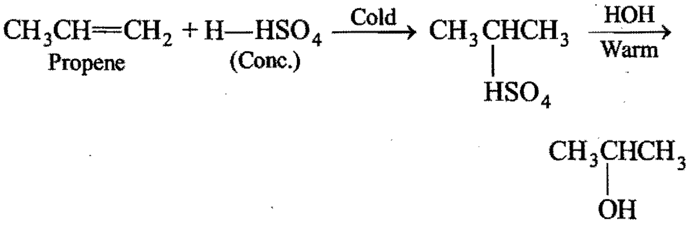
$$CH_3CH_2HSO_4 \longrightarrow H_2C=CH_2 + H_2SO_4$$

Ethanol is obtained when alkyl hydrogen sulphate (an ester) is boiled with water.

$$CH_3CH_2HSO_4 + HOH \xrightarrow{\text{Hydrolysis}} CH_3CH_2OH + H_2SO_4$$

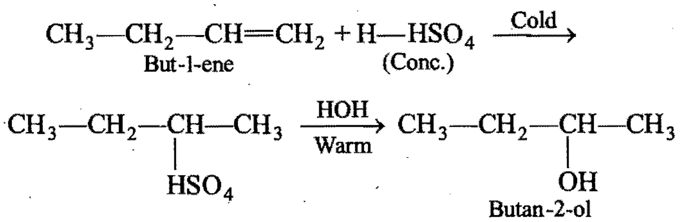
Hence, the reaction is used for the preparation of alcohols as alkenes are readily available from the cracking of petroleum.

Conversion of alk-1-ene to alkan-2-ol (reaction with cold and conc. H_2SO_4).



$$\underset{\text{Propene}}{CH_3CH=CH_2} + \underset{\text{(Conc.)}}{H-HSO_4} \xrightarrow{\text{Cold}} CH_3\underset{HSO_4}{\underset{|}{CH}}CH_3 \xrightarrow[\text{Warm}]{\text{HOH}} CH_3\underset{OH}{\underset{|}{CH}}CH_3$$

Propan-2-ol

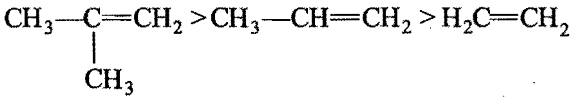


$$\underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2} + \underset{\text{(Conc.)}}{H-HSO_4} \xrightarrow{\text{Cold}}$$

$$CH_3-CH_2-\underset{HSO_4}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{Warm}]{\text{HOH}} CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$$

Butan-2-ol

Acid catalysed hydration to alkenes with Markownikoff's rule are **regioselective** reactions. The order of hydration is:



$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2 > CH_3-CH=CH_2 > H_2C=CH_2$$

Note : **To obtain alkan-1-ol from alk-1-ene,** the following procedure should be adopted. Alk-1-ene is treated first with diborane, the boron compound formed is then reacted with H_2O_2 to get the desired alcohol. This addition of borane followed by oxidation is known as **Hydroboration Oxidation reaction.**

For example,

$$\underset{\text{Propene}}{CH_3CH=CH_2} + \underset{\text{Diborane}}{(BH_3)_2} \longrightarrow CH_3CH_2CH_2BH_2$$

$$\xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_2BH \xrightarrow{CH_3CH=CH_2}$$

$$(CH_3CH_2CH_2)_3B \xrightarrow{H_2O_2,\ OH^-} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + \underset{\text{Boric acid}}{B(OH)_3}$$

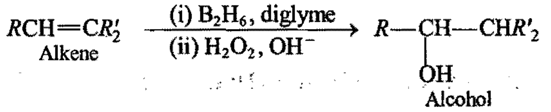
This reaction involves two steps, *i.e.*, addition of borane (BH_3) to double bond called hydroboration and oxidation followed by hydrolysis to give alcohol.

$$\underset{\text{But-1-ene}}{6CH_3-CH_2-CH=CH_2} + B_2H_6 \longrightarrow \underset{\text{Tributylborane}}{2(CH_3-CH_2-CH_2-CH_2)_3B}$$

$$(CH_3CH_2CH_2CH_2)_3B + 3H_2O_2 \longrightarrow \underset{\text{Butan-1-ol}}{3CH_3CH_2CH_2CH_2OH} + H_3BO_3$$

With diborane B_2H_6 alkenes undergo addition reaction **(Hydroboration)** to yield trialkyl boranes, which are used for the synthesis of primary alcohols by the reaction with alkaline aqueous solution of hydrogen peroxide **(oxidation).**

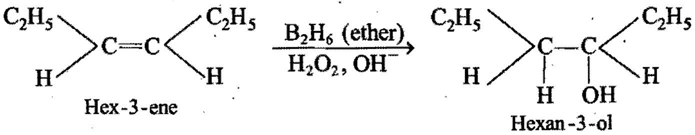
$$\underset{\text{Alkene}}{6(R-CH=CH_2)} + B_2H_6 \longrightarrow \underset{\text{Trialkyl borane}}{2(R-CH_2CH_2)_3B} \xrightarrow[+6H_2O_2]{(OH^-)} \underset{\text{Primary alcohol}}{6(R-CH_2CH_2OH)} + 2H_3BO_3$$



$$\underset{\text{Alkene}}{RCH=CR'_2} \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } B_2H_6,\text{ diglyme}} R-\underset{OH}{\underset{|}{CH}}-CHR'_2$$

Alcohol

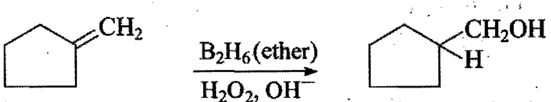
The overall result of the above reactions, appears to be anti-Markownikoff's addition of water (hydration) to a double bond **(Hydroboration oxidation).**



Hex-3-ene

Hexan-3-ol

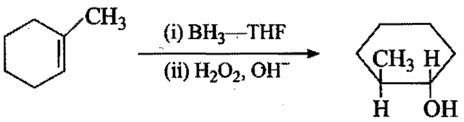
+ Enantiomer



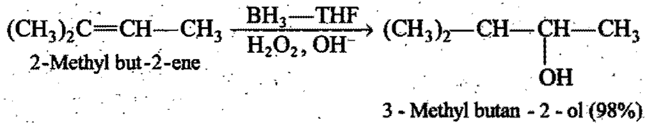
Methylene cyclopentane

Cyclopentylmethanol

Addition of —H and —OH is *syn.* addition.



Another convenient hydroborating agent is the borane-tetrahydrofuran (BH_3 — THF) complex. It is very reactive and the reaction is carried out in THF (tetrahydrofuran), ether or diglyme (diethylene glycol methyl ether, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$).



$$\underset{\text{2-Methyl but-2-ene}}{(CH_3)_2C{=}CH{-}CH_3} \xrightarrow[H_2O_2,\ OH^-]{BH_3{-}THF} \underset{\text{3 - Methyl butan - 2 - ol (98\%)}}{(CH_3)_2{-}CH{-}\underset{OH}{\underset{|}{CH}}{-}CH_3}$$

$$\underset{\text{3-Methyl but-1-ene}}{(CH_3)_2CH{-}CH{=}CH_2} \xrightarrow[H_2O_2,\ OH^-]{BH_3{-}THF} \underset{\text{3-Methyl butan-1-ol}}{(CH_3)_2CH{-}CH_2CH_2OH}$$

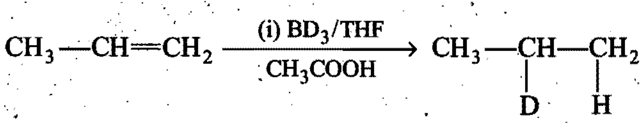
$$\underset{\text{Dec-1-ene}}{CH_3(CH_2)_7CH{=}CH_2} \xrightarrow[H_2O_2,\ OH^-]{B_2H_6\ \text{(diglyme)}} \underset{\text{Decan-1-ol (93\%)}}{CH_3(CH_2)_7CH_2CH_2OH}$$

The hydroboration reaction was discovered by H. C. Brown, who was awarded Nobel Prize in 1980 for the synthetic uses of the reaction. Trialkyl borane on decomposition by acetic acid forms alkane.

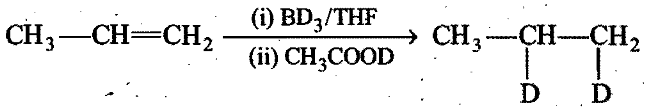
Trialkyl borane reacts with organic acid, generally acetic acid, to give alkane corresponding to alkanes.

$$\underset{\text{Trialkyl borane}}{R_3B} \xrightarrow{CH_3COOH} \underset{\text{Alkane}}{3RH}$$

$$\underset{\text{Propene}}{3CH_3CH{=}CH_2} \xrightarrow{BH_3} \underset{\text{Tripropylborane}}{(CH_3CH_2CH_2)_3B} \xrightarrow{CH_3COOH} \underset{\text{Propane}}{3CH_3CH_2CH_3}$$



$$CH_3{-}CH{=}CH_2 \xrightarrow[CH_3COOH]{\text{(i) }BD_3/THF} CH_3{-}\underset{D}{\underset{|}{CH}}{-}\underset{H}{\underset{|}{CH_2}}$$



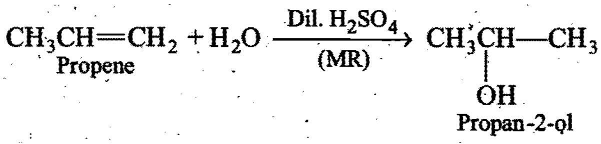
$$CH_3{-}CH{=}CH_2 \xrightarrow[\text{(ii) }CH_3COOD]{\text{(i) }BD_3/THF} CH_3{-}\underset{D}{\underset{|}{CH}}{-}\underset{D}{\underset{|}{CH_2}}$$

Trialkyl boranes undergo coupling reaction in presence of $AgNO_3/NaOH$.

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} \xrightarrow[\text{(ii) }AgNO_3/NaOH]{\text{(i) }BH_3/THF} \underset{n\text{-Hexane}}{CH_3{-}(CH_2)_4{-}CH_3}$$

(f) Addition of water (Hydration) : Alkenes add up water molecule in presence of acids or catalyst BF_3 or Mn phosphate, etc., to yield alcohols. This addition also follows Markownikoff's rule. A carbocation is an intermediate and is captured by a molecule of water acting as a nucleophile. For synthetic purposes, this reaction ordinarily works well for the preparation of secondary or tertiary alcohol. For example,

(i)

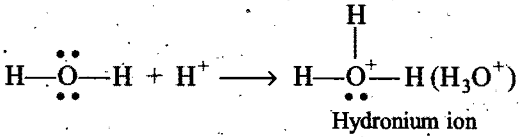


$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + H_2O \xrightarrow[\text{(MR)}]{\text{Dil. }H_2SO_4} \underset{\text{Propan-2-ol}}{CH_3\underset{OH}{\underset{|}{CH}}{-}CH_3}$$

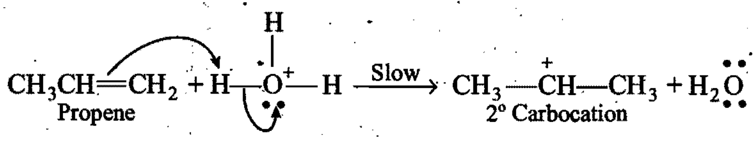
Mechanism: The mechanism of acid catalysed addition of water (hydration) to alkenes involves the following three steps:

Step 1. Electrophilic attack by hydronium ion (H_3O^+) on alkene gives an intermediate, carbocation.

$$(H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-})$$

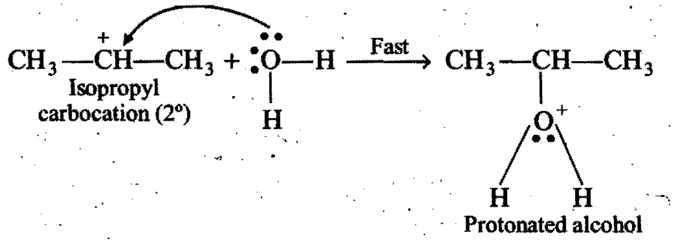


$$H{-}\ddot{\underset{\cdot\cdot}{O}}{-}H + H^+ \longrightarrow \underset{\text{Hydronium ion}}{H{-}\overset{\overset{H}{|}}{\underset{\cdot\cdot}{O^+}}{-}H\ (H_3O^+)}$$



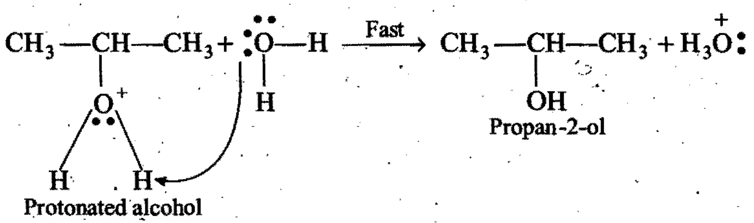
$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + H{-}\overset{\overset{H}{|}}{\underset{\cdot\cdot}{O^+}}{-}H \xrightarrow{\text{Slow}} \underset{2^\circ\ \text{Carbocation}}{CH_3{-}\overset{+}{CH}{-}CH_3} + H_2\ddot{\underset{\cdot\cdot}{O}}$$

Step 2. Nucleophilic attack by water on carbocation to yield protonated alcohol.



$$\underset{\text{Isopropyl carbocation (2°)}}{CH_3-\overset{+}{C}H-CH_3} + H-\ddot{O}-H \xrightarrow{\text{Fast}} \underset{\text{Protonated alcohol}}{CH_3-CH(\overset{+}{O}H_2)-CH_3}$$

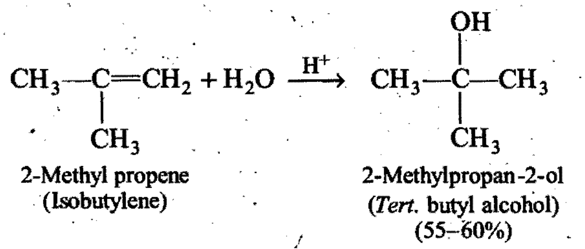
Step 3. Deprotonation (loss of proton) to form an alcohol.



$$\underset{\text{Protonated alcohol}}{CH_3-CH(\overset{+}{O}H_2)-CH_3} + H-\ddot{O}-H \xrightarrow{\text{Fast}} \underset{\text{Propan-2-ol}}{CH_3-CH(OH)-CH_3} + H_3\overset{+}{O}:$$

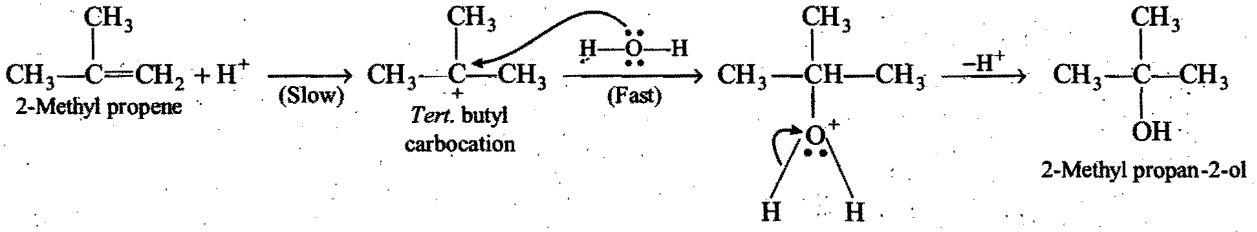
Other examples are,

(a)



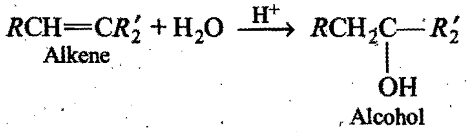
$$\underset{\substack{\text{2-Methyl propene}\\\text{(Isobutylene)}}}{CH_3-C(CH_3)=CH_2} + H_2O \xrightarrow{H^+} \underset{\substack{\text{2-Methylpropan-2-ol}\\\text{(Tert. butyl alcohol)}\\\text{(55–60\%)}}}{CH_3-C(OH)(CH_3)-CH_3}$$

Mechanism:



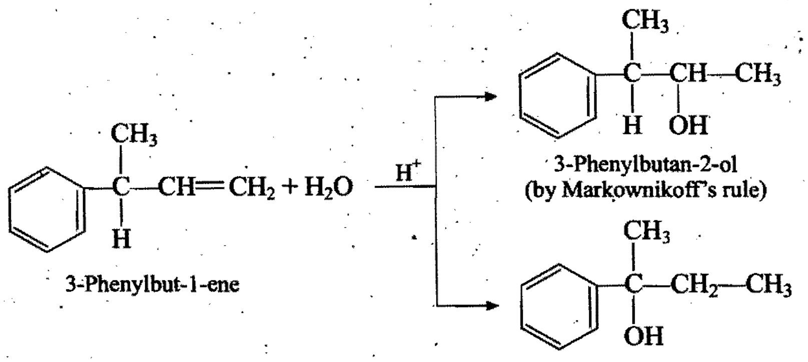
$$\underset{\text{2-Methyl propene}}{CH_3-C(CH_3)=CH_2} + H^+ \xrightarrow[\text{(Slow)}]{} \underset{\text{Tert. butyl carbocation}}{CH_3-\overset{+}{C}(CH_3)-CH_3} \xrightarrow[\text{(Fast)}]{H-\ddot{O}-H} CH_3-C(CH_3)(\overset{+}{O}H_2)-CH_3 \xrightarrow{-H^+} \underset{\text{2-Methyl propan-2-ol}}{CH_3-C(CH_3)(OH)-CH_3}$$

(b)



$$\underset{\text{Alkene}}{RCH=CR_2'} + H_2O \xrightarrow{H^+} \underset{\text{Alcohol}}{RCH_2C(OH)-R_2'}$$

(c)

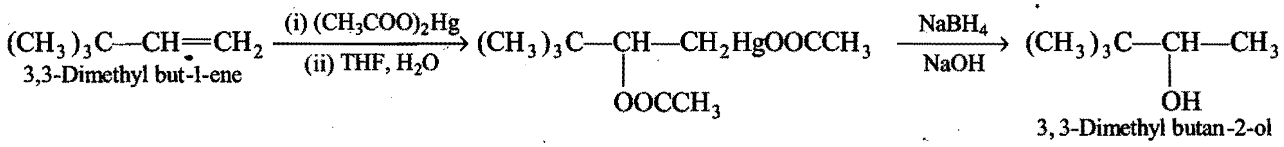


3-Phenylbut-1-ene

3-Phenylbutan-2-ol
(by Markownikoff's rule)

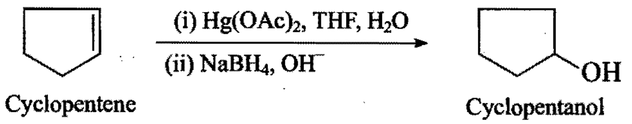
2-Phenylbutan-2-ol
(by 1,2-hydride shift)

(ii) Oxymercuration-demercuration : With mercuric acetate (in THF) followed by reduction with $NaBH_4/NaOH$ is also an example of **hydration of alkene according to Markownikoff's rule.** The regioselectivity of this reaction is identical with that of acid-catalysed hydration.



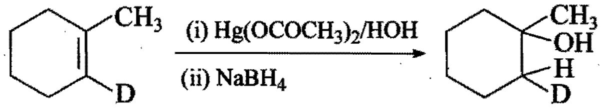
$$\underset{\text{3,3-Dimethyl but-1-ene}}{(CH_3)_3C{-}CH{=}CH_2} \xrightarrow[\text{(ii) THF, }H_2O]{\text{(i) }(CH_3COO)_2Hg} (CH_3)_3C{-}\underset{OOCCH_3}{\underset{|}{C}H}{-}CH_2HgOOCCH_3 \xrightarrow[NaOH]{NaBH_4} (CH_3)_3C{-}\underset{OH}{\underset{|}{C}H}{-}CH_3$$

3, 3-Dimethyl butan-2-ol



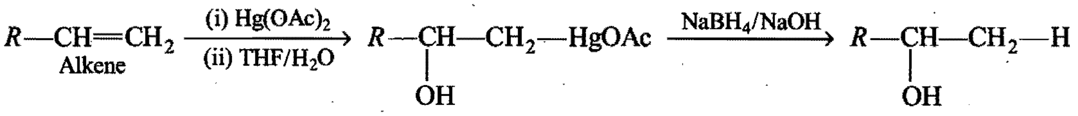
Cyclopentene Cyclopentanol

Experimentally, it has been found that the product of the reaction is a result of the anti-addition reaction. For example,



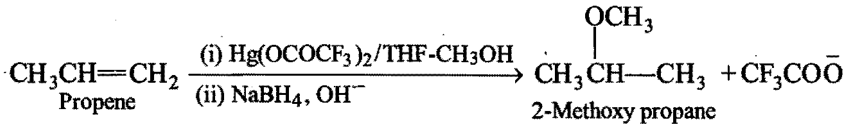
Anti-addition can only be obtained if product formation takes place by the formation of cyclic intermediate.

Oxymercuration-demercuration is a better process of hydration of alkene than catalytic hydration by dil. H_2SO_4, because it avoids rearrangement (due to the absence of free carbocation involvement in this mechanism).



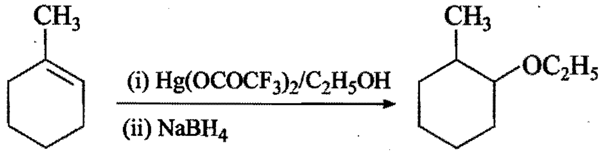
$$\underset{\text{Alkene}}{R{-}CH{=}CH_2} \xrightarrow[\text{(ii) THF/}H_2O]{\text{(i) Hg(OAc)}_2} R{-}\underset{OH}{\underset{|}{C}H}{-}CH_2{-}HgOAc \xrightarrow{NaBH_4/NaOH} R{-}\underset{OH}{\underset{|}{C}H}{-}CH_2{-}H$$

If alcohol is used in place of water as nucleophile, then this reaction is called **alkoxy mercuration-demercuration** and the product of the reaction is ether. Addition of alcohol works better in the presence of mercuric trifluoroacetate.



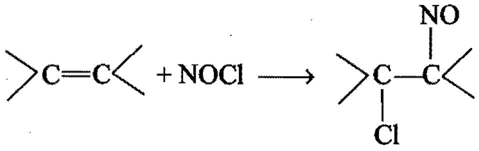
$$\underset{\text{Propene}}{CH_3CH{=}CH_2} \xrightarrow[\text{(ii) }NaBH_4,\ OH^-]{\text{(i) }Hg(OCOCF_3)_2/THF\text{-}CH_3OH} CH_3\overset{OCH_3}{\overset{|}{C}}H{-}CH_3 + CF_3CO\bar{O}$$

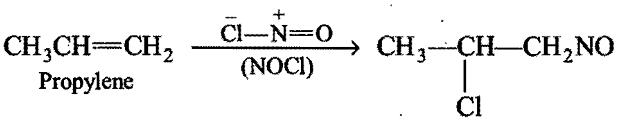
2-Methoxy propane



(g) Addition of nitrosyl chloride (Tildens Reagent) : Nitrosyl chloride (NOCl) or bromide adds to a carbon-carbon double bond to yield halonitroso derivatives.

$(NOCl \longrightarrow {}^{-}Cl{-}{}^{+}N{=}O)$; $(NOBr \longrightarrow {}^{-}Br{-}{}^{+}NO)$

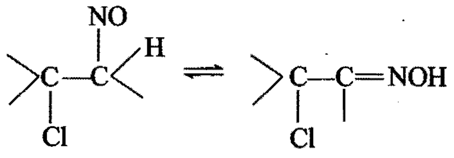




$$\underset{\text{Propylene}}{CH_3CH{=}CH_2} \xrightarrow[\text{(NOCl)}]{\bar{C}l{-}\overset{+}{N}{=}O} CH_3{-}\underset{Cl}{\underset{|}{C}H}{-}CH_2NO$$

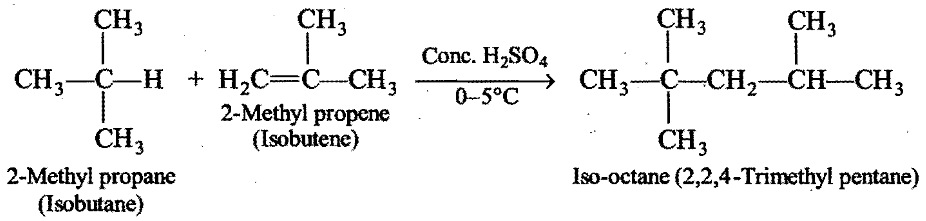
Propylene nitrosochloride

The product is stable when the carbon atom bearing —NO group does not contain hydrogen. However, if hydrogen is attached to the carbon atom, the product changes to more stable oxime.



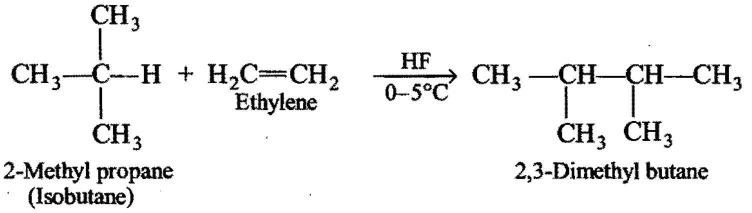
Oxime

(h) Addition of alkanes : Highly branched alkanes add to alkenes in the presence of conc. H_2SO_4 or HF **(Alkylation of alkenes).**



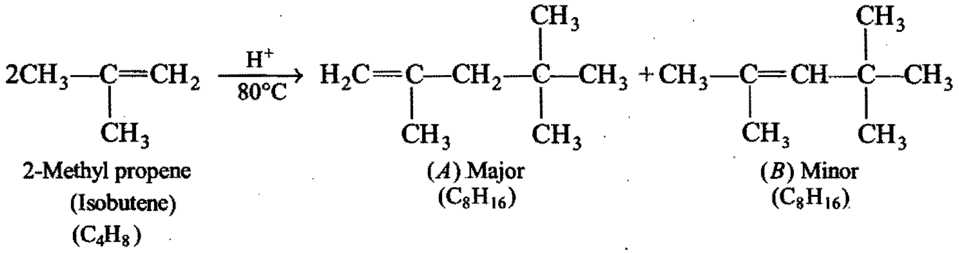
$$\underset{\substack{\text{2-Methyl propane}\\ \text{(Isobutane)}}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-H} + \underset{\substack{\text{2-Methyl propene}\\ \text{(Isobutene)}}}{H_2C=\overset{\overset{CH_3}{|}}{C}-CH_3} \xrightarrow[0\text{–}5^\circ C]{\text{Conc. } H_2SO_4} \underset{\text{Iso-octane (2,2,4-Trimethyl pentane)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3}$$

This reaction is used in the manufacture of iso-octane.



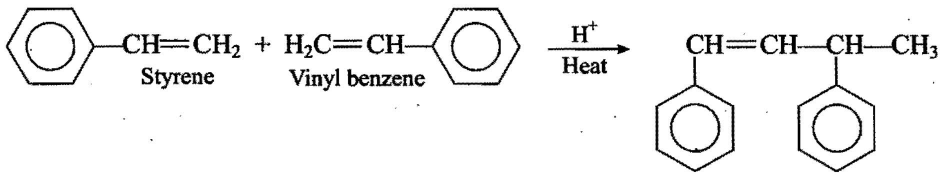
$$\underset{\substack{\text{2-Methyl propane}\\ \text{(Isobutane)}}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-H} + \underset{\text{Ethylene}}{H_2C=CH_2} \xrightarrow[0\text{–}5^\circ C]{HF} \underset{\text{2,3-Dimethyl butane}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3}$$

(i) Alkenylation of alkenes (Dimerisation) : Two molecules of isobutene (C_4H_8) add together in the presence of H_2SO_4 or H_3PO_4 at about 80°C to give an alkene, C_8H_{16} in two isomeric forms, a dimer of C_4H_8 and this is called **dimerisation.**

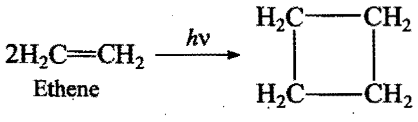


$$\underset{\substack{\text{2-Methyl propene}\\ \text{(Isobutene)}\\ (C_4H_8)}}{2CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2} \xrightarrow[80^\circ C]{H^+} \underset{\substack{(A)\text{ Major}\\ (C_8H_{16})}}{H_2C=\underset{\underset{CH_3}{|}}{C}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3} + \underset{\substack{(B)\text{ Minor}\\ (C_8H_{16})}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

Products (*A*) and (*B*) are position isomers and on hydrogenation form the same alkane, 2,2,4-trimethyl pentane. Similarly, styrene (Vinyl benzene) on dimerisation gives 1,3-diphenylbut-1-ene.

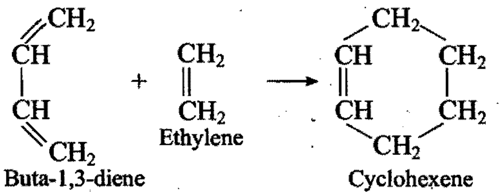


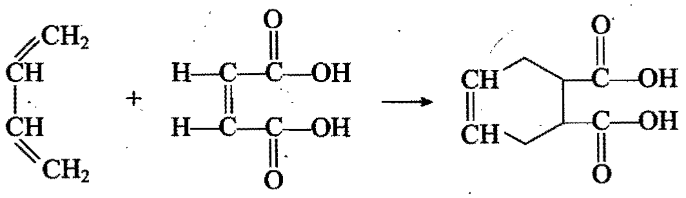
There are different types of dimerisation of alkenes in presence of sunlight forming cycloalkane.



Cyclobutane

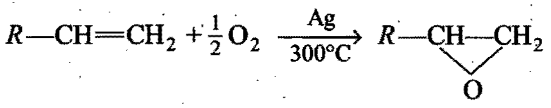
(j) Diels-Alder reaction: It is a diene-dienophile addition reaction. It forms cyclic compounds.

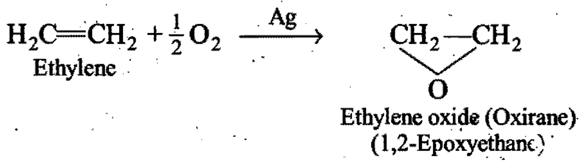


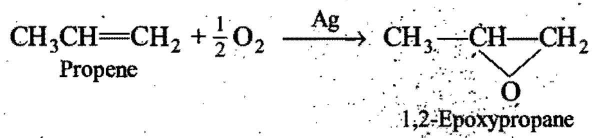


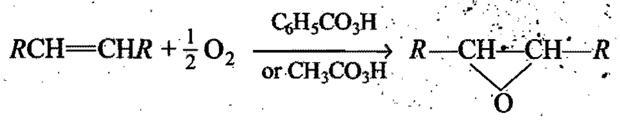
Maleic acid

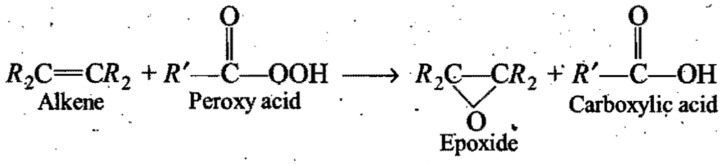
(k) Addition of oxygen : When mixed with oxygen or oxidation with peroxy acids (CH_3CO_3H, $C_6H_5CO_3H$ or CF_3CO_3H) or air and passed through a silver catalyst at high temperature (200–400°C) and pressure, lower alkenes add an atom of oxygen to form **epoxides,** (*i.e.*, cyclic ethers, in which the ether oxygen atom is a part of three membered ring). The reaction is a stereo-specific syn-addition.

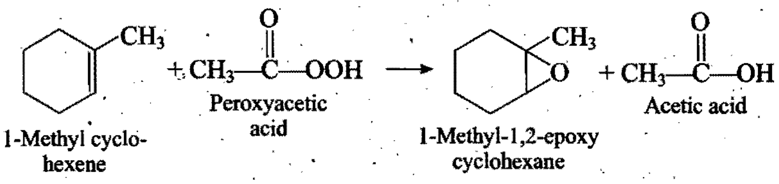






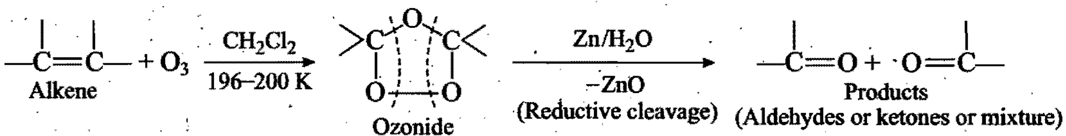




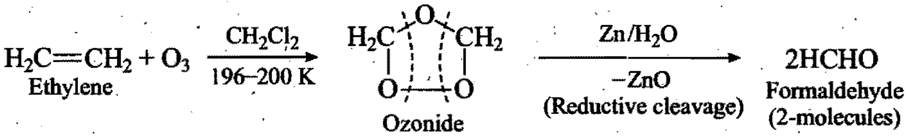


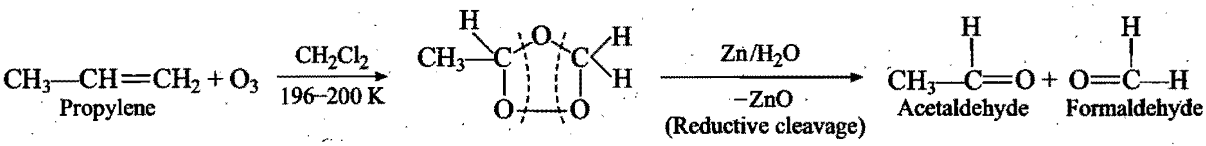
These epoxides on hydrolysis form diols or glycols.

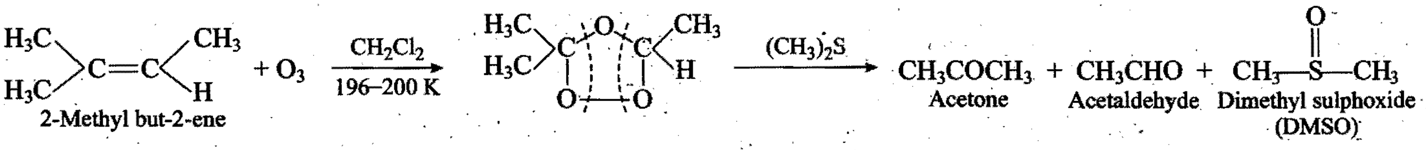
(l) Addition of ozone (Ozonolysis) : When a stream of ozone or ozonised oxygen is passed through a solution of alkene in an inert solvent (ether or CH_2Cl_2 or $CHCl_3$ or CCl_4), at low temperature (196–200 K), the molecule adds up to form ozonide. Ozonide is unstable, explosive compound and easily decomposes either by reduction [with Zn/H_2O or Zn/CH_3COOH or H_2/Pd or $(CH_3)_2S$] or hydrolysis in presence of reducing agent and forms compounds having $>C=O$ group. This process is known as ozonolysis.



Zinc dust is added to prevent the formation of H_2O_2 produced by the reaction of H_2O and O **(Reductive ozonolysis).**

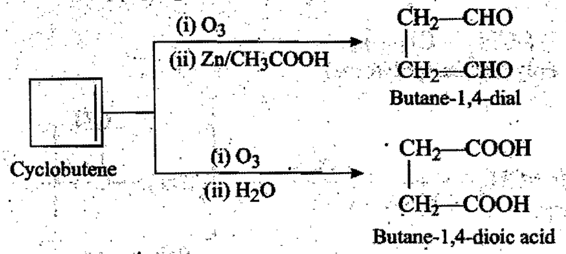




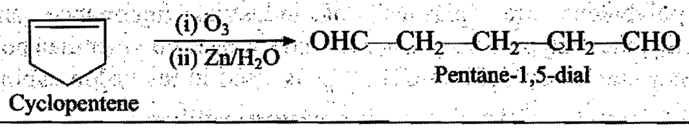


Knowing the number and arrangement of carbon atoms in these aldehydes and ketones, the structure of the original alkene can be worked out.

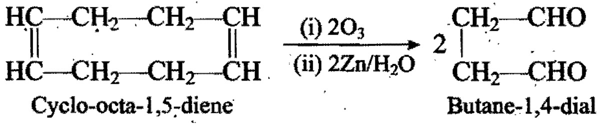
Note : (a) An alkene of type $RCH{=}CHR'$ gives a mixture of two aldehydes.
(b) An alkene of type $R_2C{=}CHR'$ gives a mixture of aldehyde and ketone.
(c) An alkene of the type $R_2C{=}CR'_2$ gives a mixture of two ketones. R and R' may be same or different.
(d) Ethene ($H_2C{=}CH_2$) gives only formaldehyde.
(e) But-2-ene ($CH_3CH{=}CHCH_3$) gives only acetaldehyde.
(f) $(CH_3)_2C{=}C(CH_3)_2$ (2,3-dimethylbut-2-ene) gives only acetone (propanone).
(g) Cyclobutene gives the product containing equal number of carbon atoms.

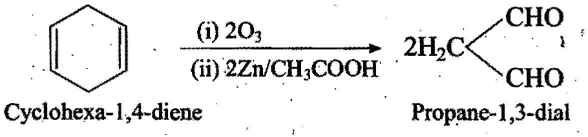


Absence of Zn/CH_3COOH will oxidise —CHO into —COOH.



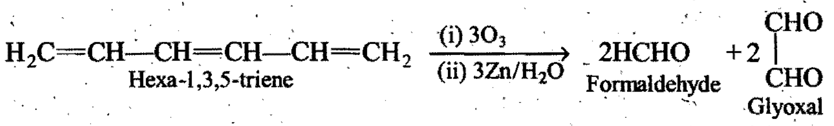
So, ozonolysis of cycloalkene gives one molecule of dialdehyde. Cycloalkadiene on ozonolysis gives two molecules of dialdehyde.





While conjugated diene and triene gives mainly glyoxal (dialdehyde) and formaldehyde.

$$\underset{\text{Buta-1,3-diene}}{H_2C{=}CH{-}CH{=}CH_2} \xrightarrow[\text{(ii) } 2Zn/H_2O]{\text{(i) } 2O_3} \underset{\text{Formaldehyde}}{2HCHO} + \underset{\text{Glyoxal}}{OHC{-}CHO}$$



$$\underset{\text{Hexa-1,3,5-triene}}{H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2} \xrightarrow[\text{(ii) } 3Zn/H_2O]{\text{(i) } 3O_3} \underset{\text{Formaldehyde}}{2HCHO} + 2\underset{\text{Glyoxal}}{\begin{array}{c}CHO\\|\\CHO\end{array}}$$

Note ; (i) Ozonide can be reduced with
(a) Zinc-acid, H_2-Raney Ni, triphenyl phosphine, etc., to give aldehydes and/or ketones.
(b) $LiAlH_4$ or $NaBH_4$ to form alcohols ($>C{=}O + 2H \longrightarrow >CHOH$)
(ii) Ozonide can be oxidised with H_2O_2, Ag_2O or per acids to form carboxylic acids and/or ketones.

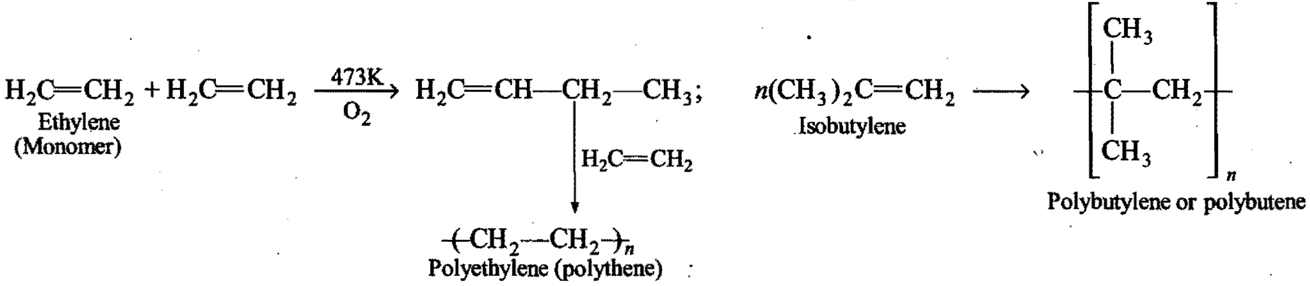
(m) Addition of HNO_3 : Nitric acid (fuming) adds to a carbon-carbon double bond to yield nitro alcohol.

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + HO{-}NO_2 \longrightarrow \underset{\text{2-Nitroethanol}}{CH_2OHCH_2NO_2}$$

(n) Addition of acetyl chloride : A molecule of acetyl chloride adds to a carbon-carbon double bond in presence of $AlCl_3$ to form chloro substituted ketone.

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + CH_3COCl \longrightarrow \underset{\text{4-Chlorobutan-2-one}}{CH_2ClCH_2COCH_3}$$

(o) Self addition or polymerisation : Alkenes in the presence of acid catalysts at high temperature (473 K) under a pressure of 1500 atmospheres and in presence of a trace of oxygen (0.001 – 0.1%) undergo self addition. Two or more molecules of an alkene link together to form a new bigger molecule of higher molecular mass. The small molecules are called monomers while the bigger (new) molecules are called macro-molecules or **polymers** and the process is called polymerisation. In such a polymerisation no atom breaks off and the molecules unite by the change in the position of double bond.

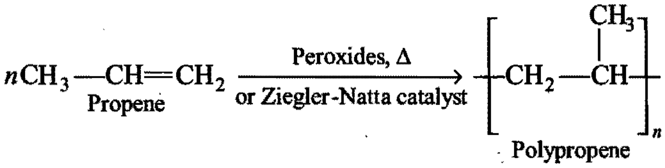


$$\underset{\substack{\text{Ethylene}\\\text{(Monomer)}}}{H_2C{=}CH_2} + H_2C{=}CH_2 \xrightarrow[O_2]{473K} H_2C{=}CH{-}CH_2{-}CH_3; \qquad n(CH_3)_2C{=}CH_2 \longrightarrow \left[\,{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}{-}CH_2{-}\right]_n$$

$$\xrightarrow{H_2C=CH_2} {-}\!(CH_2{-}CH_2)\!{-}_n$$

Polyethylene (polythene)

Polybutylene or polybutene

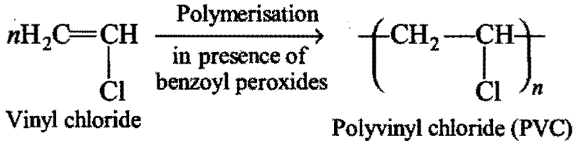


$$\underset{\text{Propene}}{nCH_3{-}CH{=}CH_2} \xrightarrow[\text{or Ziegler-Natta catalyst}]{\text{Peroxides, }\Delta} \left[{-}CH_2{-}\overset{\overset{\large CH_3}{|}}{CH}{-}\right]_n$$

Polypropene

Polythene, polypropene and polybutene are "plastics" of industrial importance and squeeze plastic bottles are moulded from high density polyethylene. Polypropene is a harder and stronger polymer than polythene and its fibres are used in carpets and automobile tyres. Polystyrene $-\!(C_6H_5CH{=}CH_2)\!-_n$ is used in television cabinets, housewares luggage and packaging, etc., *cis*-polyisoprene $\left({-}CH_2{=}\underset{\underset{\large CH_3}{|}}{C}{-}CH{=}CH_2{-}\right)_n$ is a **natural rubber.**

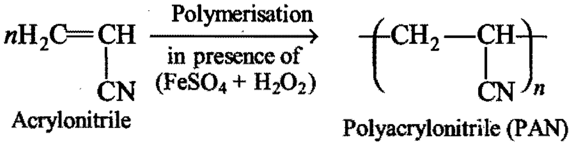
[Polymer and the original alkene have the same empirical mass but different molecular masses. The molecular mass of the polymer is generally very high. The derivatives of alkenes of the type $H_2C{=}CHX$ (X may be Cl, Br, I, CN, COOR, C_6H_5, etc.) are also used as monomers and undergo polymerisation to form useful plastics.]



$$\underset{\text{Vinyl chloride}}{nH_2C{=}\underset{\underset{\large Cl}{|}}{CH}} \xrightarrow[\substack{\text{in presence of}\\\text{benzoyl peroxides}}]{\text{Polymerisation}} \left({-}CH_2{-}\underset{\underset{\large Cl}{|}}{CH}{-}\right)_n$$

Polyvinyl chloride (PVC)

PVC is used for making plastic bottles, sheets, pipes, raincoats, hand bags, table mats, records, etc.



$$\underset{\text{Acrylonitrile}}{nH_2C{=}\underset{\underset{\large CN}{|}}{CH}} \xrightarrow[\substack{\text{in presence of}\\(FeSO_4\,+\,H_2O_2)}]{\text{Polymerisation}} \left({-}CH_2{-}\underset{\underset{\large CN}{|}}{CH}{-}\right)_n$$

Polyacrylonitrile (PAN)

Polyacrylonitrile is used for making *Orlon* and *Acrilan* fibres used for making clothes, carpets and blankets, etc.

$$\underset{\text{Tetra fluoroethene}}{nF_2C{=}CF_2} \xrightarrow[\text{High pressure}]{(NH_4)_2S_2O_8} \underset{\substack{\text{Polytetra fluoroethene (PTFE)}\\\text{(Teflon)}}}{{-}\!\!\left[CF_2{-}CF_2\right]\!\!{-}_n}$$

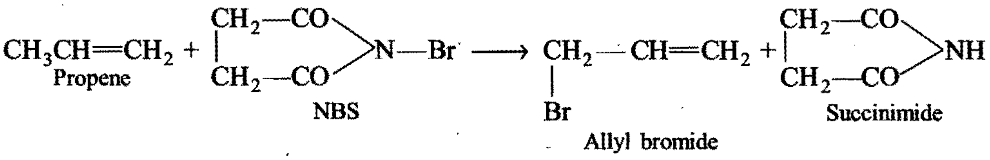
Teflon is chemically inert and a heat resistant polymer. It is very tough, electrical resistant and is used for making non-stick surface coating particularly for cooking utensils. It is also used in the manufacture of pipes and surgical tubes.

2. Substitution reactions (Halogenation) : The alkyl group of the alkenes undergo substitution at high temperature. Chlorine or bromine replace hydrogen of the alpha carbon atom with respect to the double bond of alkyl group at about 500°C without breaking the double bond **(allylic substitution).** The substitution proceeds by free radical mechanism. If the alkyl group contains more than one carbon atom, then the substitution occurs at the α-carbon to the double bond.

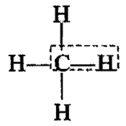
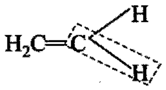
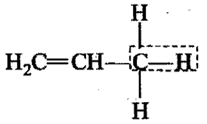
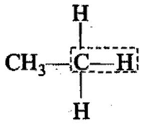
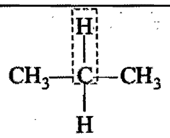
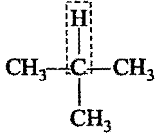
$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + Cl_2 \xrightarrow[\text{Heat}]{500°C} \underset{\substack{\text{Allyl chloride}\\ \text{(3-Chloroprop-1-ene)}}}{ClCH_2{-}CH{=}CH_2} + HCl$$

$$\underset{\text{But-1-ene}}{CH_3CH_2CH{=}CH_2} + Cl_2 \xrightarrow[\text{Heat}]{500°C} \underset{\text{3-Chlorobut-1-ene}}{CH_3CHClCH{=}CH_2} + HCl$$

NBS (N-bromosuccinimide) is a reagent used for the specific purpose of brominating alkenes at the allylic position.



Bond energy of C—H bond in the different environment :

Type of Hydrogen	**Example**	**(Hydrocarbon)**	**Bond Energy kcal/mol (ΔH)**
Methyl	$(H_3C—\underline{\mathbf{H}})$		103.8
Vinyl	$(H_2C{=}CH—\underline{\mathbf{H}})$		108
Allyl	$(H_2C{=}CH—CH_2—\underline{\mathbf{H}})$		88
Primary (1°)	$(CH_3—CH_2—\underline{\mathbf{H}})$		97.9
Secondary (2°)	$[(CH_3)_2CH—\underline{\mathbf{H}}]$		95
Tertiary (3°)	$[(CH_3)_3C—\underline{\mathbf{H}}]$		90

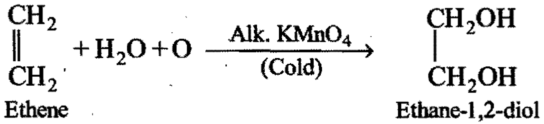
On the basis of bond dissociation energy data, abstraction reactivity for different types of hydrogen may be given as:

Allylic > 3° > 2° > 1° > methyl > vinyl

3. Oxidation reactions : Alkenes are readily oxidised. The oxidation products depend on the nature of the oxidising agent used.

(i) Oxidation with cold dilute alkaline potassium permanganate (Hydroxylation) : Alkaline potassium permanganate ($MnO_4^- + OH^-$) is known as **Baeyer's reagent.** When alkenes are treated with dilute alkaline $KMnO_4$ (1%) solution at low temperature, dihydroxy (glycol) compounds are formed. The pink colour of $KMnO_4$ solution disappears during the reaction.

Thus, this reaction is used as a test of unsaturation.

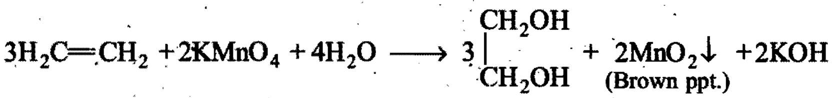


$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O + O \xrightarrow[\text{(Cold)}]{\text{Alk. }KMnO_4} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

Ethene

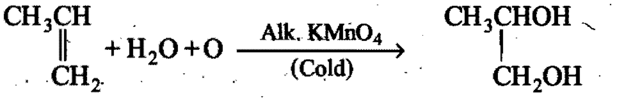
Ethane-1,2-diol
(Glycol)

or



$$3H_2C{=}CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array} + 2MnO_2\downarrow + 2KOH$$

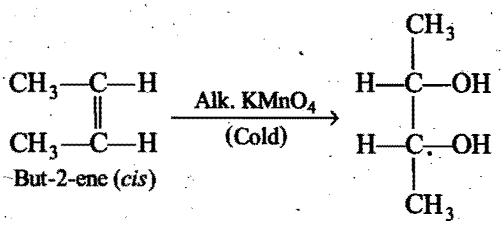
(Brown ppt.)



$$\begin{array}{l}CH_3CH\\\|\\CH_2\end{array} + H_2O + O \xrightarrow[\text{(Cold)}]{\text{Alk. KMnO}_4} \begin{array}{l}CH_3CHOH\\|\\CH_2OH\end{array}$$

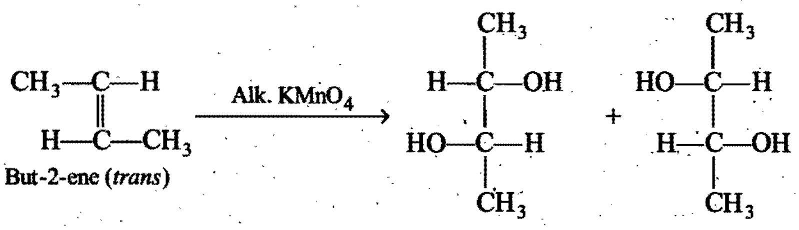
Propene

Propane-1,2-diol (Propylene glycol)



But-2-ene (*cis*)

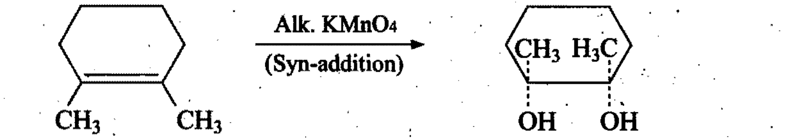
(Meso form)



But-2-ene (*trans*)

(*dl*) mixture

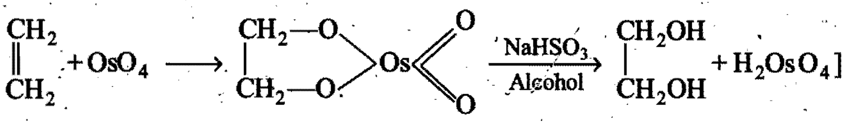
Hydroxylation by $KMnO_4$ is always syn-addition.



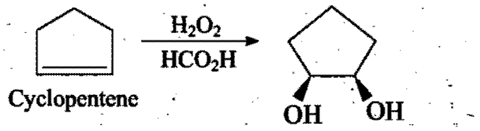
1,2-Dimethyl cyclohexene

1,2-Dimethyl cyclohexanediol (*cis*-)

[Glycols are also formed when alkenes are treated with **osmium tetraoxide** (OsO_4) and the product is refluxed with $NaHSO_3$ (alc.) or Na_2SO_3 or H_2O_2.

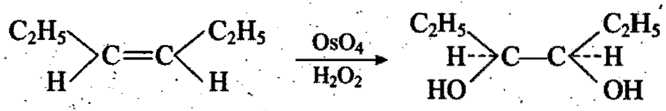


Hydroxylation using OsO_4 is syn-addition but with H_2O_2/HCO_2H is anti-addition.



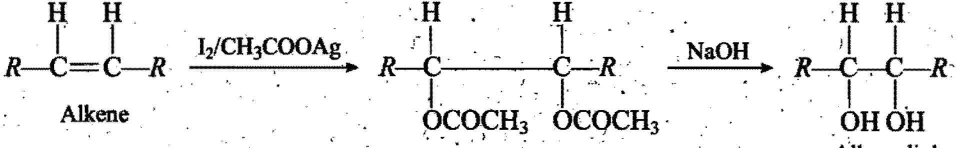
Cyclopentene

1,2-Cyclopentanediol (*trans*-)
(Anti-addition)



(Meso)

Hydroxylation using I_2/CH_3COOAg can also be used for diols formation.



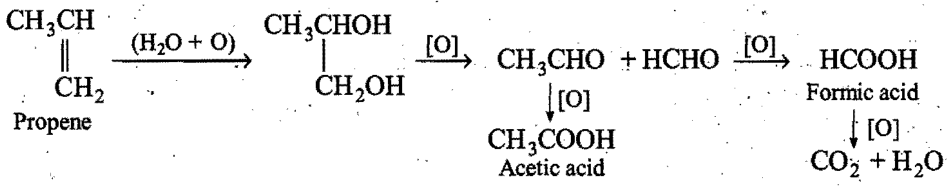
$$R{-}\overset{H}{C}{=}\overset{H}{C}{-}R \xrightarrow{I_2/CH_3COOAg} R{-}\overset{H}{\underset{OCOCH_3}{C}}{-}\overset{H}{\underset{OCOCH_3}{C}}{-}R \xrightarrow{NaOH} R{-}\overset{H}{\underset{OH}{C}}{-}\overset{H}{\underset{OH}{C}}{-}R$$

Alkene

Alkanediol

(ii) Oxidation with acidic potassium permanganate or potassium dichromate : When alkenes are treated with acidic or hot $KMnO_4$ or acidic $K_2Cr_2O_7$, glycols are first formed which are further oxidised to aldehydes, ketones or acids. Terminal formic acid is oxidised to CO_2 and H_2O.

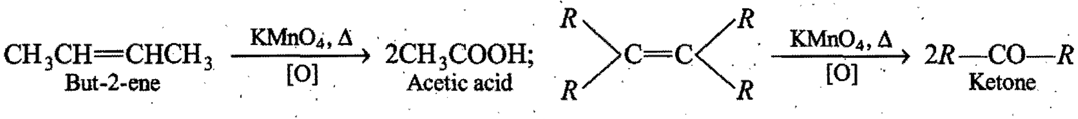
(a)



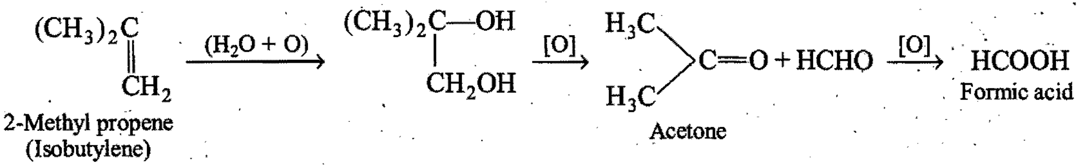
$$\underset{\text{Propene}}{\begin{matrix}CH_3CH\\ \|\\ CH_2\end{matrix}} \xrightarrow{(H_2O+O)} \begin{matrix}CH_3CHOH\\ |\\ CH_2OH\end{matrix} \xrightarrow{[O]} \begin{matrix}CH_3CHO\\ \downarrow[O]\\ \underset{\text{Acetic acid}}{CH_3COOH}\end{matrix} + HCHO \xrightarrow{[O]} \begin{matrix}\underset{\text{Formic acid}}{HCOOH}\\ \downarrow[O]\\ CO_2+H_2O\end{matrix}$$

or

$$CH_3CH{=}CH_2 + 4[O] \xrightarrow[373\text{-}383K]{\text{Hot, alk. }KMnO_4} CH_3COOH + CO_2 + H_2O$$



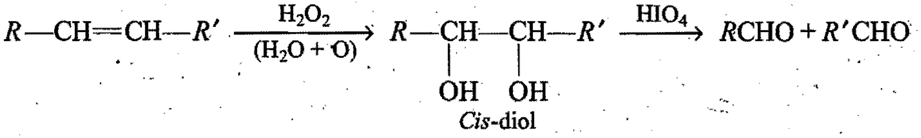
$$\underset{\text{But-2-ene}}{CH_3CH{=}CHCH_3} \xrightarrow[{[O]}]{KMnO_4,\,\Delta} \underset{\text{Acetic acid}}{2CH_3COOH}; \quad R_2C{=}CR_2 \xrightarrow[{[O]}]{KMnO_4,\,\Delta} \underset{\text{Ketone}}{2R{-}CO{-}R}$$



$$\underset{\substack{\text{2-Methyl propene}\\ \text{(Isobutylene)}}}{\begin{matrix}(CH_3)_2C\\ \|\\ CH_2\end{matrix}} \xrightarrow{(H_2O+O)} \begin{matrix}(CH_3)_2C{-}OH\\ |\\ CH_2OH\end{matrix} \xrightarrow{[O]} \underset{\text{Acetone}}{(H_3C)_2C{=}O} + HCHO \xrightarrow{[O]} \underset{\text{Formic acid}}{HCOOH}$$

(b) Same products are obtained when oxidation is done with **periodic acid** (HIO_4) or **lead tetra-acetate** $(CH_3COO)_4Pb$ or **sodium periodate** ($NaIO_4$).

The aqueous solution of sodium periodate and a trace of potassium permanganate **(Lemieux reagent)** is a better method both for determining the position of double bond and for preparing carbonyl compounds.



$$R{-}CH{=}CH{-}R' \xrightarrow[(H_2O+O)]{H_2O_2} \underset{\textit{Cis}\text{-diol}}{R{-}\underset{OH}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH}}{-}R'} \xrightarrow{HIO_4} RCHO + R'CHO$$

Formaldehyde is usually obtained from a terminal alkene. Instead of permanganate, a trace of OsO_4 has also been used by Lemieux.

(c) By passing a mixture of ethene and oxygen under pressure into an aqueous solution of **Pd and $CuCl_2$** (cupric chloride) at 50°C, the product is acetaldehyde.

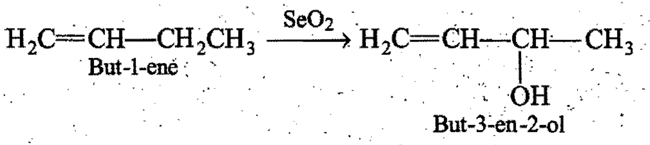
$$\underset{\text{Ethene}}{H_2C{=}CH_2} + PdCl_2 + H_2O \xrightarrow{50^\circ C} \underset{\text{Acetaldehyde}}{CH_3CHO} + Pd + 2HCl$$

$$\left[\begin{matrix} Pd + 2CuCl_2 \longrightarrow PdCl_2 + Cu_2Cl_2\\ Cu_2Cl_2 + 2HCl + \frac{1}{2}[O]_2 \longrightarrow 2CuCl_2 + H_2O\end{matrix}\right]$$

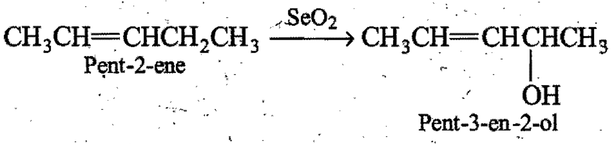
With propene, acetone is formed.

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + PdCl_2 + H_2O \longrightarrow \underset{\text{Acetone}}{CH_3COCH_3} + Pd + 2HCl$$

(d) Oxidation of alkenes by **selenium dioxide** (SeO_2) readily affects the allylic position and not the double bond.

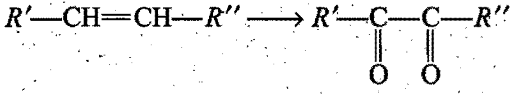


$$\underset{\text{But-1-ene}}{H_2C{=}CH{-}CH_2CH_3} \xrightarrow{SeO_2} \underset{\text{But-3-en-2-ol}}{H_2C{=}CH{-}\underset{OH}{\underset{|}{CH}}{-}CH_3}$$



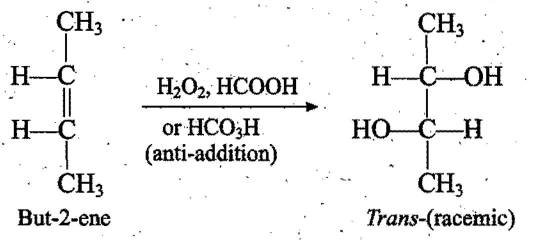
$$\underset{\text{Pent-2-ene}}{CH_3CH{=}CHCH_2CH_3} \xrightarrow{SeO_2} \underset{\text{Pent-3-en-2-ol}}{CH_3CH{=}CH\underset{OH}{\underset{|}{CH}}CH_3}$$

But the following types of alkenes are oxidised to α-diketones, *i.e.*,

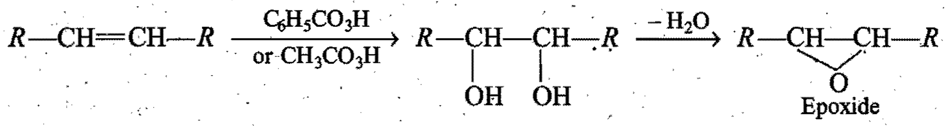


$$R'—CH=CH—R'' \longrightarrow R'—\underset{\underset{O}{\|}}{C}—\underset{\underset{O}{\|}}{C}—R''$$

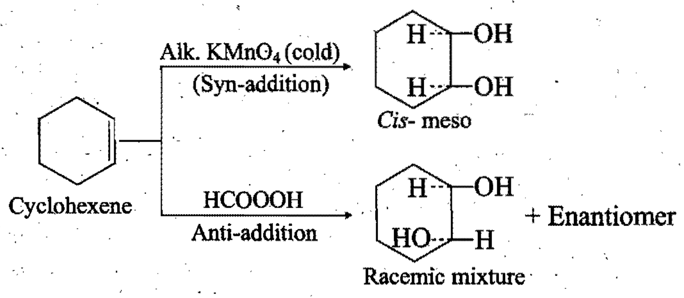
(iii) Hydroxylation using peroxy acids : A mixture of H_2O_2 and formic acid, (*i.e.*, HCO_3H) on allowing to stand with an alkene yields glycol and the addition of two —OH groups in anti-position.



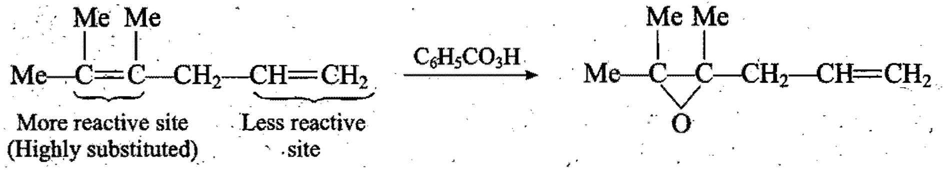
If perbenzoic acid, ($C_6H_5CO_3H$) or peroxy acetic acid, (CH_3CO_3H) is used then firstly glycols are formed and finally yields oxirane (epoxide). Peroxy formic acid forms only glycol, it is strong to decompose epoxy link.



Epoxide formation **(Epoxidation)** is also named as **Prileschaiev's reaction.**



Reactivity of alkenes for peroxy acids: More is in the substitution at double bond, greater is the reactivity.



(iv) Combustion : When burnt in air, alkenes are oxidised to carbon dioxide and water. The reaction is exothermic because heat is evolved.

$$C_nH_{2n} + \frac{3n}{2}O_2 \xrightarrow{\text{Burn}} nCO_2 + nH_2O + \text{Heat}$$

$$C_2H_4 + 3O_2 \xrightarrow{\text{Burn}} 2CO_2 + 2H_2O + \text{Heat}$$

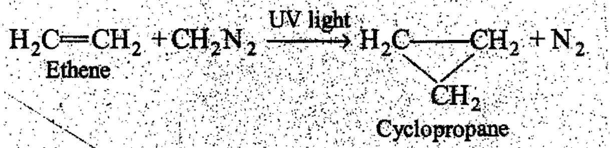
They burn with luminous flame and form explosive mixture with air or oxygen.

4. Insertion of methylene (Carbene): Photolysis of diazomethane and ketene gives methylene. Alkenes react with methylene in presence of light to form cycloalkanes.

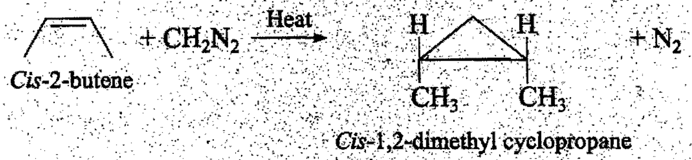
$$\underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow{h\nu} :CH_2 + N_2$$

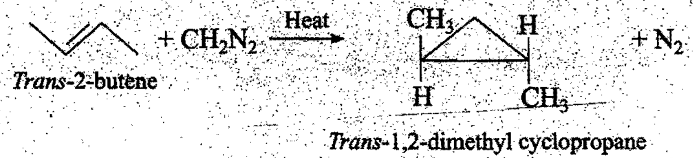
$$\underset{\text{Ketene}}{H_2C=C=O} \xrightarrow{h\nu} :CH_2 + CO$$

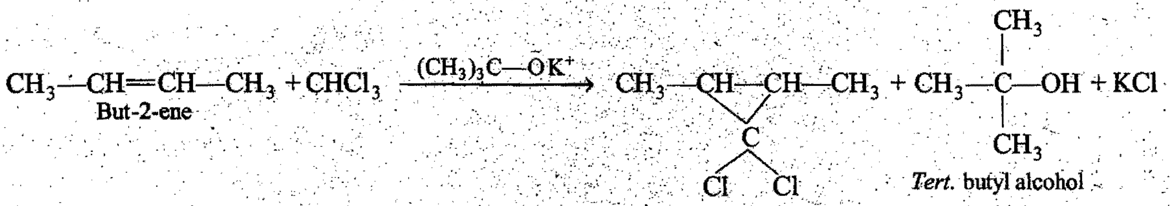
Only singlet carbene ($\ddot{C}H_2$) is involved in alkene addition reaction.



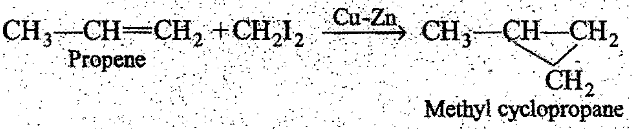
This addition is stereospecific because *cis*- and *trans*-alkenes give stereoisomers, *i.e.*, the addition is **syn**.







So, when an alkene reacts with chloroform in presence of potassium *tert.*-butoxide, there is addition of dichloromethylene (dichloro carbene $:CCl_2$). Methylene can also be added when an alkene reacts with CH_2I_2 in presence of catalyst (Cu-Zn) to form cycloalkane.



This reaction is known as **Simmons-Smith** reaction.

Uses of alkenes : Ethene is used:

(i) for the manufacture of polythene—a plastic material. Substituted alkenes upon polymerisation forms a number of useful polymers such as polypropene, PVC, teflon and natural rubber etc.

(ii) for artificial ripening of fruits;

(iii) as a general anaesthetic;

(iv) as a starting material for a large number of compounds such as glycol, ethyl halides, ethyl alcohol, ethylene oxide, etc;

(v) for making poisonous mustard gas (War gas);

(vi) for making ethylene-oxygen flame for cutting and welding metals.

7.7 ALKYNES

Alkynes contain four hydrogen atoms less than the corresponding alkanes and are characterised by the presence of a triple bond in the molecule. The first and the most important member of this series is acetylene, $HC{\equiv}CH$. Hence, the alkynes (C_nH_{2n-2}) are also called acetylenes.

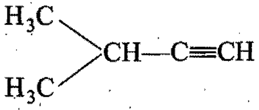
Nomenclature : There are three systems for naming alkynes:

(i) The common name system : The common names of alkynes do not bear any relationship and are based on the names of related compounds.

Formula (C_nH_{2n-2})	**Common name**
$C_2H_2(HC{\equiv}CH)$	Acetylene
$C_3H_4(CH_3C{\equiv}CH)$	Allylene
$C_4H_6(CH_3C{\equiv}CCH_3)$	Crotonylene

Except acetylene, other names are no longer used.

(ii) Derived system : In this system, the higher alkynes are regarded as alkyl derivatives of acetylene.

Formula	Derived name
$HC\equiv CH$	Acetylene
$CH_3C\equiv CH$	Methyl acetylene
$CH_3CH_2C\equiv CH$	Ethyl acetylene
$CH_3C\equiv CCH_3$	Dimethyl acetylene
	Isopropyl acetylene

(iii) IUPAC system : Names are obtained by dropping -ane of the parent alkane and adding the suffix -yne.

Alkane − ane + yne = Alkyne

When the triple bond can take up more than one position in the molecule, the carbon chain is numbered in such a way as to give minimum number to carbon atom bearing triple bond.

Formula	IUPAC name
$HC\equiv CH$	Ethyne
$CH_3C\equiv CH$	Propyne
$CH_3CH_2C\equiv CH$	But-1-yne
$CH_3C\equiv CCH_3$	But-2-yne

Alkynyl groups :

$$HC\equiv CH \xrightarrow{-H} HC\equiv C\text{—} \qquad (-e + yl) = \text{Ethynyl}$$

$$H_3C\text{—}C\equiv CH \xrightarrow{-H} H_3C\text{—}C\equiv C\text{—} (-e + yl) = \text{1-Propynyl}$$

Reactivity of alkynes: Inspite of the fact that the two π-bonds are present in alkynes, these are less reactive than alkenes towards addition reactions (due to symmetrical cylindrical nature of π-electron cloud of alkynes). Further, alkynes do not show geometrical isomerism due to their linear structure.

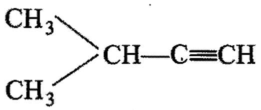
Due to greater electronegativity of *sp*-hybridized carbon atoms of a triple bond than sp^2 -hybridized carbon atoms of a doule bond, the π-electrons of alkyne are more tightly attached to the carbon atoms than π-electrons in alkene and hence are less easily available for addition reactions with electrophiles. As a result, **alkynes are less reactive than alkenes towards electrophilic addition reactions.** A majority of addition reactions of alkynes are catalysed by heavy metal ions such as Hg^{2+} and Ba^{2+}, etc., while no such catalysts are needed in case of electrophilic addition reactions to alkenes.

7.8 ISOMERISM IN ALKYNES

Ethyne does not show any type of isomerism. Other alkynes can exhibit the following types of structural isomerism:

(i) Chain isomerism : It is due to the difference in the type of carbon skeleton.

$CH_3CH_2CH_2C\equiv CH$;
Pent-1-yne



3-Methyl but-1-yne

(ii) Position isomerism : It is due to the difference in the position of triple bond in the carbon chain.

$CH_3CH_2C\equiv CH$; But-1-yne $\qquad$ $CH_3\text{—}C\equiv C\text{—}CH_3$ But-2-yne

$CH_3CH_2CH_2C\equiv CH$; Pent-1-yne $\qquad$ $CH_3CH_2C\equiv CCH_3$ Pent-2-yne

(iii) Functional isomerism : Alkynes and dienes have same molecular formulae. Alkynes contain one triple bond while dienes contain two double bonds in their molecules. C_4H_6 represents butyne and butadiene.

$CH_3CH_2C\equiv CH$; But-1-yne $\qquad$ $H_2C{=}CH\text{—}CH{=}CH_2$ Buta-1,3-diene

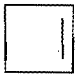
$CH_3\text{—}C\equiv CH$ Propyne $\qquad$ $H_2C{=}C{=}CH_2$ Propa-1,2-diene (Allene)

(iv) Ring chain isomerism: Alkynes and cycloalkenes having same molecular formulae are ring chain isomers.

$CH_3\text{—}C\equiv CH$;
Propyne

Cyclopropene

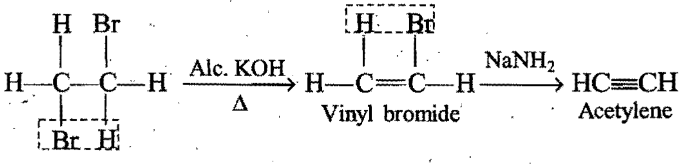
$CH_3CH_2C\equiv CH$;
But-1-yne



Cyclobutene

7.9 GENERAL METHODS OF PREPARATION OF ALKYNES

(i) By heating ethylene bromide or ethylidine bromide with alcoholic potash followed by sodamide ($NaNH_2$) in liquid ammonia **(Dehydrohalogenation of dihalides).**

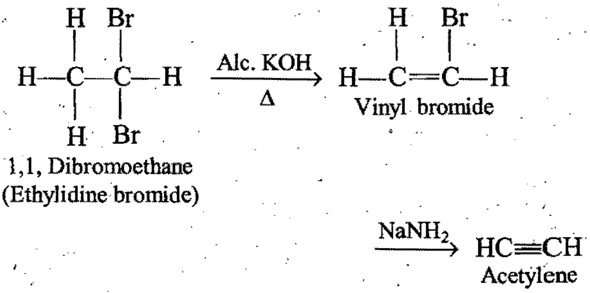


$$H\text{—}C\text{—}C\text{—}H \xrightarrow[\Delta]{\text{Alc. KOH}} H\text{—}C{=}C\text{—}H \xrightarrow{NaNH_2} HC\equiv CH$$

1,2-Dibromoethane
(Ethylene bromide)

Vinyl bromide

Acetylene



$$H\text{—}C\text{—}C\text{—}H \xrightarrow[\Delta]{\text{Alc. KOH}} H\text{—}C{=}C\text{—}H \xrightarrow{NaNH_2} HC\equiv CH$$

1,1, Dibromoethane
(Ethylidine bromide)

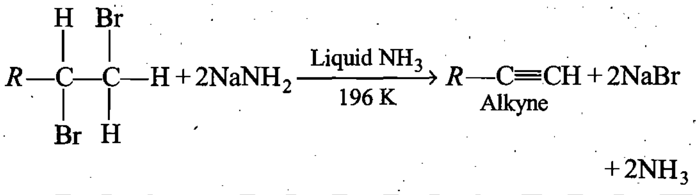
Vinyl bromide

Acetylene

(i) Heat of combustion of alkanes is greater than corresponding alkene and alkyne.

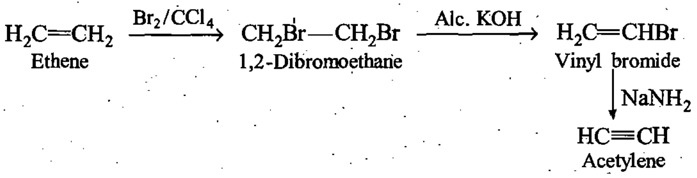
(ii) '*Cis*'-isomer has greater heat of combustion than '*trans*'-isomer because *cis*-isomer is destabilized by steric hindrance.

Sodamide ($NaNH_2$) in liquid NH_3 can be used instead of alcoholic KOH.



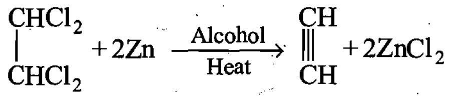
$$R-\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{Br}{C}}-H + 2NaNH_2 \xrightarrow[196\ K]{\text{Liquid } NH_3} \underset{\text{Alkyne}}{R-C{\equiv}CH} + 2NaBr + 2NH_3$$

Note : By this method, ethene can be converted into acetylene.



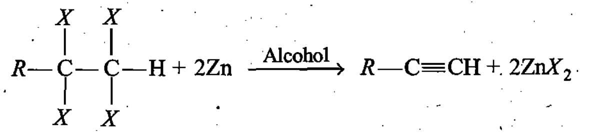
$$\underset{\text{Ethene}}{H_2C{=}CH_2} \xrightarrow{Br_2/CCl_4} \underset{\text{1,2-Dibromoethane}}{CH_2Br{-}CH_2Br} \xrightarrow{\text{Alc. KOH}} \underset{\text{Vinyl bromide}}{H_2C{=}CHBr} \xrightarrow{NaNH_2} \underset{\text{Acetylene}}{HC{\equiv}CH}$$

(ii) By heating 1,1,2,2-tetrachloroethane with zinc in methanol (Dehalogenation of tetrahalides):



$$\begin{array}{c} CHCl_2 \\ | \\ CHCl_2 \end{array} + 2Zn \xrightarrow[\text{Heat}]{\text{Alcohol}} \begin{array}{c} CH \\ ||| \\ CH \end{array} + 2ZnCl_2$$

Note : This method can be used for the purification of ethyne and higher alkynes can also be prepared.

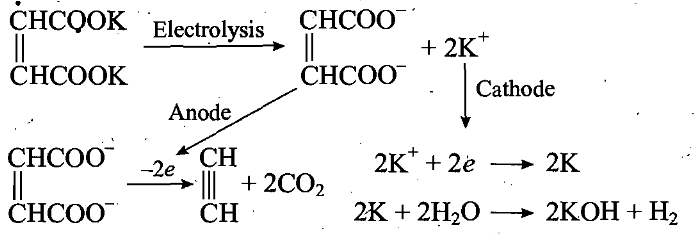


$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H + 2Zn \xrightarrow{\text{Alcohol}} R-C{\equiv}CH + 2ZnX_2$$

(iii) By heating haloform (CHX_3) with silver powder : Pure acetylene is obtained when iodoform or chloroform is heated with silver powder.

$$\underset{\text{Iodoform}}{CHI_3} + 6Ag + I_3CH \xrightarrow{\Delta} \underset{\text{Ethyne}}{HC{\equiv}CH} + 6AgI$$

(iv) By the electrolysis of aqueous solution of sodium or potassium maleate or fumarate (Kolbe's method):



$$\begin{array}{c} CHCOOK \\ \| \\ CHCOOK \end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{c} CHCOO^- \\ \| \\ CHCOO^- \end{array} + 2K^+$$

Anode

$$\begin{array}{c} CHCOO^- \\ \| \\ CHCOO^- \end{array} \xrightarrow{-2e} \begin{array}{c} CH \\ ||| \\ CH \end{array} + 2CO_2$$

Cathode

$$2K^+ + 2e \longrightarrow 2K$$

$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

(v) Laboratory method : Acetylene is prepared in the laboratory by the action of water on calcium carbide.

$$\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O \longrightarrow \underset{\text{Acetylene}}{HC{\equiv}CH} + Ca(OH)_2$$

Acetylene prepared by this method is contaminated with small amounts of phosphine, hydrogen sulphide, arsine, ammonia, etc. The evolved gas is thus, passed through acidified copper sulphate solution. There should be no flame in the vicinity of the apparatus because acetylene catches fire as it forms explosive mixture with air.

$$H_2S + CuSO_4 \longrightarrow \underset{\text{(Black ppt.)}}{CuS} + H_2SO_4$$

$$2PH_3 + 3CuSO_4 \longrightarrow \underset{\substack{\text{Cupric phosphide} \\ \text{(Black ppt.)}}}{Cu_3P_2} + 3H_2SO_4$$

(vi) Manufacture : (a) Laboratory method of preparation of acetylene is also used on a large scale for its manufacture. The start is made with limestone ($CaCO_3$). It is heated at 1000°C to form quick lime, (CaO). A mixture of quick lime and coke is then heated in an electric furnace when calcium carbide is formed.

$$CaCO_3 \xrightarrow{\text{Heat}} CaO + CO_2$$

$$CaO + 3C \xrightarrow{2000\text{–}3000°C} CaC_2 + CO$$

(b) Acetylene is manufactured by heating methane or natural gas at 1500°C in an electric arc.

$$2CH_4 \xrightarrow{\text{Electric arc}} HC{\equiv}CH + 3H_2$$

(c) A recent method for the manufacture of acetylene is the controlled partial oxidation of methane at high temperature.

$$6CH_4 + O_2 \xrightarrow{1500°C} 2HC{\equiv}CH + 2CO + 10H_2$$

(d) Propyne can be prepared by the hydrolysis of magnesium carbide.

$$Mg_2C_3 + 4H_2O \longrightarrow CH_3C{\equiv}CH + 2Mg(OH)_2$$

(vii) Synthesis (Berthelot) : Acetylene is synthesised by striking an electric arc between carbon electrodes in the atmosphere of hydrogen.

$$2C + H_2 \xrightarrow{2000\text{–}2500°C} HC{\equiv}CH$$

7.10 GENERAL CHARACTERISTICS OF ALKYNES

Physical properties :

(i) The first three members (C_2, C_3 and C_4) are colourless gases, the next eight are liquids while the higher one are solid.

(ii) Acetylene has a garlic odour due to the presence of phosphine as impurity.

(iii) Alkynes are weakly polar, lighter than water and immisible with water but highly soluble in organic solvents like ether, acetone, benzene and carbon tetrachloride. Acetylene is transported under high pressure in acetone soaked on porous material packed in steel cylinders.

(iv) The melting and boiling points of alkynes are slightly higher than those of corresponding members of alkane and alkene series. This is due to the fact that alkynes have a linear structure and therefore, their molecules are rather more closely packed in the crystal lattice as compared to alkanes and alkenes.

(v) Their melting point, boiling point and density increase with increase in molar mass.

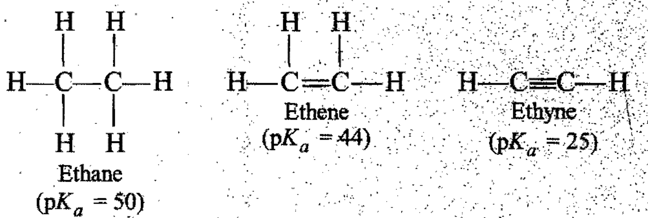
Chemical properties : (1) Acidic nature : Acetylene is acidic in nature. The acidity can be explained on the basis of percentage of *s*-character of the hybrid atomic orbital. The amount of *s*-character in various hybrid orbitals is as follows:

Hybrid orbital	Percentage of *s*-character
sp	50 (1/2)
sp^2	33.3 (1/3)
sp^3	25 (1/4)

The *s*-character of C—H bond of acetylene is higher in comparison to C—H bond of ethene and ethane. Therefore, the release of H^+ ion from an alkene and alkane molecule is difficult and they do not show acidic character.

$$\underset{K_a \approx 10^{-26}}{HC\equiv CH} > \underset{K_a \approx 10^{-36}}{H_2C=CH_2} > \underset{K_a \approx 10^{-42}}{H_3C-CH_3}$$

The hybridisation of the atom bonded to the hydrogen has a large effect on the acidity of that hydrogen as shown in the following examples:



Ethane ($pK_a = 50$) Ethene ($pK_a = 44$) Ethyne ($pK_a = 25$)

The hybridisation changes from sp^3 in ethane to sp^2 in ethene and to sp in ethyne, the acidity increases and the pK_a decreases. This is because of the relative stability of the unshared electrons in the conjugate bases of each of these compounds.

An '*s*' orbital has a lower energy than a '*p*' orbital. Therefore, the energy of a hybrid orbital decreases with the increase in '*s*' character. The energy of hybrid orbitals is in the order $sp < sp^2 < sp^3$.

The electrons of the C—H bond in acetylene are strongly held by carbon nuclei. This facilitates the removal of hydrogen as proton.

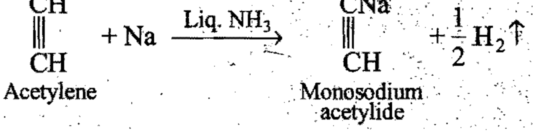
Acidic nature is $HOH > ROH > HC\equiv CH > NH_3 > RH$

Conversely, the relative basicities follow the order:

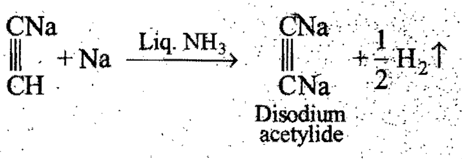
$$R^- > NH_2^- > HC\equiv C^- > RO^- > HO^-$$

On account of acidic nature, acetylene forms salts which are called **acetylides** or **alkynides.**

(a) Formation of sodium acetylides : Acetylene reacts with sodium in liquid ammonia or sodamide ($NaNH_2$) to form sodium acetylides.



$$\underset{\text{Acetylene}}{\begin{matrix}CH\\ |||\\ CH\end{matrix}} + Na \xrightarrow{\text{Liq. NH}_3} \underset{\text{Monosodium acetylide}}{\begin{matrix}CNa\\ |||\\ CH\end{matrix}} + \frac{1}{2}H_2\uparrow$$

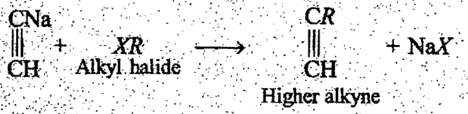


$$\begin{matrix}CNa\\ |||\\ CH\end{matrix} + Na \xrightarrow{\text{Liq. NH}_3} \underset{\text{Disodium acetylide}}{\begin{matrix}CNa\\ |||\\ CNa\end{matrix}} + \frac{1}{2}H_2\uparrow$$

$$\underset{\text{Ethyne}}{HC\equiv C-H} + \underset{\text{Sod. amide}}{2NaNH_2} \longrightarrow \underset{\text{Disodium ethynide}}{\overset{+}{Na}-\overset{-}{C}\equiv\overset{-}{C}-\overset{+}{Na}}$$

Hence, ethyne and other terminal alkynes (1-alkynes) are weakly acidic in character. During these reactions, the acetylenic hydrogen is removed as a proton to form stable carbanions (acetylide ions).

Note : This reaction is utilised for the preparation of higher alkynes.



$$\begin{matrix}CNa\\ |||\\ CH\end{matrix} + \underset{\text{Alkyl halide}}{XR} \longrightarrow \underset{\text{Higher alkyne}}{\begin{matrix}CR\\ |||\\ CH\end{matrix}} + NaX$$

$$\underset{\text{Sodium acetylide}}{HC\equiv C^{-}Na^{+}} + BrCH_3 \longrightarrow \underset{\text{Propyne}}{HC\equiv C-CH_3} + NaBr$$

$$\underset{\text{Propyne}}{CH_3-C\equiv C-H} + Na \xrightarrow{\text{Liq. NH}_3} CH_3-C\equiv C-Na$$

$$CH_3-C\equiv C-Na + ICH_3 \longrightarrow \underset{\text{But-2-yne}}{CH_3-C\equiv C-CH_3}$$

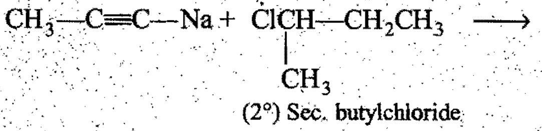
$$CH_3C\equiv C-Na + \underset{\text{Ethyl bromide}}{BrCH_2CH_3} \longrightarrow \underset{\text{Pent-2-yne}}{CH_3C\equiv C-CH_2CH_3}$$

The acetylinic and terminal H are reactive hence, salt formation is easier.

$$\underset{\text{Terminal alkyne}}{R-C\equiv C-H} \xrightarrow{\text{Liq. NH}_3} R-C\equiv C-Na$$

$$\xrightarrow{XR'} \underset{\text{Higher alkyne}}{R-C\equiv C-R'}$$

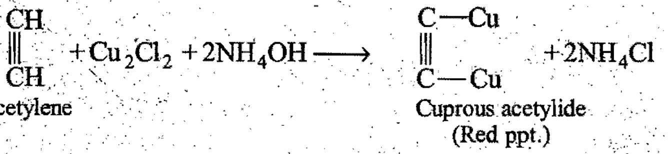
Higher alkynes are formed when $R-X$ and $R'X$ should be primary (1°) alkyl halides, since higher 2° and 3° alkyl halides give mainly alkenes when they react with sodium alkynides.



$$CH_3-C\equiv C-Na + \underset{\text{(2°) Sec. butylchloride}}{\underset{CH_3}{ClCH}-CH_2CH_3} \longrightarrow$$

$$CH_3-C\equiv CH + \underset{\text{But-2-ene}}{CH_3CH=CHCH_3} + NaCl$$

(b) Formation of copper acetylide : Acetylene when passed through an ammoniacal cuprous chloride solution, a red precipitate of cuprous acetylide is formed. This is a test of acetylene.



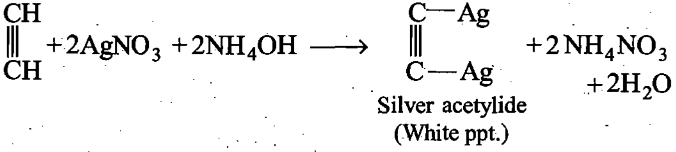
$$\underset{\text{Acetylene}}{\begin{matrix}CH\\ |||\\ CH\end{matrix}} + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{Cuprous acetylide (Red ppt.)}}{\begin{matrix}C-Cu\\ |||\\ C-Cu\end{matrix}} + 2NH_4Cl + 2H_2O$$

$$\underset{\text{Propyne}}{2CH_3-C\equiv CH} + Cu_2Cl_2 + 2NH_4OH \longrightarrow$$

$$2CH_3-C\equiv CCu + 2NH_4Cl + 2H_2O$$

$$\underset{\text{(Terminal alkyne)}}{R—C\equiv CH} + [Cu(NH_3)_2]^+\overset{-}{O}H \longrightarrow \underset{\substack{\text{Copper alkynide}\\ \text{(Red ppt.)}}}{R—C\equiv C—Cu} + H_2O + 2NH_3$$

(c) Formation of silver acetylide : Acetylene when passed through an ammoniacal solution of silver nitrate (Tollens' reagent), a white precipitate of silver acetylide is formed. This is also a test of acetylene.



$$\begin{array}{c}CH\\ |||\\ CH\end{array} + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\substack{\text{Silver acetylide}\\ \text{(White ppt.)}}}{\begin{array}{c}C—Ag\\ |||\\ C—Ag\end{array}} + 2NH_4NO_3 + 2H_2O$$

$$\underset{\text{(Terminal alkyne)}}{R—C\equiv CH} + \underset{\text{Tollens' reagent}}{[Ag(NH_3)_2]^+\overset{-}{O}H} \longrightarrow \underset{\substack{\text{Silver alkynide}\\ \text{(White ppt.)}}}{R—C\equiv C—Ag} + H_2O + 2NH_3$$

Note : Copper and silver acetylides are very sensitive to shock when dry and may explode violently. However, these can be decomposed by acids to regenerate acetylene.

$$\underset{\text{Cuprous acetylide}}{Cu—C\equiv C—Cu} + 2HCl \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + 2CuCl\downarrow$$

$$Ag—C\equiv C—Ag \xrightarrow[\text{(Dil.)}]{2HNO_3} HC\equiv CH + 2AgNO_3$$

Hence, these reactions can be utilised for the separation of acetylene from a mixture containing ethane, ethylene and acetylene.

(d) Reaction with Grignard reagent : (Alkylation of acetylene and terminal alkynes).

$$HC\equiv CH + CH_3MgI \xrightarrow[\text{ether}]{\text{Dry}} CH_4 + HC\equiv C—MgI$$

$$HC\equiv C—MgI + ICH_3 \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Propyne}}{HC\equiv C—CH_3} + MgI_2$$

$$\underset{\text{Terminal alkyne}}{R'—C\equiv CH} + RMgX \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Alkynyl G.R.}}{R'—C\equiv CMgX} + \underset{\text{Alkane}}{RH}$$

Alkynyl Grignard reagents like usual Grignard reagents can be used to prepare a variety of organic compounds.

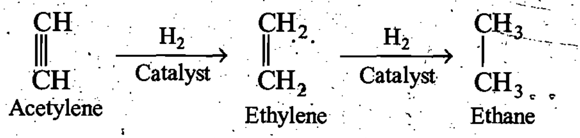
(e) Reaction with ammoniacal I_2 :

$$HC\equiv CH + I_2 + 2NH_4OH \longrightarrow IC\equiv CI + 2NH_3 + 2H_2O$$

(2) Addition reactions : Carbon-carbon triple bond is a combination of one sigma-bond and two pi-bonds. Due to the presence of excess of π-electrons, acetylene should be very reactive and should undergo addition reactions very readily but actually it is not so. Ethylene has been found to be more reactive than acetylene towards electrophilic reagents. This is quite unexpected.

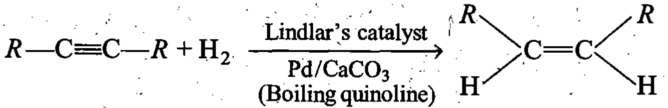
However, acetylene undergoes electrophilic addition reactions. The addition occurs in two stages. In first stage, acetylene is converted into ethylene compound and in the second stage, into ethane derivative, *i.e.*, two molecules of the reagent are used. Besides electrophilic addition reactions, nucleophilic addition reactions are also observed.

(a) Addition of hydrogen (Hydrogenation) : Acetylene reacts with hydrogen in the presence of a catalyst (Ni, Pt or Pd). The reaction occurs in two stages.

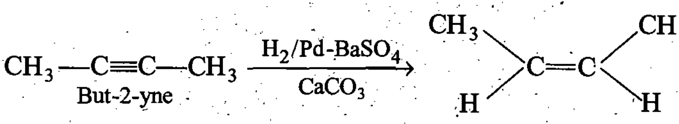


$$\underset{\text{Acetylene}}{\begin{array}{c}CH\\ |||\\ CH\end{array}} \xrightarrow[\text{Catalyst}]{H_2} \underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ ||\\ CH_2\end{array}} \xrightarrow[\text{Catalyst}]{H_2} \underset{\text{Ethane}}{\begin{array}{c}CH_3\\ |\\ CH_3\end{array}}$$

Ethylene can be obtained in very good yield if Lindlar's catalyst is used.



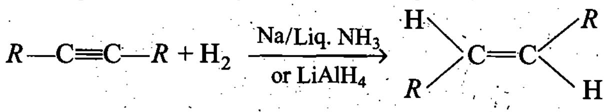
Cis-alkene



But-2-ene (*cis*) 95%

This reaction is an example of **stereoselective reaction.** Thus reaction that generates a C—C double bond or chiral carbon in a product leading to the preferential formation of one stereoisomer over another is known as a stereoselective reaction.

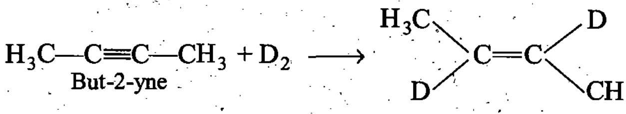
For *'trans'* product we take Na/liq. NH_3 or Li-NH_3/C_2H_5OH or $LiAlH_4$ as a reducing agent (anti-addition).



Trans-alkene

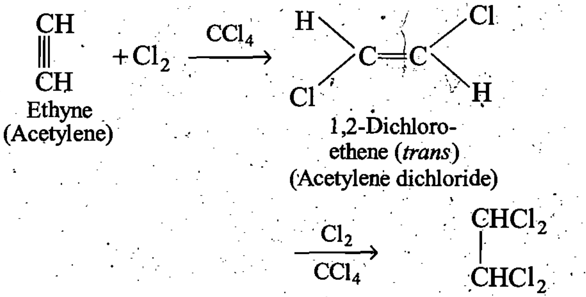
$$\underset{\text{Higher alkyne}}{R—C\equiv C—R} + 2H_2 \xrightarrow[\text{Catalyst}]{PtO_2 \text{ or } [(C_6H_5)_3P]_3} \underset{\text{Higher alkane}}{RCH_2CH_2—R}$$

Instead of H_2, the D_2 can be used to form *trans*-alkene.



But-2-ene (*trans*)

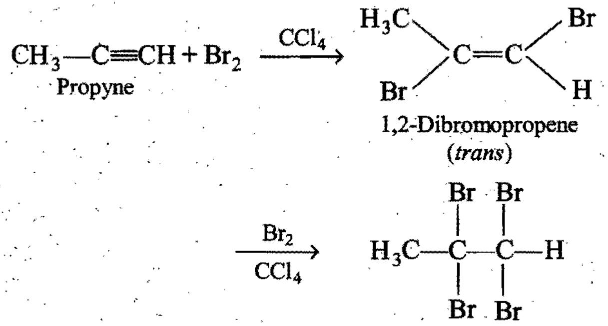
(b) Addition of halogens : Acetylene combines with gaseous chlorine or bromine in the dark to form di or tetrahalides.



1,2-Dichloro-ethene (*trans*)
(Acetylene dichloride)

1,1,2,2-Tetrachloro-ethane (Westron)
(Acetylene tetrachloride)

Mechanism(See unit 5, problem 6 on page 220)



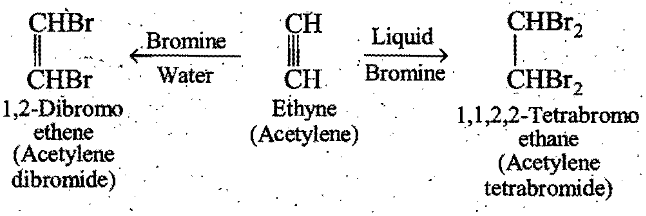
Propyne

1,2-Dibromopropene (*trans*)

1,1,2,2-Tetrabromo propane

Thus, alkynes also decolourise bromine water and this reaction gives a useful test for unsaturation.

Liquid bromine yields tetrabromo derivative while bromine water or Br_2/CCl_4 forms dibromo derivative.



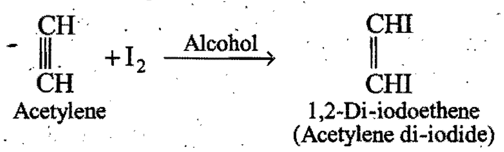
$$CHBr{=}CHBr \xleftarrow[\text{Water}]{\text{Bromine}} CH{\equiv}CH \xrightarrow[\text{Bromine}]{\text{Liquid}} CHBr_2{-}CHBr_2$$

1,2-Dibromo ethene (Acetylene dibromide)

Ethyne (Acetylene)

1,1,2,2-Tetrabromo ethane (Acetylene tetrabromide)

Iodine reacts slowly in alcohol to form di-iodo derivative.



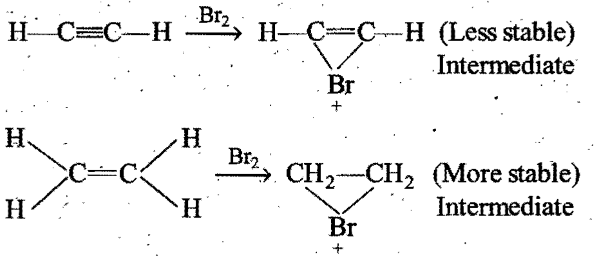
$$CH{\equiv}CH + I_2 \xrightarrow{\text{Alcohol}} CHI{=}CHI$$

Acetylene

1,2-Di-iodoethene (Acetylene di-iodide)

Dihalide derivatives are *trans*-isomers and the addition of halogens to acetylene is stereoselective reaction.

Alkynes are less reactive than alkenes towards addition of halogens because alkynes form less stable intermediate.



Alkynes undergo addition of halogens, as well as other electrophilic addition more slowly than alkenes.

$$\underset{\text{Pent-1-en-4-yne}}{HC{\equiv}C{-}CH_2{-}CH{=}CH_2} \xrightarrow[CCl_4,\ -20°C]{Br_2\ (1\ \text{mole})}$$

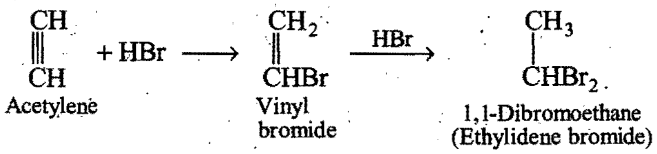
$$\underset{\text{4,5-Dibromopent-1-yne (90\%)}}{HC{\equiv}C{-}CH_2{-}CH(Br){-}CH_2(Br)}$$

This reaction clearly shows that alkynes are less reactive than alkenes towards electrophilic reagents.

Thus, the order of reactivity of halogens is:

$$Cl_2 > Br_2 > I_2$$

(c) Addition of halogen acids: Addition of one molecule of halogen acid gives vinyl halide which then adds another molecule of hydrogen halide to form gem-dihalide. The addition follows Markownikoff's rule.



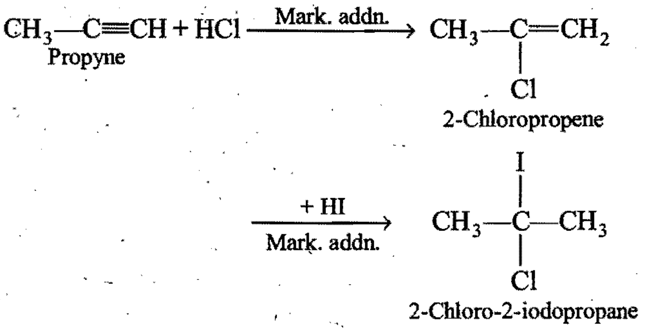
$$CH{\equiv}CH + HBr \longrightarrow CH_2{=}CHBr \xrightarrow{HBr} CH_3{-}CHBr_2$$

Acetylene

Vinyl bromide

1,1-Dibromoethane (Ethylidene bromide)

Mechanism (See unit 5, problem 5 on page 220)



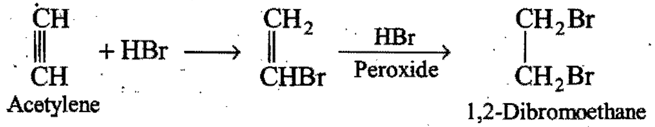
$$\underset{\text{Propyne}}{CH_3{-}C{\equiv}CH} + HCl \xrightarrow{\text{Mark. addn.}} CH_3{-}C(Cl){=}CH_2$$

2-Chloropropene

$$\xrightarrow[\text{Mark. addn.}]{+HI} CH_3{-}C(I)(Cl){-}CH_3$$

2-Chloro-2-iodopropane

In presence of peroxides, anti-Markownikoff product is obtained.

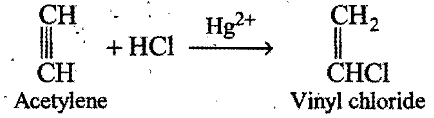


$$CH{\equiv}CH + HBr \longrightarrow CH_2{=}CHBr \xrightarrow[\text{Peroxide}]{HBr} CH_2Br{-}CH_2Br$$

Acetylene

1,2-Dibromoethane

By passing acetylene into dilute hydrochloric acid at 60–65°C in presence of mercuric ion (catalyst), only one molecule is added to give vinyl chloride.



$$CH{\equiv}CH + HCl \xrightarrow{Hg^{2+}} CH_2{=}CHCl$$

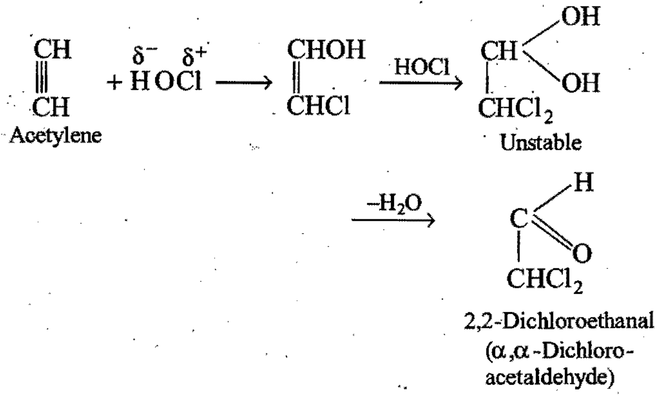
Acetylene

Vinyl chloride

Vinyl chloride polymerises to yield **polyvinyl chloride** (PVC), an addition polymer used in making PVC sheets, water pipes, hoses and hand bags, etc.

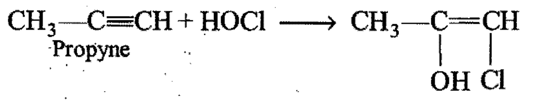
The order of reactivity of halogen acids is HI > HBr > HCl > HF, but HF adds only under pressure.

(d) Addition of hypochlorous acid (Chlorohydroxylation by chlorine water): Acetylene when passed into hypochlorous acid solution forms dichloroacetaldehyde.

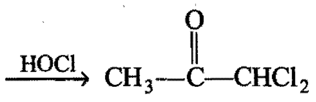


Acetylene

2,2-Dichloroethanal (α,α-Dichloro-acetaldehyde)

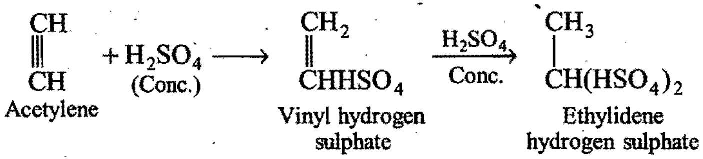


$$\underset{\text{Propyne}}{CH_3{-}C{\equiv}CH} + HOCl \longrightarrow CH_3{-}C(OH){=}CH(Cl)$$



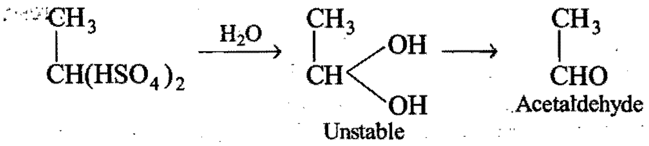
$$\xrightarrow{HOCl} \underset{\text{1,1-Dichloroacetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CHCl_2}$$

(e) Addition of sulphuric acid : Acetylene gas when passed through conc. H_2SO_4, it gets absorbed forming ethylidene hydrogen sulphate.



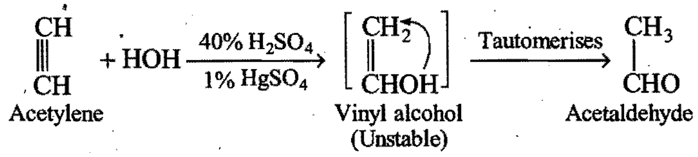
$$\underset{\text{Acetylene}}{\overset{CH}{\underset{CH}{|||}}} + \underset{\text{(Conc.)}}{H_2SO_4} \longrightarrow \underset{\text{Vinyl hydrogen sulphate}}{\overset{CH_2}{\underset{CHHSO_4}{\|}}} \xrightarrow[\text{Conc.}]{H_2SO_4} \underset{\text{Ethylidene hydrogen sulphate}}{\overset{CH_3}{\underset{CH(HSO_4)_2}{|}}}$$

Ethylidene hydrogen sulphate on boiling with water produces acetaldehyde.

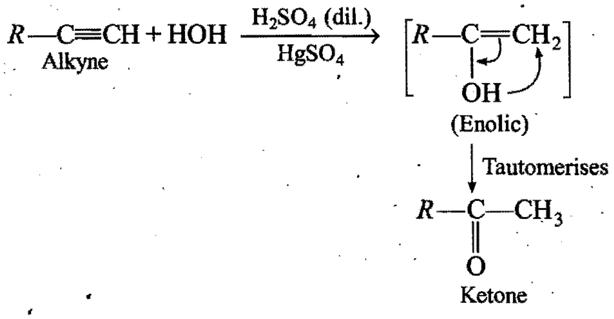


$$\overset{CH_3}{\underset{CH(HSO_4)_2}{|}} \xrightarrow{H_2O} \underset{\text{Unstable}}{\overset{CH_3}{\underset{CH(OH)_2}{|}}} \longrightarrow \underset{\text{Acetaldehyde}}{\overset{CH_3}{\underset{CHO}{|}}}$$

(f) Addition of water (Hydration) : Alkynes cannot be hydrated more easily than alkenes because of their low reactivity towards electrophilic addition reactions. Further when acetylene is passed through 40% H_2SO_4 containing 1% $HgSO_4$ at 80°C, a water molecule adds upto give acetaldehyde.



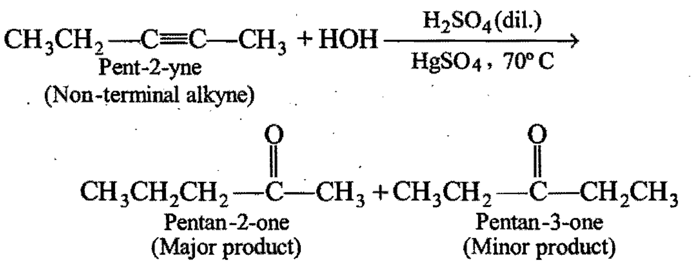
$$\underset{\text{Acetylene}}{\overset{CH}{\underset{CH}{|||}}} + HOH \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} \underset{\text{Vinyl alcohol (Unstable)}}{\left[\overset{CH_2}{\underset{CHOH}{\|}}\right]} \xrightarrow{\text{Tautomerises}} \underset{\text{Acetaldehyde}}{\overset{CH_3}{\underset{CHO}{|}}}$$



$$\underset{\text{Alkyne}}{R-C\equiv CH} + HOH \xrightarrow[HgSO_4]{H_2SO_4\text{ (dil.)}} \underset{\text{(Enolic)}}{\left[R-\underset{OH}{\underset{|}{C}}=CH_2\right]} \xrightarrow{\text{Tautomerises}} \underset{\text{Ketone}}{R-\underset{O}{\underset{\|}{C}}-CH_3}$$

This is called **keto-enol tautomerism.**

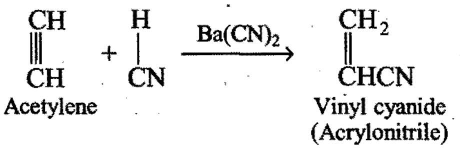
However, if the unsymmetrical alkyne is non-terminal, a mixture of two isomeric ketones is obtained in which methyl ketone predominates. For example,



$$\underset{\text{Pent-2-yne (Non-terminal alkyne)}}{CH_3CH_2-C\equiv C-CH_3} + HOH \xrightarrow[HgSO_4,\ 70^\circ C]{H_2SO_4\text{(dil.)}}$$

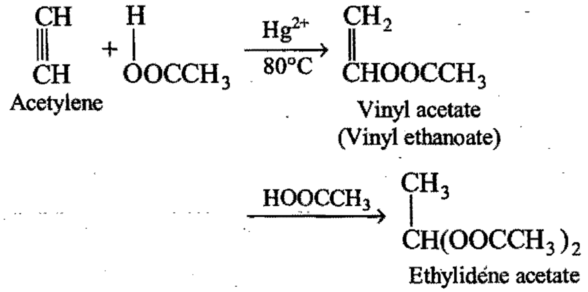
$$\underset{\text{Pentan-2-one (Major product)}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{\text{Pentan-3-one (Minor product)}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3}$$

(g) Addition of hydrogen cyanide : The addition of a molecule of HCN occurs in the presence of barium cyanide or CuCl/HCl (catalyst). Vinyl cyanide is formed. This is an important reagent for making polymers such as **Orlon** (Poly acrylonitrile or **PAN**) and **Buna-N rubber.**



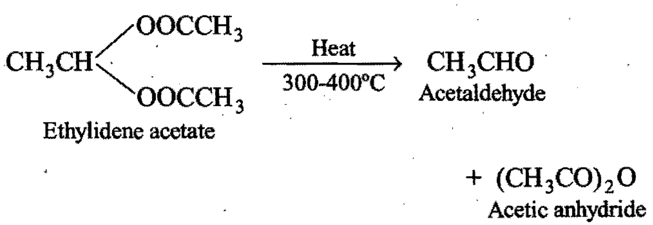
$$\underset{\text{Acetylene}}{\overset{CH}{\underset{CH}{|||}}} + \overset{H}{\underset{CN}{|}} \xrightarrow{Ba(CN)_2} \underset{\text{Vinyl cyanide (Acrylonitrile)}}{\overset{CH_2}{\underset{CHCN}{\|}}}$$

(h) Addition of acetic acid : Acetylene combines with acetic acid in presence of mercuric sulphate or zinc acetate or BF_3 (as catalyst) at 160°C. It first forms vinyl acetate and then ethylidene acetate.



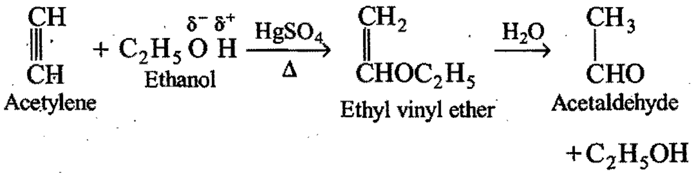
$$\underset{\text{Acetylene}}{\overset{CH}{\underset{CH}{|||}}} + \overset{H}{\underset{OOCCH_3}{|}} \xrightarrow[80^\circ C]{Hg^{2+}} \underset{\text{Vinyl acetate (Vinyl ethanoate)}}{\overset{CH_2}{\underset{CHOOCCH_3}{\|}}} \xrightarrow{HOOCCH_3} \underset{\text{Ethylidene acetate}}{\overset{CH_3}{\underset{CH(OOCCH_3)_2}{|}}}$$

Vinyl acetate on polymerisation forms polyvinyl acetate (PVA), used in plastic industry and ethylidene acetate on heating at 300–400°C yields acetaldehyde and acetic anhydride.

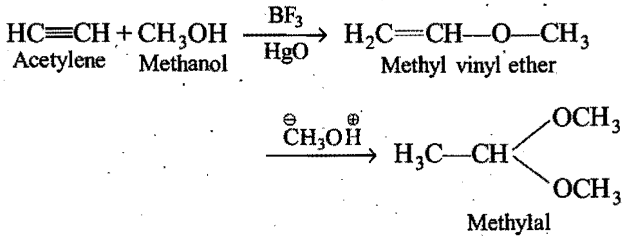


$$\underset{\text{Ethylidene acetate}}{CH_3CH(OOCCH_3)_2} \xrightarrow[300\text{-}400^\circ C]{\text{Heat}} \underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

(i) Addition of alcohol : In presence of NaOH or KOH or a mercury salt, acetylene reacts with alcohol (Alcoholation of alkynes) to form ethyl vinyl ether.



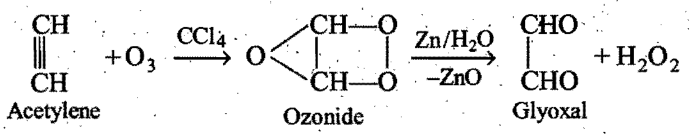
$$\underset{\text{Acetylene}}{\overset{CH}{\underset{CH}{|||}}} + \underset{\text{Ethanol}}{C_2H_5\overset{\delta^-}{O}\overset{\delta^+}{H}} \xrightarrow[\Delta]{HgSO_4} \underset{\text{Ethyl vinyl ether}}{\overset{CH_2}{\underset{CHOC_2H_5}{\|}}} \xrightarrow{H_2O} \underset{\text{Acetaldehyde}}{\overset{CH_3}{\underset{CHO}{|}}} + C_2H_5OH$$



$$\underset{\text{Acetylene}}{HC\equiv CH} + \underset{\text{Methanol}}{CH_3OH} \xrightarrow[HgO]{BF_3} \underset{\text{Methyl vinyl ether}}{H_2C=CH-O-CH_3} \xrightarrow{\overset{\ominus}{C}H_3\overset{\oplus}{O}H} \underset{\text{Methylal}}{H_3C-CH(OCH_3)_2}$$

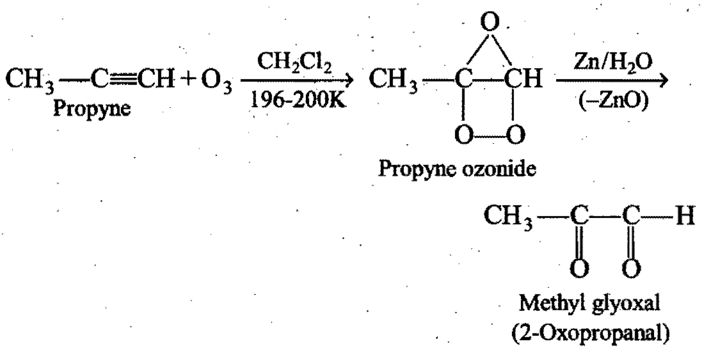
Such a reaction is termed vinylation.

(j) Addition of ozone (Ozonolysis) : Acetylene combines with ozone in presence of some inert solvents such as CCl_4, $CHCl_3$ or CH_2Cl_2 at low temperature (196–200 K) to form an ozonide which on decomposition with zinc dust and water or H_2/Pd (reductive cleavage) yields glyoxal.

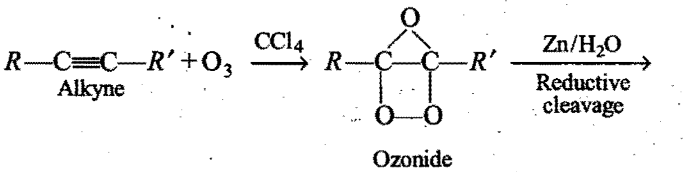


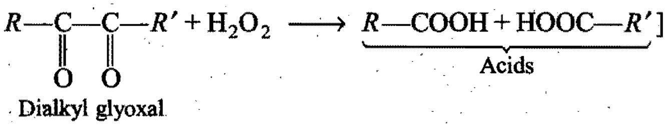
$\longrightarrow 2HCOOH$ Formic acid

Glyoxal is further converted into formic acid.



[Higher alkynes form diketones which are further oxidised to carboxylic acids.

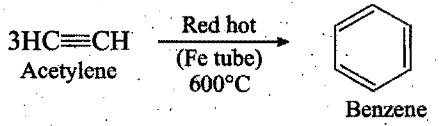




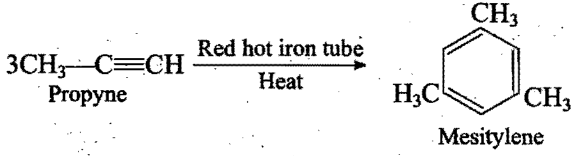
$$\underset{\text{Dialkyl glyoxal}}{R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R'} + H_2O_2 \longrightarrow \underbrace{R-COOH + HOOC-R'}_{\text{Acids}}]$$

(k) Self addition or polymerisation : Acetylene undergoes polymerisation yielding different types of polymeric compounds under different conditions :

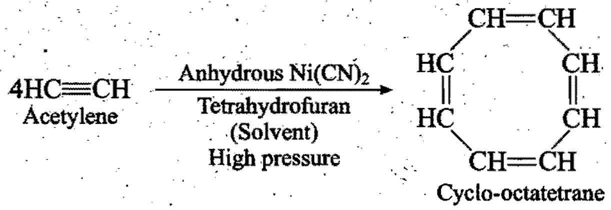
(i) Cyclic polymerisation : When acetylene is passed through a red-hot metallic tube at 600°C, cyclic polymerisation takes place with the formation of benzene.



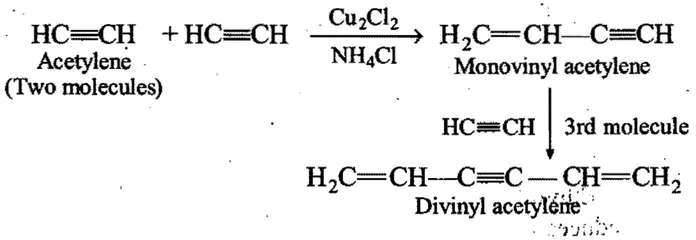
Propyne on heating trimerises under similar conditions and forms mesitylene (1,3,5-trimethyl benzene).



(ii) Acetylene dissolved in tetrahydrofuran polymerises into cyclo-octa-1,3,5,7-tetrene in presence of $Ni(CN)_2$ and under high pressure.



(iii) Linear polymerisation : When acetylene is passed into cuprous chloride solution containing NH_4Cl, linear polymerisation occurs forming monovinyl acetylene and divinyl acetylene.



$$\underset{\substack{\text{Acetylene}\\\text{(Two molecules)}}}{HC\equiv CH} + HC\equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{Monovinyl acetylene}}{H_2C=CH-C\equiv CH}$$

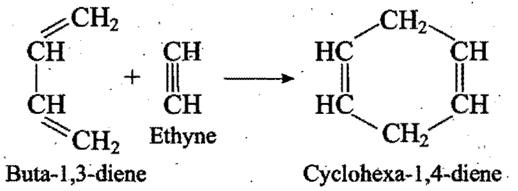
$$\xrightarrow[\text{3rd molecule}]{HC\equiv CH} \underset{\text{Divinyl acetylene}}{H_2C=CH-C\equiv C-CH=CH_2}$$

Vinyl acetylene on reduction with H_2/Pt in presence of $BaSO_4$ forms buta-1,3-diene.

$$\underset{\text{Vinyl acetylene}}{H_2C=CH-C\equiv CH} \xrightarrow[(BaSO_4)]{H_2/Pt} \underset{\text{Buta-1,3-diene}}{H_2C=CH-CH=CH_2}$$

Butadiene and vinyl cyanide form polymer **Buna N-synthetic rubber.**

Butadiene adds to acetylene **(Diels-Alder reaction)** to form addition product.

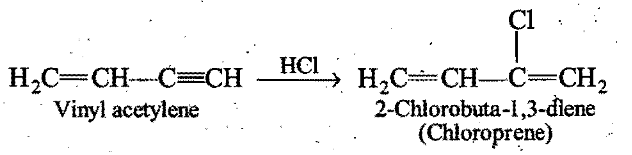


But if 1-alkynes react with Cu_2Cl_2 containing NH_4Cl and air, oxidative coupling takes place and dimerised products are formed.

$$HC\equiv CH + HC\equiv CH \xrightarrow[NH_4Cl,\ air]{Cu_2Cl_2} HC\equiv C-C\equiv CH + H_2$$

$$2R-C\equiv CH \xrightarrow[NH_4Cl,\ air]{Cu_2Cl_2} R-C\equiv C-C\equiv C-R + H_2$$

When monovinyl acetylene is treated with HCl, it forms chloroprene which is used for making synthetic rubber like substance; **neoprene.**



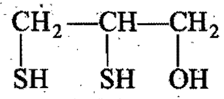
$$\underset{\text{Vinyl acetylene}}{H_2C=CH-C\equiv CH} \xrightarrow{HCl} \underset{\substack{\text{2-Chlorobuta-1,3-diene}\\\text{(Chloroprene)}}}{H_2C=CH-\overset{\overset{Cl}{|}}{C}=CH_2}$$

(iv) When acetylene is heated in presence of spongy copper or its oxides, a cork like substance **cuprene** is produced. This is used in the manufacture of **linoleum.**

(l) Addition of arsenic trichloride : In the presence of anhydrous aluminium chloride, acetylene combines with $AsCl_3$ to yield Lewisite, a powerful poisonous gas.

$$\underset{\text{Acetylene}}{HC\equiv CH} + Cl-AsCl_2 \longrightarrow \underset{\substack{\text{2-Chlorovinyldichloroarsenic}\\\text{(Lewisite)}}}{ClCH=CHAsCl_2}$$

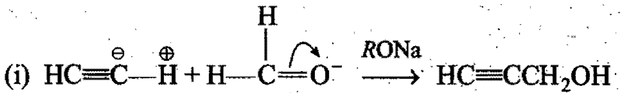
It is more poisonous than mustard gas and was used in World War-II. The British chemists developed an antidote for Lewisite and named it as **BAL** (British Anti Lewisite).



$$\underset{SH}{CH_2}-\underset{SH}{CH}-\underset{OH}{CH_2}$$

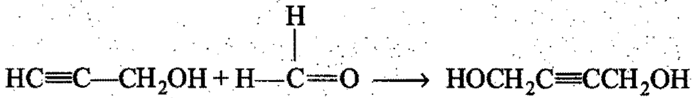
BAL

(m) Alkynylation of carbonyl compounds : Terminal alkynes (containing ≡CH, a **methine** hydrogen atom) can add on to >C=O group in presence of sodium alkoxide or copper acetylide catalyst and form alkyndiol (along with small amount of alkyneol). This is called alkynylation or ethinylation.



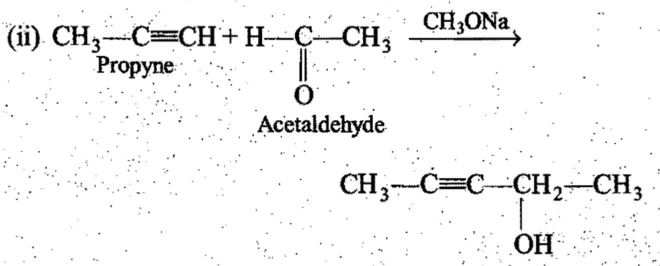
$$\text{(i) } HC\equiv\overset{\ominus}{C}-\overset{\oplus}{H}+H-\overset{H}{\overset{|}{C}}=O^- \xrightarrow{RONa} HC\equiv CCH_2OH$$

Ethyne Formaldehyde Prop-2-yn-1-ol



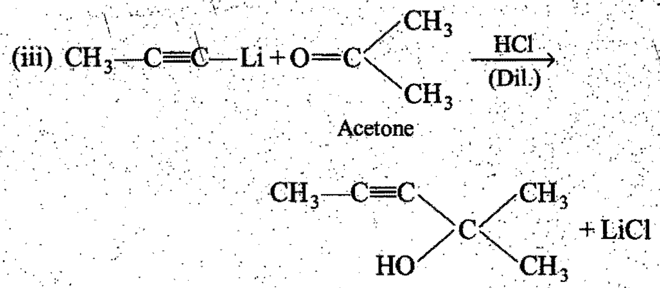
$$HC\equiv C-CH_2OH+H-\overset{H}{\overset{|}{C}}=O \longrightarrow HOCH_2C\equiv CCH_2OH$$

But-2-yn-1,4-diol



$$\text{(ii) } \underset{\text{Propyne}}{CH_3-C\equiv CH}+\underset{\text{Acetaldehyde}}{H-\underset{O}{\underset{\|}{C}}-CH_3} \xrightarrow{CH_3ONa} CH_3-C\equiv C-\underset{OH}{\underset{|}{CH}}-CH_3$$

Pent-3-yn-2-ol



(iii) $CH_3-C\equiv C-Li+O=C(CH_3)_2 \xrightarrow[\text{(Dil.)}]{HCl} CH_3-C\equiv C-C(OH)(CH_3)_2+LiCl$

Acetone

(iv) Terminal alkyne ($R-C\equiv C-H$) on reaction with certain hydroxy compounds can also undergo ethinylation with the removal of H_2O.

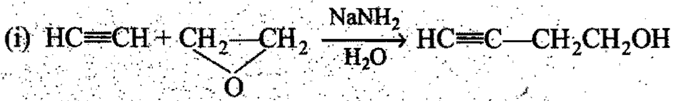
$$H-C\equiv C-H+HOCH_2NR_2 \longrightarrow H-C\equiv C-CH_2NR_2+H_2O$$

(n) Carbonylation : Acetylene reacts with $(CO+H_2O)$ or $(CO+ROH)$ in presence of nickel catalyst and forms α, β-unsaturated acid or ester.

$$HC\equiv CH+CO+H_2O \xrightarrow{Ni} \underset{\text{Prop-2-enoic acid}}{H_2C=CHCOOH}$$

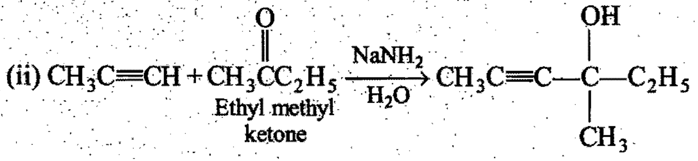
$$HC\equiv CH+CO+HOCH_3 \xrightarrow{Ni} \underset{\text{Ester}}{H_2C=CHCOOCH_3}$$

(o) Some other addition reactions can be summerised as:



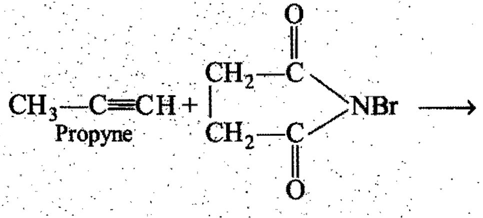
(i) $HC\equiv CH+CH_2-CH_2(O) \xrightarrow[H_2O]{NaNH_2} HC\equiv C-CH_2CH_2OH$

Ethylene oxide



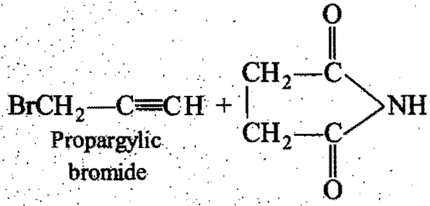
$$\text{(ii) } CH_3C\equiv CH+\underset{\text{Ethyl methyl ketone}}{CH_3\overset{O}{\overset{\|}{C}}C_2H_5} \xrightarrow[H_2O]{NaNH_2} CH_3C\equiv C-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-C_2H_5$$

(iii) Propargylic bromination



Propyne

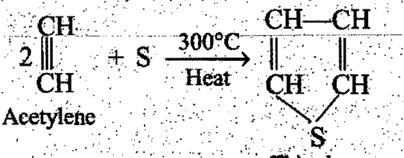
N-Bromosuccinimide



Propargylic bromide

(3) Reactions with sulphur, nitrogen and ammonia :

(a) When acetylene is passed over heated iron pyrites at 300°C, it combines with sulphur to form **thiophene.**

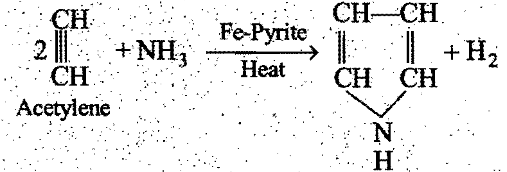


Thiophene

(b) When an electric spark is passed through a mixture of acetylene and nitrogen, hydrocyanic acid is formed.

$$C_2H_2+N_2 \xrightarrow[\text{spark}]{\text{Electric}} 2HCN$$

(c) Acetylene combines with ammonia at high temperature to form **pyrrole.**



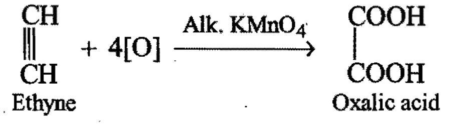
Pyrrole

(4) Oxidation : Different oxidation products are obtained with different reagents:

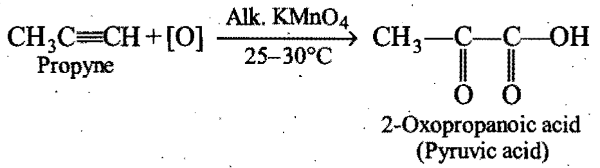
(a) Burning (Combustion) : Acetylene burns with smoky flame in excess of air. Under controlled supply of air, it burns with a bright light which is injurious to eyes. The burning is highly exothermic and a large amount of heat is produced. The oxy-acetylene flame (blue flame) is used for welding and cutting purposes and gives a temperature of about 3500°C.

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O; \ \Delta H = -1300 \text{ kJ}$$

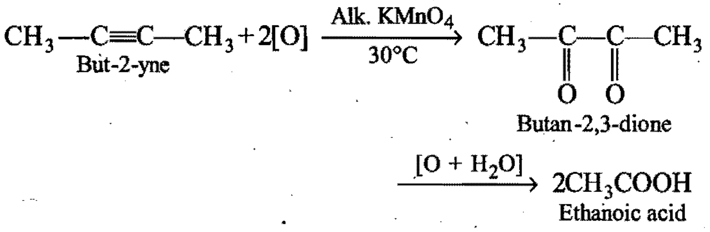
(b) With alk. $KMnO_4$ solution : Acetylene is finally converted into oxalic acid with cold, dilute alk. $KMnO_4$ solution and pink colour of the solution is discharged.



$$\underset{\text{Ethyne}}{\begin{matrix}CH\\|||\\CH\end{matrix}} + 4[O] \xrightarrow{\text{Alk. KMnO}_4} \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}}$$



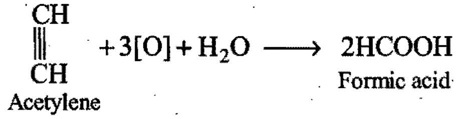
$$\underset{\text{Propyne}}{CH_3C{\equiv}CH} + [O] \xrightarrow[\text{25–30°C}]{\text{Alk. KMnO}_4} \underset{\substack{\text{2-Oxopropanoic acid}\\\text{(Pyruvic acid)}}}{CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OH}$$



$$\underset{\text{But-2-yne}}{CH_3-C{\equiv}C-CH_3} + 2[O] \xrightarrow[\text{30°C}]{\text{Alk. KMnO}_4} \underset{\text{Butan-2,3-dione}}{CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3}$$

$$\xrightarrow{[O + H_2O]} \underset{\text{Ethanoic acid}}{2CH_3COOH}$$

(c) With acidified $KMnO_4$: Acetylene is converted into formic acid with a rupture of triple bond at high temperature.



$$\underset{\text{Acetylene}}{\begin{matrix}CH\\|||\\CH\end{matrix}} + 3[O] + H_2O \longrightarrow \underset{\text{Formic acid}}{2HCOOH}$$

$$R-C{\equiv}CH + 3[O] + H_2O \xrightarrow{\text{Heat}} RCOOH + HCOOH$$

(d) With hot acidic or alkaline $KMnO_4$:

$$\underset{\text{Propyne}}{CH_3-C{\equiv}CH} + [O] \xrightarrow[\text{KMnO}_4]{\text{100-110°C}} CH_3COOH + CO_2$$

In contrast, non-terminal alkynes on oxidation with hot alkaline $KMnO_4$ gives only carboxylic acids.

For example,

$$\underset{\text{But-2-yne}}{CH_3-C{\equiv}C-CH_3} + 4[O] \xrightarrow[\text{100-110°C}]{\text{Alk. KMnO}_4}$$

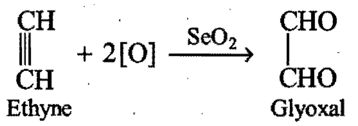
$$\underset{\text{Ethanoic acid (2 moles)}}{CH_3COOH + HOOCCH_3}$$

$$\underset{\text{Pent-2-yne}}{CH_3CH_2C{\equiv}C-CH_3} + 4[O] \xrightarrow[\text{100-110°C}]{\text{Alk. KMnO}_4}$$

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} + \underset{\text{Ethanoic acid}}{HOOCCH_3}$$

So, it is possible to determine the position of triple bond in an alkyne molecule by alkaline oxidation with $KMnO_4$.

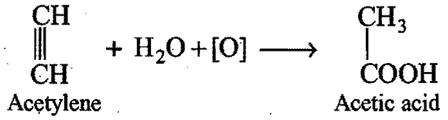
(e) With SeO_2 (Selenium dioxide) : Acetylene is oxidised to glyoxal (ethane-1,2-dial) with SeO_2.



$$\underset{\text{Ethyne}}{\begin{matrix}CH\\|||\\CH\end{matrix}} + 2[O] \xrightarrow{SeO_2} \underset{\text{Glyoxal}}{\begin{matrix}CHO\\|\\CHO\end{matrix}}$$

$$\underset{\text{Propyne}}{CH_3-C{\equiv}CH} + 2[O] \xrightarrow{SeO_2} \underset{\text{2-Ketopropanal}}{CH_3COCHO}$$

(f) With chromic acid ($K_2Cr_2O_7 + H_2SO_4$) : Acetylene is converted into acetic acid and orange colour of the dilute acidified dichromate changes to light green.



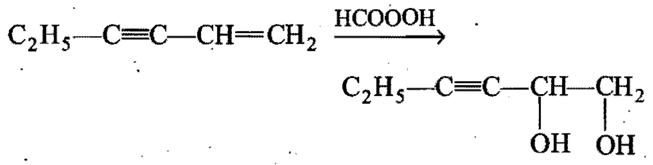
$$\underset{\text{Acetylene}}{\begin{matrix}CH\\|||\\CH\end{matrix}} + H_2O + [O] \longrightarrow \underset{\text{Acetic acid}}{\begin{matrix}CH_3\\|\\COOH\end{matrix}}$$

Oxidation of alkyne is slower than that of alkene. Thus, only double bond can be oxidised leaving behind triple bond.

$$CH_3C{\equiv}CCH_2CH{=}CHC_2H_5 \xrightarrow[\text{AcOH}]{\text{CrO}_3 \text{ in}}$$

$$CH_3C{\equiv}CCH_2COOH + C_2H_5COOH$$

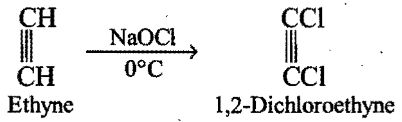
Peroxy formic acid (HCO_3H) hydroxylates C=C without affecting C≡C bond.



$$C_2H_5-C{\equiv}C-CH{=}CH_2 \xrightarrow{\text{HCOOOH}}$$

$$C_2H_5-C{\equiv}C-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$$

(5) Substitution reactions : When acetylene is passed through sodium hypochlorite solution at 0°C in absence of light, hydrogen atoms are replaced by chlorine atoms with the formation of 1,2-dichloroethyne.



$$\underset{\text{Ethyne}}{\begin{matrix}CH\\|||\\CH\end{matrix}} \xrightarrow[\text{0°C}]{\text{NaOCl}} \underset{\text{1,2-Dichloroethyne}}{\begin{matrix}CCl\\|||\\CCl\end{matrix}}$$

(6) Isomerisation : (a) On heating with alcoholic KOH or $NaNH_2$ in inert solvent, the triple bond of 1-alkyne is shifted towards the centre to form an isomeric 2-alkyne.

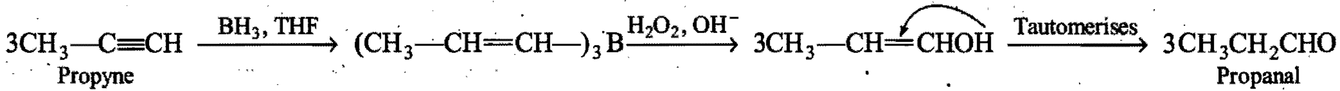
$$\underset{\text{But-1-yne}}{CH_3CH_2-C{\equiv}CH} \xrightarrow[\text{(Heat)}]{\text{Alcoholic KOH}} \underset{\text{But-2-yne}}{CH_3-C{\equiv}C-CH_3}$$

(b) On heating with sodamide ($NaNH_2$ in liquid NH_3), the triple bond shifts towards the end.

$$\underset{\text{But-2-yne}}{CH_3-C{\equiv}C-CH_3} \xrightarrow[(-NH_3)]{NaNH_2} \underset{\text{Sodium alkynide}}{CH_3CH_2-C{\equiv}CNa} \xrightarrow{H_2O}$$

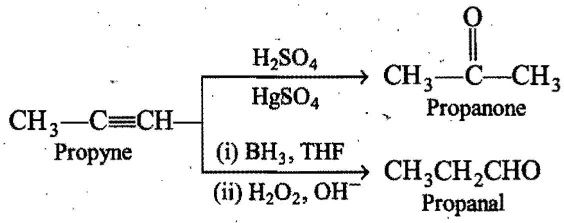
$$\underset{\text{But-1-yne}}{CH_3CH_2-C{\equiv}CH}$$

(7) Oxidative-Hydroboration : Alkynes react with BH_3 (in THF) and finally converted into carbonyl compounds.



$$\underset{\text{Propyne}}{3CH_3{-}C{\equiv}CH} \xrightarrow{BH_3,\ THF} (CH_3{-}CH{=}CH{-})_3B \xrightarrow{H_2O_2,\ OH^-} 3CH_3{-}CH{=}CHOH \xrightarrow{\text{Tautomerises}} \underset{\text{Propanal}}{3CH_3CH_2CHO}$$

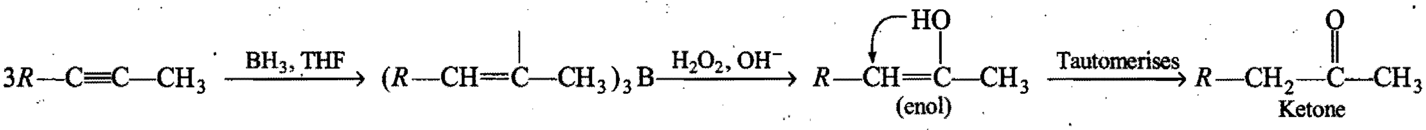
Thus, this method is useful for preparing aldehyde from terminal alkyne, which is otherwise not possible by hydration.



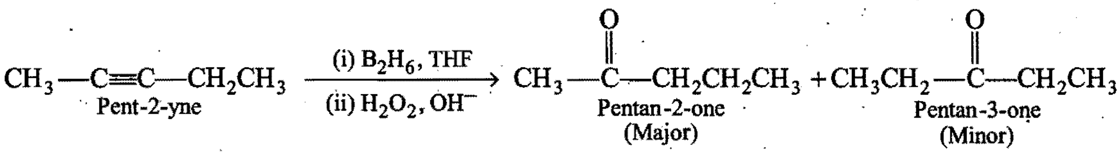
$$\underset{\text{Propyne}}{CH_3{-}C{\equiv}CH} \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{Propanone}}{CH_3{-}\overset{\overset{\Large O}{\|}}{C}{-}CH_3}$$

$$\underset{\text{Propyne}}{CH_3{-}C{\equiv}CH} \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } BH_3,\ THF} \underset{\text{Propanal}}{CH_3CH_2CHO}$$

Higher ketones can also be prepared by this method.



$$3R{-}C{\equiv}C{-}CH_3 \xrightarrow{BH_3,\ THF} (R{-}CH{=}\overset{|}{C}{-}CH_3)_3B \xrightarrow{H_2O_2,\ OH^-} \underset{\text{(enol)}}{R{-}CH{=}\overset{HO}{\overset{|}{C}}{-}CH_3} \xrightarrow{\text{Tautomerises}} \underset{\text{Ketone}}{R{-}CH_2{-}\overset{\overset{\Large O}{\|}}{C}{-}CH_3}$$



$$\underset{\text{Pent-2-yne}}{CH_3{-}C{\equiv}C{-}CH_2CH_3} \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } B_2H_6,\ THF} \underset{\substack{\text{Pentan-2-one}\\ \text{(Major)}}}{CH_3{-}\overset{\overset{\Large O}{\|}}{C}{-}CH_2CH_2CH_3} + \underset{\substack{\text{Pentan-3-one}\\ \text{(Minor)}}}{CH_3CH_2{-}\overset{\overset{\Large O}{\|}}{C}{-}CH_2CH_3}$$

Aldehydes can likewise be prepared from terminal alkynes, but to avoid complications due to double addition of diborane, bulky sterically hindered boranes such as (1,2-dimethylpropyl) borane commonly known as **disiamylborane** (R_2BH) is used in place of B_2H_6.

$$\underset{\text{Propyne}}{CH_3C{\equiv}CH} \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } R_2BH} \underset{\text{Propanal}}{CH_3CH_2CHO}$$

Here, R_2BH (abreviated as Sia_2BH) is disiamylborane, *i.e.*, $[(CH_3)_2CH{-}\underset{\underset{CH_3}{|}}{CH}{-}]_2BH$.

Uses : (i) Acetylene is used as an illuminant.

(ii) It is used for the production of oxy-acetylene flame. The temperature of the flame is above 3000°C. It is employed for cutting and welding of metals.

(iii) Acetylene is used for artificial ripening of fruits.

(iv) It is used as a general anaesthetic under the name **Naracylene.**

(v) Acetylene has synthetic applications in synthesis of *cis* and *trans* alkenes and methyl ketones. It serves as a starting material for the manufacture of a large variety of substance like acetic acid, ethyl alcohol, vinyl plastics, synthetic rubbers such as **Buna N** and synthetic fibres such as **Orlon.**

(vi) On electrical decomposition acetylene produces finely divided carbon and hydrogen. Hydrogen is used in airships.

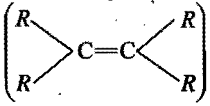
7.11 TESTS OF UNSATURATION

Unsaturation means the presence of double or triple bond/bonds in the molecule of the compound. The tests of unsaturation are actually the tests for the detection of double or triple bond. The following two tests are generally performed for unsaturation.

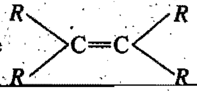
1. Baeyer's reagent : It is 1% $KMnO_4$ solution containing sodium carbonate. It has pink colour. To an aqueous solution of the compound a few drops of Baeyer's reagent are added. The pink colour of the solution disappears on shaking and a brown precipitate of MnO_2 appears. The decolourisation of pink colour indicates the presence of unsaturation in the compound.

Note : (a) This test is also given by aldehydes or primary and secondary alcohols which are readily oxidised.

(b) Alkenes without any hydrogen atom on the carbon forming the double bond do not show this test.



2. Bromine-carbon tetrachloride test : The compound is dissolved in carbon tetrachloride or chloroform and then a few drops of 5% bromine solution in carbon tetrachloride are added to it. If the colour of the bromine is discharged, *i.e.*, disappears, it indicates the presence of unsaturation in the compound.

Note : This test also fails in the case of alkenes of the type  $R_2C=CR_2$

Besides the above two tests, 1-alkynes give a white precipitate when passed through ammoniacal silver nitrate solution (Tollens' reagent).

The double and triple bonds are located by the identification of the products of ozonolysis.

Degree of Unsaturation

The number of pairs of hydrogen atoms that a molecular formula lacks to be an alkane (C_nH_{2n+2}) is called *degree of unsaturation* and this value is also called the *index of hydrogen deficiency.*

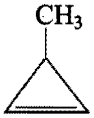
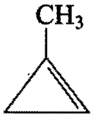
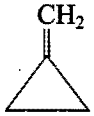
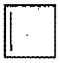
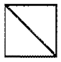
For example, a molecular formula, C_4H_6 has 2° of unsaturation, because a molecule with four carbon atom needs 10H atoms to be an alkane. It has 4H atoms (or two pairs of hydrogen atoms) less than alkane.

$$(C_4H_6 + 2H_2 \longrightarrow C_4H_{10})$$

So, C_4H_6 with 2° of unsaturation can have the following possible isomers:

(i) $H_2C{=}CH{-}CH{=}CH_2$, or $H_2C{=}C{=}CH{-}CH_3$;

(ii) $HC{\equiv}C{-}CH_2{-}CH_3$, or $H_3C{-}C{\equiv}C{-}CH_3$;

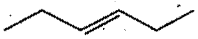
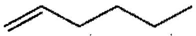
(iii)  or  or  or ; (iv) 

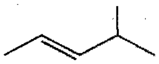
The number of degree of unsaturation in a hydrocarbon is given by:

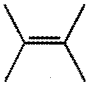
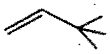
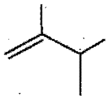
$$= \frac{2n_1 + 2 - n_2}{2}, \quad \text{where, } n_1 \text{ is the number of carbon atoms; } n_2 \text{ is the number of hydrogen atoms.}$$

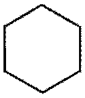
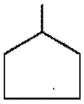
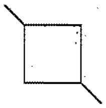
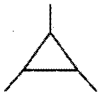
For example, in C_6H_{12}, the degree of unsaturation is $= \frac{2 \times 6 + 2 - 12}{2} = 1$

So, C_6H_{12} with 1° of unsaturation can have different arrangements.

(i)  or  or 

(ii)  or  or 

(iii)  or  or 

(iv)  or  or  or 

Other examples have the following degree of unsaturation:

(i) $C_6H_6 \longrightarrow 4°$ (ii) $C_5H_8 \longrightarrow 2°$

(iii) $C_7H_{10} \longrightarrow 3°$ (iv) $C_8H_{12} \longrightarrow 3°$

(v) $C_{10}H_{16} \longrightarrow 3°$ (vi) $C_{12}H_{10} \longrightarrow 8°$

(vii) $C_3H_3Cl_3$ (It is like C_3H_6) $\longrightarrow 1°$ (viii) C_3H_4O (It is like C_3H_4) $\longrightarrow 2°$

(ix) C_4H_5N (It is like C_4H_4) $\longrightarrow 3°$ (x) C_5H_9Cl (It is like C_5H_{10}) $\longrightarrow 1°$

Hence, degree of unsaturation induces double bonds, triple bonds and rings.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. The shape of but-2-ene is:
   (a) planar (b) tetrahedral
   (c) linear (d) pyramidal
   [Ans. (a)]

2. The molecule that will have dipole moment is:
   (a) *trans*-3-hexene
   (b) *trans*-2-pentene
   (c) 2,2-dimethyl propane
   (d) 2,2,3,3-tetramethyl butane
   [Ans. (b)]
3. Which of the following cannot be obtained by oxidation of alkenes with potassium permanganate followed by acid hydrolysis?
   (a) Carboxylic acid (b) Aldehydes
   (c) Ketones (d) CO_2
   [Ans. (b)]
4. Find the identity of compound $[B]$ in the following reaction sequence;

$$HC{\equiv}C{-}Na + CH_3CH_2CH_2CH_2Br \longrightarrow [A],$$

$$\underset{1\text{ mole}}{[A]} + \underset{1\text{ mole}}{Cl_2} \longrightarrow [B]$$

   (a) *cis*-1,2-dichlorobutane
   (b) *trans*-2,3-dichloro-2-hexene
   (c) *cis*-1,2-dichloro-1-hexene
   (d) *trans*-1,2-dichloro-1-hexene
   [Ans. (d)]
5. 1-Phenyl-2-chloropropane on treatment with alcoholic KOH gives mainly:
   (a) 1-phenyl propan-1-ol (b) 1-phenyl propan-2-ol
   (c) 1-phenyl propene (d) 2-phenyl propene
   [Ans. (c)]
6. Allene (C_3H_4) contains:
   (a) one triple and two double bonds
   (b) two double and four single bonds
   (c) two triple and one double bond
   (d) one double bond and one triple bond
   [Ans. (b)]

7.12 INTERCONVERSIONS

(i) Conversion of ethane into ethene : (Alkane into alkene)

$$\underset{\text{Ethane}}{CH_3{-}CH_3} \xrightarrow[h\nu]{Br_2} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow[KOH]{\text{Alc.}} \underset{\text{Ethene}}{H_2C{=}CH_2}$$

(ii) Ethene into ethane : (Alkene into alkane)

$$\underset{\text{Ethene}}{H_2C{=}CH_2} \xrightarrow[\text{Ni, }300°C]{H_2} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

(iii) Ethane into ethyne (acetylene) : *i.e.*, alkane into alkyne

$$\underset{\text{Ethane}}{CH_3{-}CH_3} \xrightarrow[h\nu]{Br_2} CH_3CH_2Br \xrightarrow[KOH]{\text{Alc.}} \underset{\text{Ethene}}{H_2C{=}CH_2} \xrightarrow[CCl_4]{Br_2} \underset{\text{1,2-Dibromoethane}}{CH_2Br{-}CH_2Br} \xrightarrow[\text{or } NaNH_2]{\text{Alc. KOH}} \underset{\text{Ethyne}}{HC{\equiv}CH}$$

(iv) Ethyne into ethane : (Alkyne into alkane)

$$\underset{\text{Ethyne}}{HC{\equiv}CH} \xrightarrow[\text{Ni, }300°C]{H_2} \underset{\text{Ethene}}{H_2C{=}CH_2} \xrightarrow[\text{Ni, }300°C]{H_2} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

(v) Ethene into propene : Ascending in alkene series.

$$\begin{tikzcd}
\underset{\text{Ethene}}{H_2C{=}CH_2} \arrow[r, "HI"] & \underset{\text{Iodoethane}}{CH_3CH_2I} \arrow[r, "KCN"] & \underset{\substack{\text{Propane nitrile}\\ \text{(Ethyl cyanide)}}}{CH_3CH_2CN} \arrow[r, "{[H]}", "\text{Reduction}"'] & \underset{\text{Propan-1-amine}}{CH_3CH_2CH_2NH_2} \arrow[r, "HNO_2"] & \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} \arrow[d, "PBr_3"] \\
 & & & \underset{\text{Propene}}{CH_3CH{=}CH_2} & \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \arrow[l, "\text{Alc.}"', "KOH"]
\end{tikzcd}$$

Or

$$\underset{\text{Ethene}}{H_2C{=}CH_2} \xrightarrow{HI} \underset{\text{Iodoethane}}{CH_3CH_2I} \xrightarrow{Li(CH_3)_2Cu} \underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[h\nu]{Cl_2} \underset{\substack{\text{1-Chloropropane}\\ \text{or (2-Chloropropane)}}}{CH_3CH_2CH_2Cl} \xrightarrow[KOH]{\text{Alc.}} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$

Or $$\underset{}{H_2C{=}CH_2} \xrightarrow{HI} CH_3CH_2I \xrightarrow{CH_3I/Na} \underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[h\nu]{Cl_2} \underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} \xrightarrow[KOH]{Alc.} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$

(vi) Propene into ethene : Descending an alkene series.

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} \xrightarrow{O_3/H_2O} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[LiAlH_4]{[H]} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[170°C]{H_2SO_4} \underset{\text{Ethene}}{H_2C{=}CH_2}$$

(vii) Acetylene into propyne (methyl acetylene) : (Ascent)

$$\underset{\text{Acetylene}}{HC{\equiv}CH} \xrightarrow{Na} \underset{\substack{\text{Monosodium}\\\text{acetylide}}}{HC{\equiv}CNa} \xrightarrow{CH_3I} \underset{\text{Propyne}}{HC{\equiv}C{-}CH_3}$$

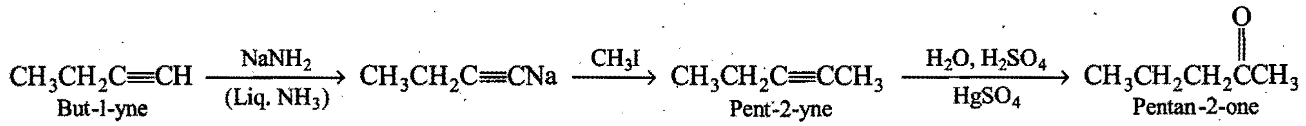
(viii) Propyne into acetylene : (Descent)

$$\underset{\text{Propyne}}{CH_3C{\equiv}CH} \xrightarrow{\text{Lindlar's catalyst}} \underset{\text{Propylene}}{CH_3CH{=}CH_2} \xrightarrow{O_3/H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{PCl_5} \underset{\substack{\text{Ethylidene}\\\text{chloride}}}{CH_3CHCl_2} \xrightarrow[KOH]{Alc.} \underset{\text{Acetylene}}{HC{\equiv}CH}$$

(ix) 1-Butyne into 2-pentyne : (Ascent)

$$\underset{\text{But-1-yne}}{CH_3CH_2C{\equiv}CH} \xrightarrow{NaNH_2} CH_3CH_2C{\equiv}C{-}Na \xrightarrow{CH_3I} \underset{\text{Pent-2-yne}}{CH_3CH_2{-}C{\equiv}CCH_3}$$

(x) 1-Butyne into 2-pentanone : (not more than three steps)



$$\underset{\text{But-1-yne}}{CH_3CH_2C{\equiv}CH} \xrightarrow[(Liq.\ NH_3)]{NaNH_2} CH_3CH_2C{\equiv}CNa \xrightarrow{CH_3I} \underset{\text{Pent-2-yne}}{CH_3CH_2C{\equiv}CCH_3} \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} \underset{\text{Pentan-2-one}}{CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3}$$

7.13 SEPARATION OF ALKANE, ALKENE AND ALKYNE OR SEPARATION OF METHANE OR ETHANE, ETHYLENE AND ACETYLENE

The gaseous mixture is passed through ammoniacal cuprous chloride solution. The alkyne (acetylene) reacts with Cu_2Cl_2 and forms a red precipitate. It is filtered. The alkyne or acetylene is recovered by decomposition of the precipitate with an acid.

$$C_2H_2 + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{(Red ppt.)}}{C_2Cu_2} + 2NH_4Cl + 2H_2O$$

$$C_2Cu_2 + 2HNO_3 \longrightarrow C_2H_2 + Cu_2(NO_3)_2$$

The remaining gaseous mixture is passed through concentrated sulphuric acid. Alkene (ethylene) is absorbed. The hydrogen sulphate derivative is heated at 170°C.

$$C_2H_4 + H_2SO_4 \longrightarrow C_2H_5HSO_4 \xrightarrow[170°C]{Heat} C_2H_4 + H_2SO_4.$$

The methane or ethane is left behind.

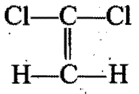
7.14 DISTINCTION BETWEEN ALKANES, ALKENES AND ALKYNES OR DISTINCTION BETWEEN ETHANE, ETHENE AND ETHYNE

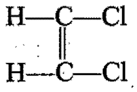
Property	Alkane (Ethane)	Alkene (Ethene)	Alkyne (Ethyne)
1. Molecular formula	$C_nH_{2n+2}(C_2H_6)$	$C_nH_{2n}(C_2H_4)$	$C_nH_{2n-2}(C_2H_2)$
2. Nature	Saturated. Single bond between carbon atoms. Each carbon atom is sp^3-hybridized. $>C-C<$ Bond length : 1.54 Å Bond energy : 83 kcal mol^{-1}	Unsaturated. Double bond between two carbon atoms. Both carbon atoms are sp^2-hybridized. $>C=C<$ 1.34Å 144 kcal mol^{-1}	Unsaturated. Triple bond between two carbon atoms. Both carbon atoms are sp-hybridized. $-C\equiv C-$ 1.20Å 192 kcal mol^{-1}
3. Burning	Burns with nonluminous flame. $C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$	Burns with luminous flame. $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$	Burns with smoky flame. $C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O$
4. Reaction with H_2	—	Forms alkane $C_nH_{2n} + H_2 \xrightarrow[300°C]{Ni} \underset{\text{Alkane}}{C_nH_{2n+2}}$ $C_2H_4 + H_2 \longrightarrow C_2H_6$	Forms alkene and alkane. $C_nH_{2n-2} + H_2 \xrightarrow[300°C]{Ni} \underset{\text{Alkene}}{C_nH_{2n}}$ $C_nH_{2n} + H_2 \xrightarrow[300°C]{Ni} \underset{\text{Alkane}}{C_nH_{2n+2}}$
5. Reaction with conc. H_2SO_4 and hydrolysis	—	Addition. $C_2H_4 + H_2SO_4 \longrightarrow C_2H_5HSO_4 \xrightarrow{H_2O} \underset{\text{Alcohol}}{C_2H_5OH}$	Addition. $C_2H_2 \longrightarrow CH_3CH(HSO_4)_2 \xrightarrow{H_2O} \underset{\text{Aldehyde}}{CH_3CHO}$
6. Br_2/CCl_4	—	Decolourises. Dibromo derivatives, $C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$	Decolourises. Tetrabromo derivatives, $C_2H_2Br_4$.
7. Baeyer's reagent (Alk. $KMnO_4$)	—	Decolourises. Glycol is formed. $\begin{array}{c}CH_2\\ \Vert\\ CH_2\end{array} + H_2O + O \longrightarrow \begin{array}{c}CH_2OH\\ \vert\\ CH_2OH\end{array}$	Decolourises. Oxalic acid is formed. $\begin{array}{c}CH\\ \vert\vert\vert\\ CH\end{array} + 4O \longrightarrow \begin{array}{c}COOH\\ \vert\\ COOH\end{array}$
8. Ammoniacal Cu_2Cl_2	—	—	Red precipitate $\begin{array}{c}CH\\ \vert\vert\vert\\ CH\end{array} + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{(Red)}}{\begin{array}{c}CCu\\ \vert\vert\vert\\ CCu\end{array}} + 2NH_4Cl + 2H_2O$
9. Ammoniacal silver nitrate	—	—	White precipitate $\begin{array}{c}CH\\ \vert\vert\vert\\ CH\end{array} + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\text{(White)}}{\begin{array}{l}C-Ag\\ \vert\vert\vert\\ C-Ag\end{array}} + 2NH_4NO_3 + 2H_2O$

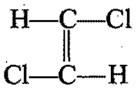
SOME SOLVED PROBLEMS

Problem 1. *Write the structures of all the isomers of dichloroethene. Which one of them will have zero dipole moment?*

Solution : There are three isomers of dichloroethene.


1,1-Dichloroethene
(i)


Cis-1,2-Dichloroethene
(ii)


Trans-1,2-Dichloroethene
(iii)

The structure (iii), *i.e.*, *trans*-isomer has zero dipole moment.

Problem 2. *Propene reacts with* HBr *to give isopropyl bromide but does not give n-propyl bromide.*

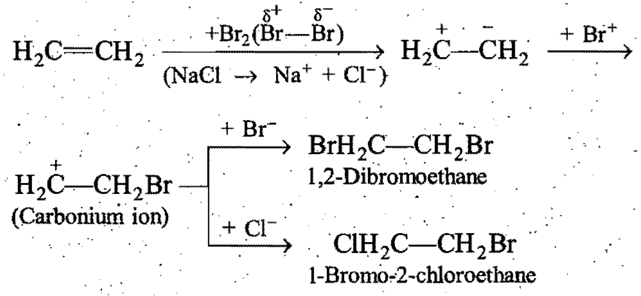
Solution : The addition of HBr on propene takes place in accordance to Markownikoff's rule, *i.e.*, negative part of the additive goes to that carbon atom which is linked with lesser number of hydrogen atoms. The addition of an electrophile involves the intermediate formation of a more stable carbonium ion. $(CH_3)_2\overset{+}{C}H$ is more stable than $CH_3CH_2\overset{+}{C}H_2$ carbonium ion.

Problem 3. *Acetylene is acidic but it does not react with* NaOH *or* KOH. *Give reason.*

Solution : Acetylene is very weak acid. The value of K_a is near about 10^{-25}. Thus, it does not react with NaOH or KOH but reacts with very strong base such as $NaNH_2$.

Problem 4. *Ethene on treating with* Br_2 *in presence of sodium chloride forms a mixture of* CH_2ClCH_2Br *and* CH_2BrCH_2Br. *Give reason.*

Solution : The addition of Br_2 follows ionic mechanism. The intermediate carbonium ion formed is attacked by Br^- as well as by Cl^- given by NaCl.


$$H_2C{=}CH_2 \xrightarrow[(NaCl\ \rightarrow\ Na^+ + Cl^-)]{+Br_2(\overset{\delta+}{Br}-\overset{\delta-}{Br})} H_2\overset{+}{C}-\overset{-}{C}H_2 \xrightarrow{+\ Br^+}$$

$$\underset{\text{(Carbonium ion)}}{H_2\overset{+}{C}-CH_2Br} \xrightarrow{+\ Br^-} \underset{\text{1,2-Dibromoethane}}{BrH_2C-CH_2Br}$$

$$\underset{\text{(Carbonium ion)}}{H_2\overset{+}{C}-CH_2Br} \xrightarrow{+\ Cl^-} \underset{\text{1-Bromo-2-chloroethane}}{ClH_2C-CH_2Br}$$

Problem 5. *How can you prepare benzene from lime?*

Solution : $$\underset{\text{Lime}}{CaO} + \underset{\text{Coke}}{3C} \xrightarrow[\text{furnace}]{\text{Electric}} CaC_2 + CO$$

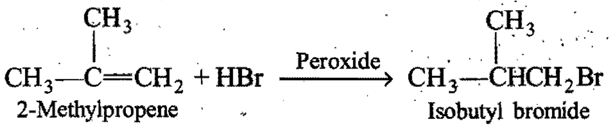
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

$$3C_2H_2 \xrightarrow[\text{Polymerization}]{\text{Red hot tube}} \underset{\text{Benzene}}{C_6H_6}$$

Problem 6. (*a*) *2-Methylpropene can be converted into isobutyl bromide by hydrogen bromide. Write the condition.*

(*b*) *Ethyne and its derivatives will give white precipitate with ammoniacal silver nitrate solution. Mention the condition under which this statement is true.*

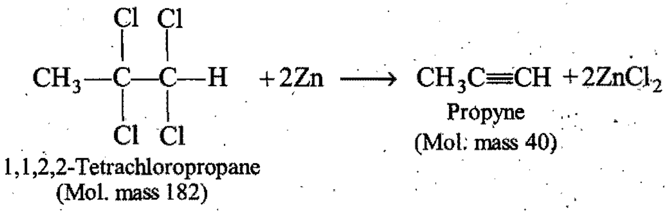
Solution : (a) 2-Methylpropene reacts with HBr in presence of peroxide as the addition occurs through anti-Markownikoff's rule.


$$\underset{\text{2-Methylpropene}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{Isobutyl bromide}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2Br}$$

(b) Only those derivatives of ethyne will give white precipitate with ammoniacal silver nitrate which possess acidic hydrogen atom, *i.e.*, $R-C{\equiv}CH$. The derivatives $R_1C{\equiv}C-R_2$ do not give precipitate with ammoniacal silver nitrate.

Problem 7. 36.4 *g of* 1,1,2,2-*tetrachloropropane was heated with zinc dust and the product was bubbled through ammoniacal* $AgNO_3$. *What is the mass of precipitate obtained? Give equations for the reactions involved.*

Solution :


$$\underset{\substack{\text{1,1,2,2-Tetrachloropropane}\\ \text{(Mol. mass 182)}}}{CH_3-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-H} + 2Zn \longrightarrow \underset{\substack{\text{Propyne}\\ \text{(Mol. mass 40)}}}{CH_3C{\equiv}CH} + 2ZnCl_2$$

Mass of propyne obtained from 36.4 g of

$$\text{1,1,2,2-tetrachloropropane} = \frac{40}{182} \times 36.4 = 8\text{ g}$$

$$CH_3C{\equiv}CH + AgNO_3 + NH_4OH \longrightarrow \underset{\substack{\text{Ag-salt}\\ \text{(Mol. mass 147)}}}{CH_3C{\equiv}C-Ag} + NH_4NO_3 + H_2O$$

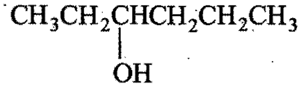
Mass of precipitate obtained from 8 g of propyne

$$= \frac{147}{40} \times 8 = 29.4\text{ g}$$

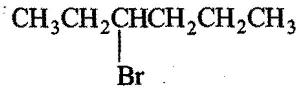
Problem 8. *Compound* (*A*) *contains only carbon and hydrogen. It decolourises bromine in* CCl_4 *solution and reacts slowly with concentrated* H_2SO_4. *Compound* (*A*) *reacts with* HBr *to form* (*B*). (*B*) *reacts with* NaOH *to form* (*C*). *On oxidation* (*C*) *gives hexanone-3. Write the structural formulae of* (*A*), (*B*), (*C*) *and explain the reactions involved.*

Solution : (*A*) is an alkene as it decolourises bromine in CCl_4 and reacts with H_2SO_4.

(*C*) is a secondary alcohol as it forms hexanone-3 on oxidation. The structure of (*C*) should be


$$CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{C}HCH_2CH_2CH_3 \quad \text{(Hexan-3-ol)}$$

(*B*) on hydrolysis with NaOH gives (*C*) thus, (*B*) should be



$$CH_3CH_2\underset{\substack{|\\ Br}}{C}HCH_2CH_2CH_3$$

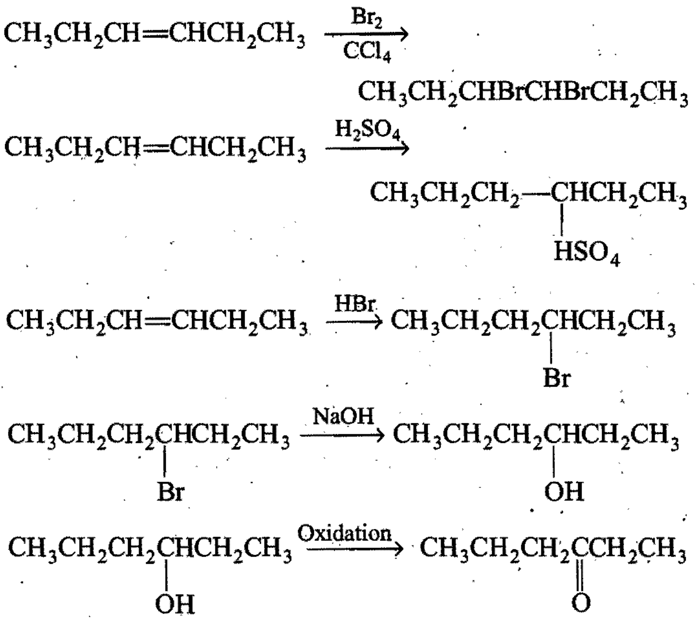
(3-Bromohexane)

(*A*) on HBr addition gives (*B*) hence, (*A*) is

$$CH_3CH_2CH{=}CHCH_2CH_3$$

(Hex-3-ene)

Reactions :



$$CH_3CH_2CH{=}CHCH_2CH_3 \xrightarrow[CCl_4]{Br_2} CH_3CH_2CHBrCHBrCH_2CH_3$$

$$CH_3CH_2CH{=}CHCH_2CH_3 \xrightarrow{H_2SO_4} CH_3CH_2CH_2{-}\underset{\substack{|\\ HSO_4}}{C}HCH_2CH_3$$

$$CH_3CH_2CH{=}CHCH_2CH_3 \xrightarrow{HBr} CH_3CH_2CH_2\underset{\substack{|\\ Br}}{C}HCH_2CH_3$$

$$CH_3CH_2CH_2\underset{\substack{|\\ Br}}{C}HCH_2CH_3 \xrightarrow{NaOH} CH_3CH_2CH_2\underset{\substack{|\\ OH}}{C}HCH_2CH_3$$

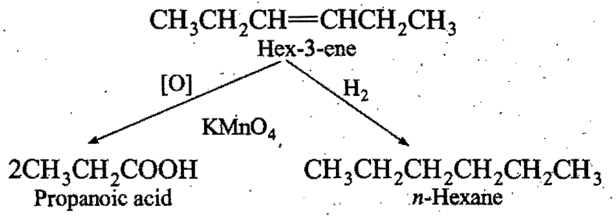
$$CH_3CH_2CH_2\underset{\substack{|\\ OH}}{C}HCH_2CH_3 \xrightarrow{Oxidation} CH_3CH_2CH_2\underset{\substack{\|\\ O}}{C}CH_2CH_3$$

Problem 9. *An organic compound (A), having carbon and hydrogen, adds one mole of hydrogen in the presence of platinum catalyst to form normal hexane. On vigorous oxidation with* $KMnO_4$, *it gives a single carboxylic acid containing three carbon atoms. Assign structure to the compound (A).*

Solution : The compound combines with hydrogen to form normal hexane by consuming one mole of hydrogen, hence the hydrocarbon is *n*-hexene.

$$\underset{n\text{-Hexene}}{C_6H_{12}} + H_2 \longrightarrow \underset{n\text{-Hexane}}{C_6H_{14}}$$

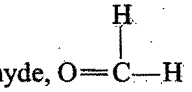
The position of double bond is indicated by its oxidation to propanoic acid. Thus, the double bond is present in the middle of the chain (a symmetrical alkene).



Problem 10. *How is the structure of an alkene determined?*

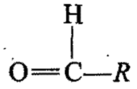
Solution : Ozonolysis is the best method for locating the double bond position in unknown alkene. An alkene is treated with ozone in an inert solvent to form an ozonide. The ozonide is treated with Zn/H_2O to obtain the carbonyl compounds. The structure of the carbonyl compounds depends upon the structure of the alkene. The following points should be kept in mind while deciding the structure of the alkene:

1. $=CH_2$ group gives formaldehyde,



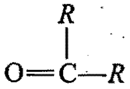
$$O{=}\overset{\substack{H\\ |}}{C}{-}H$$

$=CHR$ group gives aldehyde,



$$O{=}\overset{\substack{H\\ |}}{C}{-}R$$

$=CR_2$ group gives ketone,



$$O{=}\overset{\substack{R\\ |}}{C}{-}R$$

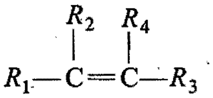
2. When only one aldehyde or one ketone is obtained, the alkene is symmetrical with respect to double bond.

3. The structures of carbonyl compounds are written in such a way that the carbonyl groups face each other.

$$\underset{(A)}{R_1{-}\overset{\substack{R_2\\ |}}{C}{=}O} \qquad \underset{(B)}{O{=}\overset{\substack{R_4\\ |}}{C}{-}R_3}$$

(*A*) (*B*)

4. The $=O$ of both the compounds is removed and linked through a double bond. This is the structure of unknown alkene.

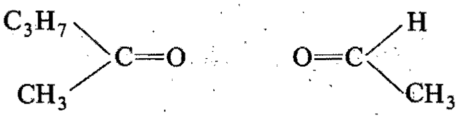


$$R_1{-}\overset{\substack{R_2\\ |}}{C}{=}\overset{\substack{R_4\\ |}}{C}{-}R_3$$

R_1, R_2, R_3, R_4 are either hydrogen atoms or alkyl groups or both.

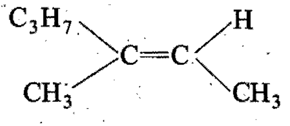
Problem 11. *An olefin was treated with ozone and the resulting ozonide on hydrolysis gave 2-pentanone and acetaldehyde. What is the structure of the original olefin? Write equations for the reactions involved.*

Solution : The products of ozonolysis are 2-pentanone and acetaldehyde. Writing the structure of both the carbonyl compounds.



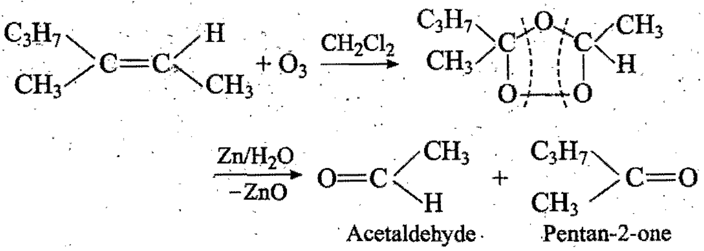
Pentan-2-one Acetaldehyde

Removing $=O$ of the compounds and linking both through double bond, we get the alkene.



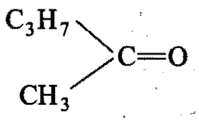
Thus, the alkene is 3-methyl hex-2-ene.

Reaction :

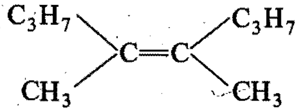


Problem 12. *Write the structure and give the IUPAC name of the alkene which gives only pentan-2-one on reductive ozonolysis. Give equations.*

Solution : As the alkene gives only pentan-2-one, it is symmetrical. Writing the structure of pentan-2-one,

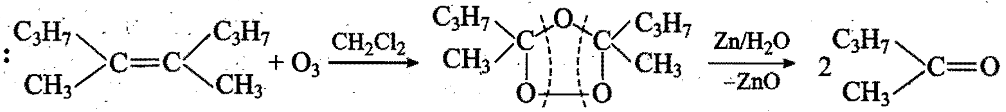


Hence, the alkene is,



The IUPAC name of the alkene is 4,5-dimethyloct-4-ene.

Reaction :

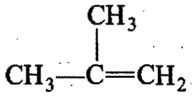


Problem 13. *Write the structure of the isomeric butenes and name them. Give the products obtained on reductive ozonolysis.*

Solution : Butene exists in three isomeric forms:

$CH_3—CH_2—CH=CH_2$
But-1-ene

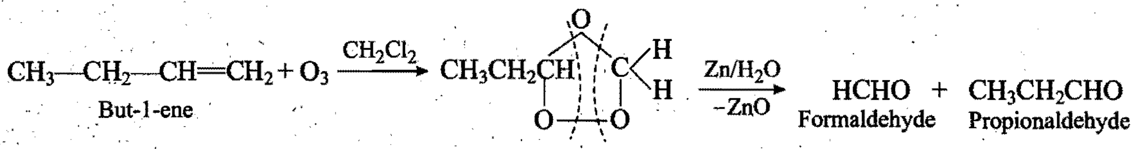
$CH_3—CH=CH—CH_3$
But-2-ene



$CH_3—\overset{CH_3}{\overset{|}{C}}=CH_2$

2-Methylprop-1-ene

But-1-ene on reductive ozonolysis gives propionaldehyde and formaldehyde.



But-2-ene on reductive ozonolysis gives only acetaldehyde.
2-Methylprop-1-ene on reductive ozonolysis gives acetone and formaldehyde.

Problem 14. *Effect the following transformations:*

(*a*) $CH_3CH_2CH_2CH_2I$ *to* $CH_3CH_2CH_2CH_2Br$
(*b*) $CH_3CHBrCH_3$ *to* $CH_3CHClCH_3$
(*c*) $CH_3CH_2CH_2OH$ *to* $CH_3CHOHCH_2Cl$

Solution :

(a) $$CH_3CH_2CH_2CH_2I \xrightarrow[KOH]{Alc.} CH_3CH_2CH=CH_2 \xrightarrow[\substack{R—O—O—R \\ \text{(Peroxide)}}]{HBr} CH_3CH_2CH_2CH_2Br$$

(b) $$CH_3CHBrCH_3 \xrightarrow[KOH]{Alc.} CH_3—CH=CH_2 \xrightarrow{HCl} CH_3CHClCH_3$$

(c) $$CH_3CH_2CH_2OH \xrightarrow[Heat]{H_2SO_4} CH_3—CH=CH_2 \xrightarrow{HOCl} CH_3CHOHCH_2Cl$$

Problem 15. *Account for the following* :

(*a*) *The* C≡C *distance is shorter than* C=C *and* C—C *distance.*
(*b*) *The stability of alkenes is in decreasing order of substitution by R.*

Solution : (a) The carbon-carbon distance depends upon the shielding of carbon nuclei by bonded electrons. In C≡C, the carbon nuclei is shielded by six electrons while in C=C and C—C by four and two electrons respectively. As a result of this, the carbon atoms come closer and undergoing more of overlapping of atomic orbitals and thus form stronger bonds.

It can also be explained on the basis of hybridization concept. In C≡C, each carbon atom is *sp*-hybridized while in C=C and C—C, each carbon atom is sp^2- and sp^3-hybridized respectively. More the *s*-character of the orbital, shorter will be bond formed by the orbital. In *sp*, the *s*-character is maximum, hence C≡C distance is minimum.

(b) According to Saytzeff's rule, stability of alkenes depends upon the substitution in C═C bond. More of substitution by *R*, the more stable is the alkene. Hence, the order of stability is:

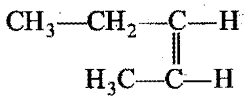
$$R_2C{=}CR_2 > R_2C{=}CHR > RCH{=}CHR > RCH{=}H_2C > H_2C{=}CH_2$$

Problem 16. *Write the structural and stereoisomers of pentene,* C_5H_{10} *and compare their stabilities.*

Solution : Pentene exist in the following isomeric forms:

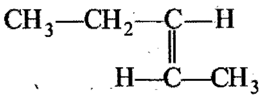
$CH_3CH_2CH_2—CH{=}CH_2$;

Pent-1-ene



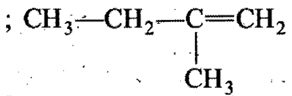
$$\begin{matrix} CH_3—CH_2—C—H \\ \| \\ H_3C—C—H \end{matrix}$$

Pent-2-ene (*cis*)



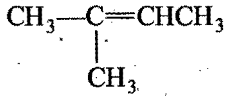
$$\begin{matrix} CH_3—CH_2—C—H \\ \| \\ H—C—CH_3 \end{matrix}$$

Pent-2-ene (*trans*)



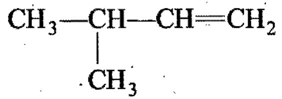
$$CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

2-Methylbut-1-ene



$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_3$$

2-Methylbut-2-ene



$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH{=}CH_2$$

3-Methylbut-1-ene

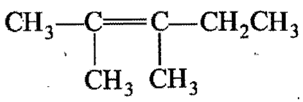
and the stability order is:

Pent-1-ene < pent-2-ene (*cis*) < pent-2-ene (*trans*) < 2-methylbut-2-ene

(since, stability increases with increasing number of electron releasing alkyl groups.)

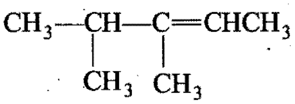
Problem 17. *What are the possible products, in order of decreasing yield, obtained from the reaction of* 3-*bromo*-2,3-*dimethylpentane with alc.* KOH?

Solution :



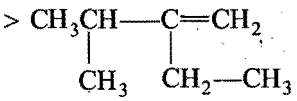
$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}{=}\underset{\displaystyle CH_3}{\underset{|}{C}}—CH_2CH_3 >$$

($R_2C{=}CR_2$, tetrasubstituted)



$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_3$$

($R_2C{=}CHR$, trisubstituted)



$$> CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}—\underset{\displaystyle CH_2—CH_3}{\underset{|}{C}}{=}CH_2$$

($R_2C{=}CH_2$ disubstituted)

Problem 18. *Prepare the following from* 1-*pentene* :

(*i*) $CH_3CH_2CH_2CHDCH_3$ (*A*),

(*ii*) $CH_3CH_2CH_2CH_2CH_2D$ (*B*),

(*iii*) $CH_3CH_2CH_2CHDCH_2D$ (*C*).

Solution :

(i) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{BD_3/THF}$

$(CH_3CH_2CH_2CHDCH_2)_3B \xrightarrow{HOAc} (A)$

(ii) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{BH_3/THF}$

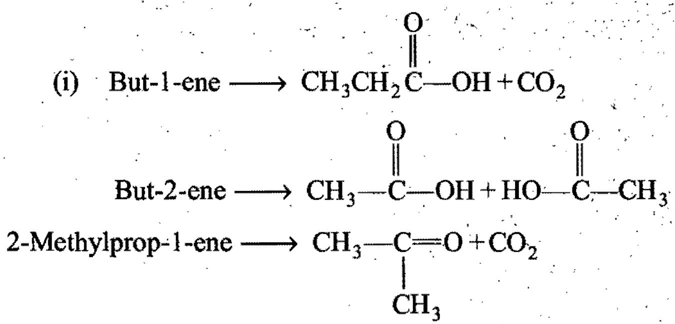
$(CH_3CH_2CH_2CH_2CH_2)_3B \xrightarrow{DOAc} (B)$

(iii) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{BD_3/THF}$

$(CH_3CH_2CH_2CHDCH_2)_3B \xrightarrow{DOAc} (C)$

Problem 19. *Write the expected products formed from hot* $KMnO_4$ *oxidation of* (*i*) *alkenes*, C_4H_8, (*ii*) *cyclobutene*, (*iii*) 1-*methylcyclobutene*, (*iv*) 1,2-*dimethylcyclobutene*.

Solution :

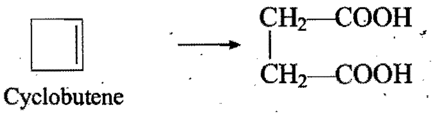


$$\text{(i) But-1-ene} \longrightarrow CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}—OH + CO_2$$

$$\text{But-2-ene} \longrightarrow CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—OH + HO—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3$$

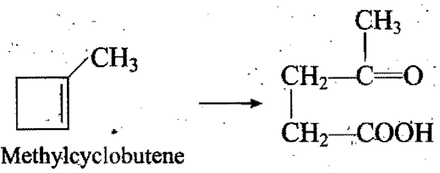
$$\text{2-Methylprop-1-ene} \longrightarrow CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}{=}O + CO_2$$

(ii)



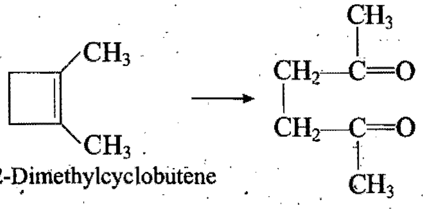
Cyclobutene

(iii)



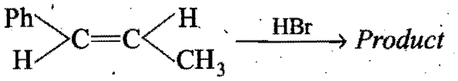
1-Methylcyclobutene

(iv)



1,2-Dimethylcyclobutene

Problem 20. *Predict the product of the reaction,*

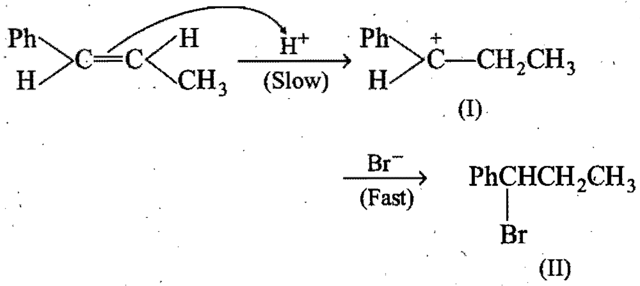


$$\begin{matrix} Ph \\ H \end{matrix}\!\!>\!C{=}C\!<\!\!\begin{matrix} H \\ CH_3 \end{matrix} \xrightarrow{HBr} \text{Product}$$

[AIPMT (Mains) 2008]

Solution :

In the first step of electrophilic addition reaction, H^+ adds to that carbon atom of the double bond which carries CH_3 group since, it produces carbocation (I) which is stabilized by +*R*-effect of the Ph group. In the second step, the nucleophile Br^- attacks the carbocation (I) to give 1-bromo-1-phenylpropane (II).

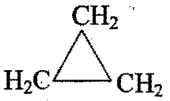


(II)
1-Bromo-1-phenylpropane

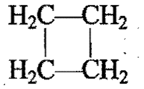
SUPPLEMENTARY READING

7.15 CYCLOALKANES

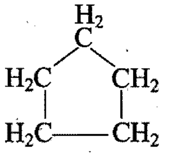
Cycloalkanes are carbocyclic saturated hydrocarbons in which carbon atoms are joined by single covalent bonds to form a ring. They form a homologous series of general formula C_nH_{2n}. They are also termed **alicyclic** because of their similarity to aliphatic compounds. Some of the members of this series are:



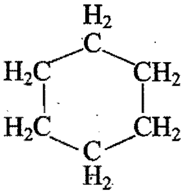
Cyclopropane
(Trimethylene)



Cyclobutane
(Tetramethylene)



Cyclopentane
(Pentamethylene)



Cyclohexane

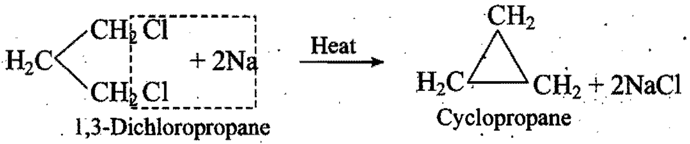
Note : For nomenclature see Chapter 3.

Cycloalkanes are usually represented by simple geometrical figures: a triangle (△) represents cyclopropane; a square (□) cyclobutane, a pentagon (⬠) cyclopentane; a hexagon (⬡) cyclohexane and so on. Each corner of the geometrical figure represents a —CH_2— (methylene) group.

Hydrocarbons having medium size rings (C_5 or C_6) are quite stable and closely resemble alkanes. But the compounds having rings with carbon atoms fewer than five show chemical properties somewhat intermediate between alkanes and alkenes.

Methods of preparation : Cycloalkanes are synthesised from aliphatic compounds by using suitable reactions which bring about cyclization. They are also obtained from aromatic compounds. Some of the common methods used are:

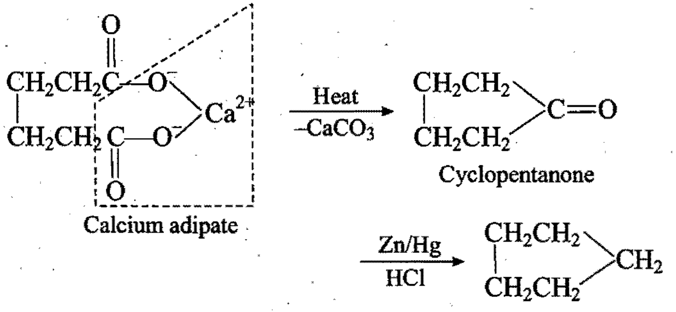
(i) From dihalogen compounds (Freund reaction) : α,ω-Dihalides when treated with sodium or zinc form cycloalkanes.



1,3-Dichloropropane
Cyclopropane

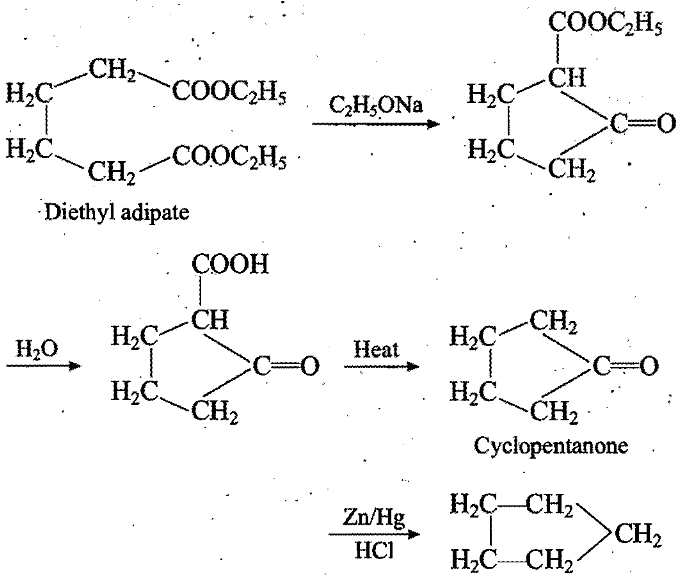
This reaction can be regarded as intramolecular Wurtz reaction. It is useful for the preparation of three to six membered rings.

(ii) From calcium salts of dicarboxylic acids : When calcium salts of dicarboxylic acids are heated, cyclic ketones are formed which yield cycloalkanes by **Clemmensen reduction.**



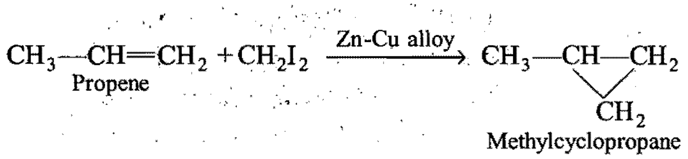
Calcium adipate
Cyclopentanone
Cyclopentane

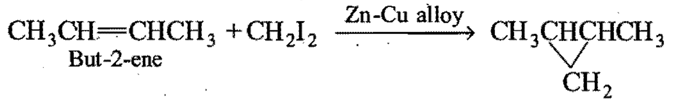
(iii) Dieckmann cyclization—From esters of dicarboxylic acids : Esters of dicarboxylic acids undergo intramolecular Claisen condensation in presence of sodium or sodium ethoxide yielding cyclic β-ketoesters. The β-ketoesters on subsequent hydrolysis and heating (decarboxylation) give cycloketones. These on reduction yield cyclic alkanes.



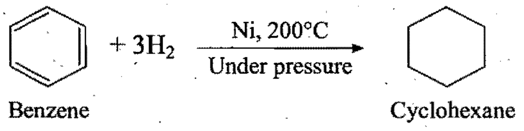
Diethyl adipate
Cyclopentanone
Cyclopentane

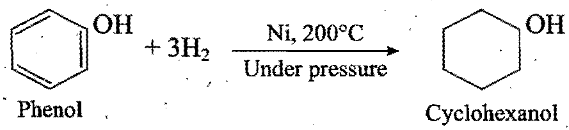
(iv) From alkenes : Cyclopropane derivatives are formed when alkenes are treated with methylene iodide (CH_2I_2) in the presence of Zn–Cu couple or diazomethane (CH_2N_2) and ultraviolet light.





(v) From aromatic compounds : Six membered cycloalkane compounds are conveniently prepared by the catalytic reduction of benzene and its derivatives.





Physical properties : (a) First two members are gases, next three members are liquids and higher ones are solids.

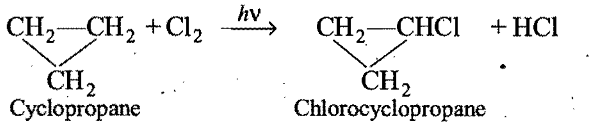
(b) They are insoluble in water but soluble in alcohol and ether.

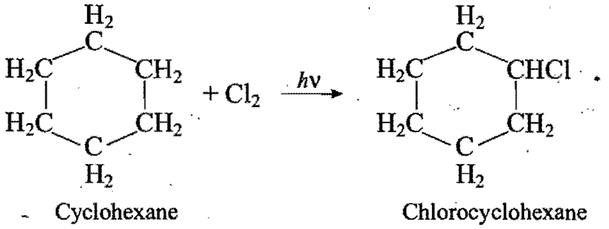
(c) Their boiling points show a gradual increase with increase of molecular mass. Their boiling points are higher than those of isomeric alkenes or corresponding alkanes.

(d) Their density increase gradually with increase of molecular mass.

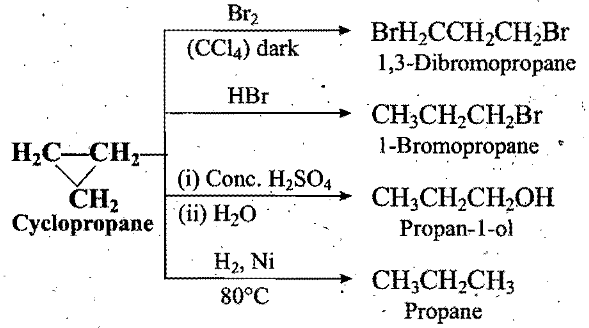
Chemical properties : Cycloalkanes resemble alkanes in their chemical properties. However, the first two members, *i.e.*, cyclopropane and cyclobutane are exceptions which are comparatively less stable and tend to break open like a double bond and give addition reactions. The similarity of cycloalkanes with alkanes can be attributed to the fact that all the carbon atoms in cycloalkanes are sp^3-hybridized forming sigma bonds with two neighbouring carbons and two hydrogens. It has been observed that cycloalkanes from cyclopentane onwards show high degree of stability and are not affected by acids, alkalies and common oxidising agents under usual conditions.

(1) Free radical substitution with Cl_2 and Br_2 : Cycloalkanes undergo halogenation in presence of sunlight or ultraviolet light.

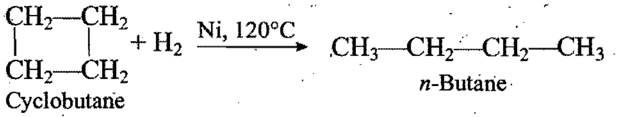




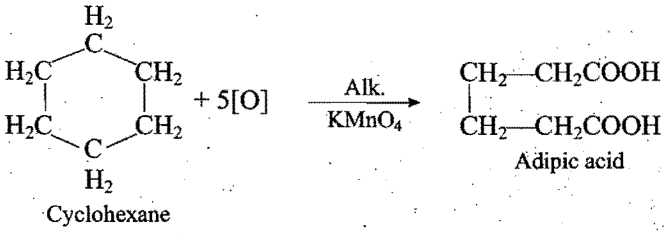
(2) Addition reactions : Like alkenes cyclopropane undergoes electrophilic addition reactions with ring fission. Some of the examples are:



Cyclobutane is not as reactive as cyclopropane as it does not undergo addition reactions under ordinary conditions. However, it can be hydrogenated to *n*-butane at 120°C.



(3) Oxidation : Cycloalkanes are oxidised by alkaline potassium permanganate to dicarboxylic acids with ring fission.



7.16 BAEYER'S STRAIN THEORY

In 1885, Adolf Baeyer proposed his famous theory in order to explain the relative stability of cycloalkanes. The theory is based on a purely mechanical concept of bonding. The main assumptions of the theory are:

(i) Since carbon atom is tetrahedral in nature with all the four valencies directed towards four corners of a regular tetrahedron, the angle between any two bonds should be 109°28′. Any deviation from this angle would result in internal strain in the molecule.

(ii) All cycloalkanes are planar, *i.e.*, cyclopropane ring is equilateral triangle; cyclobutane ring is a square and other cycloalkane rings are polygons. In the formation of these rings, there is deviation from the normal bond angle causing a lot of strain in the molecule. This strain, commonly referred to as angle strain, would depend upon the extent of such deviation.

(iii) The deviations from normal tetrahedral angle can be calculated as follows:

$$\text{Deviation} = \frac{1}{2}\,[109^\circ 28' - \text{bond angle in the planar ring}]$$

Compound	Geometry	Bond angle in planar ring	Deviation
Cyclopropane	Equilateral triangle	60°	$\frac{1}{2}(109°28' - 60°) = 24°44'$
Cyclobutane	Square planar	90°	$\frac{1}{2}(109°28' - 90°) = 9°44'$
Cyclopentane	Regular pentagon	108°	$\frac{1}{2}(109°28' - 108°) = 0°44'$
Cyclohexane	Regular hexagon	120°	$\frac{1}{2}(109°28' - 120°) = -5°16'$
Cycloheptane	Regular heptagon	128°34′	$\frac{1}{2}(109°28' - 128°34') = -9°33'$

The positive values of deviation mean that the bond angles are compressed while negative values mean expansion of the bond angle from the tetrahedral angle. In both the cases the molecule has been strained.

It is observed that the angle strain is maximum in the case of cyclopropane. Thus, cyclopropane molecule is a highly strained molecule and consequently most unstable. The ring opens up on slight provocation and thus releasing the strain. The angle strain in cyclobutane is less than that in cyclopropane. Thus, it has higher stability than cyclopropane. It undergoes ring opening reactions only under drastic conditions as expected. The angle strain is minimum in cyclopentane and thus, it is most stable and does not undergo ring opening reactions.

From cyclohexane onwards the angle strain continuously increases. According to Baeyer's strain theory, higher cycloalkanes should become increasingly unstable and hence more reactive. But, cyclohexane and higher members are found to be quite stable. Thus, it is concluded that the theory is valid for first three members only.

In order to account for the stability of cyclohexane and higher members, **Sachse** and **Mohr** (1918) proposed that such rings can become free from strain if all the ring carbons are not forced into one plane but assume a strain-free puckered configuration in which each carbon atom retains its normal valency angle. On this basis Sachse proposed two models for cyclohexane—called the boat and chair forms. Mohr supported this proposal and the theory became known as Sachse-Mohr theory of strainless rings.

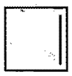

Boat form

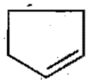

Chair form

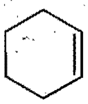
The reactivity of unsaturated hydrocarbons (alkenes and alkynes) is explained with the help of Baeyer's strain theory. When carbon atoms are linked by double bond, the valency bonds undergo bending and are distorted from their normal directions. This bending produces strain in the molecule with the result that it becomes unstable and hence more reactive. In acetylene, there is greater strain and hence is reactive. The strain disappears when addition occurs.

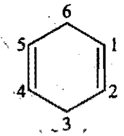
7.17 CYCLOALKENES

Carbocyclic compounds with double bonds in the ring are called cycloalkenes. Some of the common cycloalkenes are:


Cyclobutene

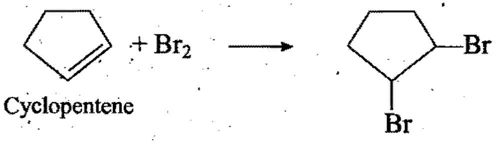

Cyclopentene


Cyclohexene

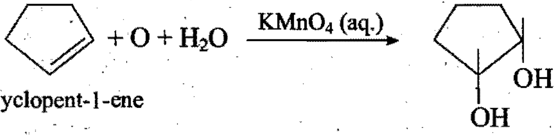


Cyclohexa-1,4-diene

Cycloalkenes can be easily obtained by Diels-Alder reaction. These compounds undergo the electrophilic addition reactions which are characteristic of alkenes, while the ring remains intact. Cycloalkenes decolourise the purple colour of dilute cold $KMnO_4$ or red colour of bromine in carbon tetrachloride.



Cyclopentene
1,2-Dibromo-cyclopentane



Cyclopent-1-ene
Cyclopentane-1,2-diol

7.18 DIENES

These are hydrocarbons with two carbon-carbon double bonds. Dienes are of three types:

(i) Conjugated dienes : Double bonds are separated by one single bond. For example,

Buta-1,3-diene $H_2C{=}CH{-}CH{=}CH_2$

(ii) Cumulative dienes : Double bonds are adjacent to each other. For example,

Allene (Propadiene) $H_2C{=}C{=}CH_2$

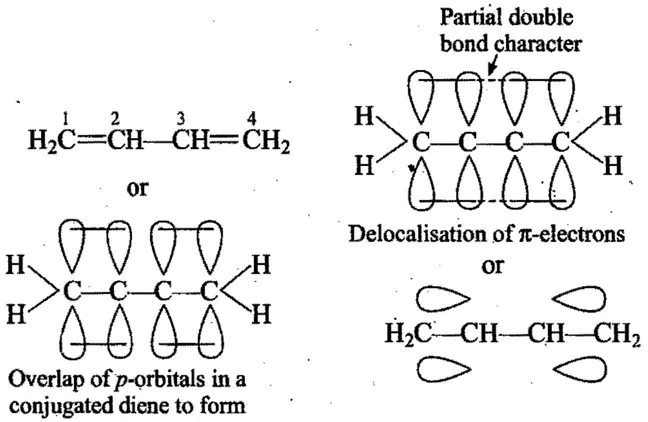
Buta-1,2-diene $CH_3{-}CH{=}C{=}CH_2$

(iii) Isolated or Non-conjugated dienes : Double bonds are separated by more than one single bond. For example,

Penta-1,4-diene $H_2C{=}CH{-}CH_2{-}CH{=}CH_2$

The general formula of dienes is C_nH_{2n-2}. Dienes are isomeric with alkynes. The most important class of dienes is that of conjugated dienes. Their chemical properties are different from those of ordinary alkenes. The predominent member of this class is Buta-1,3-diene.

Delocalisation of electrons and stability of conjugated dienes : In buta-1,3-diene, all the carbon atoms are in a state of sp^2-hybridization. The three sp^2-hybrid orbitals of each carbon lie in the same plane and are at angle of 120° to each other. Each carbon atom in buta-1,3-diene has an unhybridised p-orbital of C_1 or that of C_3. Similarly, the orbital at C_3 can overlap with that of C_2 or C_4 to form π-bonds. Therefore, the four π-electrons of buta-1,3-diene are delocalised over all the four carbon atoms. This delocalisation of π-electrons makes the molecule more stable.



Delocalisation of π-electrons

Overlap of p-orbitals in a conjugated diene to form two double bonds

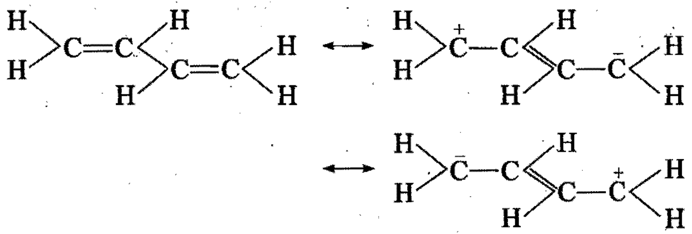
The central carbon atoms in this molecule are close to each other and there is a possibility of overlapping between p-orbitals of C_2 and C_3. This gives the partial double bond character to the central bond. Rotation of the molecule about atoms C_2 and C_3 requires only about 5 kcal/mol whereas that about the double bond in ethylene, the barrier is 60 kcal/mol.

The stability of conjugated dienes are supported by bond length measurement and study of heat of hydrogenation and heat of combustion, etc.

The heat of hydrogenation of monosubstituted alkenes ($R—CH=CH_2$) is 30.3 kcal/mol (or 126 kJ/mol). The heat of hydrogenation of butadiene, having two double bonds, should be $2 \times 30.3 = 60.6$ kcal/mol (or 252 kJ/mol). The experimental (observed) value is 57.1 kcal/mol (or 236 kJ/mol). Thus butadiene is more stable by about 3.5 kcal (15 kJ/mol). This is resonance energy of butadiene. These values support that conjugated dienes are more stable.

The $C_2—C_3$ bond length in butadiene is 1.48 Å and for $C_1—C_2$ and $C_3—C_4$ bond length is 1.37 Å. The $C_2—C_3$ bond length is shorter than the C—C bond length in ethane (1.54 Å).

The resonance structures of buta-1,3-diene are as follows:



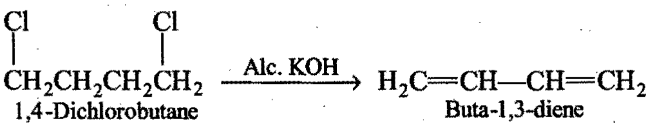
Buta-1,3-diene, $H_2C=CH—CH=CH_2$

Buta-1,3-diene may be prepared:

(i) From acetylene : Acetylene in presence of Cu_2Cl_2 and NH_4Cl dimerise to form vinyl acetylene which on reduction with Lindlar's catalyst yields buta-1,3-diene.

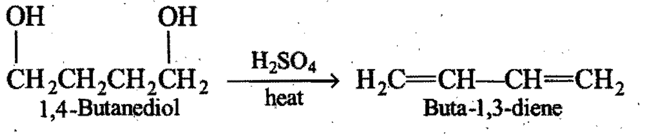
$$\underset{\text{Acetylene}}{2HC\equiv CH} \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{Vinyl acetylene}}{HC\equiv C—CH=CH_2} \xrightarrow[Pd/BaSO_4]{H_2} \underset{\text{Buta-1,3-diene}}{H_2C=CH—CH=CH_2}$$

(ii) From 1,4-dichlorobutane : 1,4-Dichlorobutane is heated with alcoholic KOH when dehydrohalogenation occurs with formation of buta-1,3-diene.



$$\underset{\text{1,4-Dichlorobutane}}{\overset{Cl}{CH_2}CH_2CH_2\overset{Cl}{CH_2}} \xrightarrow{\text{Alc. KOH}} \underset{\text{Buta-1,3-diene}}{H_2C=CH—CH=CH_2}$$

(iii) From 1,4-butanediol : Acid-catalysed dehydration is done by heating 1,4-butanediol with conc. H_2SO_4.

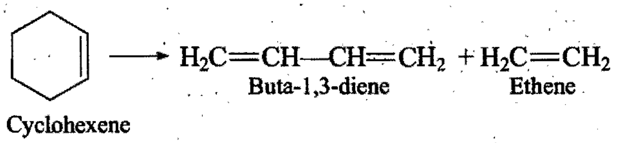


$$\underset{\text{1,4-Butanediol}}{\overset{OH}{CH_2}CH_2CH_2\overset{OH}{CH_2}} \xrightarrow[\text{heat}]{H_2SO_4} \underset{\text{Buta-1,3-diene}}{H_2C=CH—CH=CH_2}$$

(iv) From butane : Buta-1,3-diene is obtained by passing the butane vapours over heated catalyst (Cr_2O_3 on an alumina support) at 600°C.

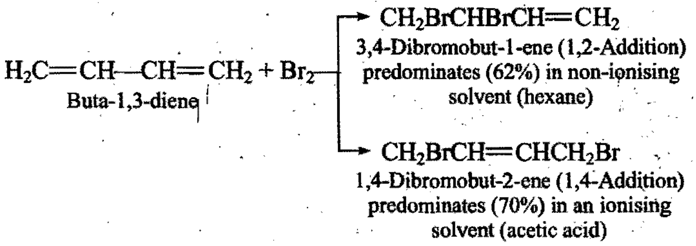
$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[600°C]{\text{Catalyst}} \underset{\text{Buta-1,3-diene}}{H_2C=CH—CH=CH_2}$$

(v) From cyclohexene : Buta-1,3-diene may be prepared by passing cyclohexene over a heated nichrome wire.



Properties : Buta-1,3-diene is a gas. It shows the following reactions:

(i) Addition of halogens : Buta-1,3-diene reacts with halogens (Br_2 or Cl_2) in the presence of an inert solvent (CCl_4) to yield a mixture of 1,2- and 1,4-addition products.

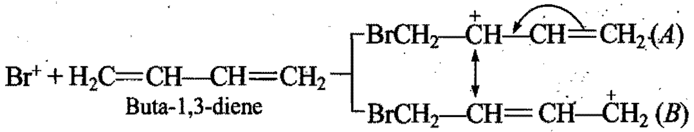


The **mechanism** of the above reaction involves the following steps:

1st step : The halogen molecule (Br_2) undergoes heterolytic fission.

$$\underset{\text{Bromonium ion}}{Br^+} + \underset{\text{Bromide ion}}{:Br^-} \longleftarrow Br_2$$

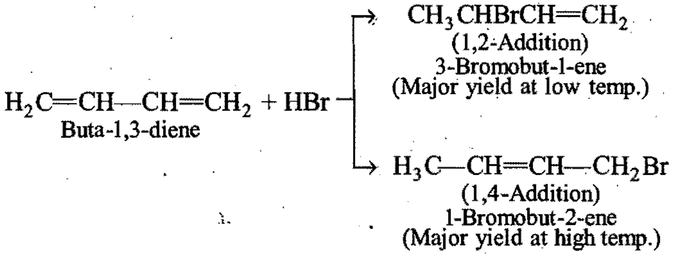
2nd step : The bromonium ion attacks the double bond to give a resonance stabilized carbocation.



$$\underset{\text{Buta-1,3-diene}}{Br^+ + H_2C{=}CH{-}CH{=}CH_2} \longrightarrow BrCH_2{-}\overset{+}{C}H{-}CH{=}CH_2\,(A) \longleftrightarrow BrCH_2{-}CH{=}CH{-}\overset{+}{C}H_2\,(B)$$

3rd step : The bromide ion combines with (*A*) to form 3,4-dibromobut-1-ene (1,2-addition). It combines with (*B*) to form 1,4-dibromobut-2-ene (1,4-addition).

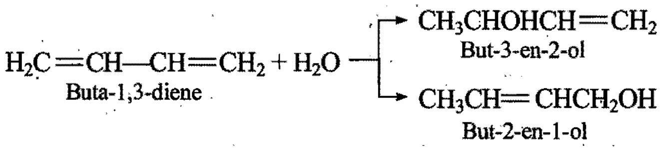
(ii) Addition of halogen acids : A mixture of two compounds is formed when buta-1,3-diene reacts with halogen acids (H*X*).



$$\underset{\text{Buta-1,3-diene}}{H_2C{=}CH{-}CH{=}CH_2} + HBr \longrightarrow \underset{\substack{\text{(1,2-Addition)}\\ \text{3-Bromobut-1-ene}\\ \text{(Major yield at low temp.)}}}{CH_3CHBrCH{=}CH_2}$$

$$\longrightarrow \underset{\substack{\text{(1,4-Addition)}\\ \text{1-Bromobut-2-ene}\\ \text{(Major yield at high temp.)}}}{H_3C{-}CH{=}CH{-}CH_2Br}$$

(iii) Addition of water : Buta-1,3-diene reacts with water in the presence of H_2SO_4 to give a mixture of 1,2- and 1,4-addition products.



$$\underset{\text{Buta-1,3-diene}}{H_2C{=}CH{-}CH{=}CH_2} + H_2O \longrightarrow \underset{\text{But-3-en-2-ol}}{CH_3CHOHCH{=}CH_2}$$

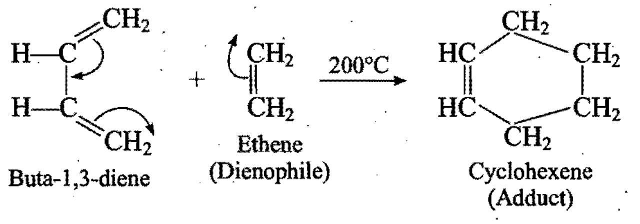
$$\longrightarrow \underset{\text{But-2-en-1-ol}}{CH_3CH{=}CHCH_2OH}$$

(iv) Addition of hydrogen : A mixture of but-1-ene and but-2-ene is formed when buta-1,3-diene reacts with H_2 in the presence of a catalyst (Pt).

(v) Polymerisation : It undergoes polymerisation in the presence of peroxides to form polybutadiene (Buna rubber).

$$\underset{\text{Buta-1,3-diene}}{nCH_2{=}CHCH{=}CH_2} \xrightarrow{\text{Peroxide}} \underset{\text{Buna rubber}}{\left[CH_2CH{=}CHCH_2\right]_n}$$

(vi) Diels-Alder reaction : This is a reaction between a conjugated diene and an alkene or alkyne called dienophile. This reaction does not require any catalyst. It involves the formation of two sigma-bonds and a pi-bond at the expense of three original pi-bonds. The product is called adduct, a six membered aromatic ring and involves an addition at positions 1,4.



Buta-1,3-diene Ethene (Dienophile) Cyclohexene (Adduct)

The presence of electron attracting groups such as —CN, —CHO, —CO*R*, —COOH, —COO*R*, etc., on dienophile facilitates the reaction. This reaction is widely used in the synthesis of six membered ring compounds.

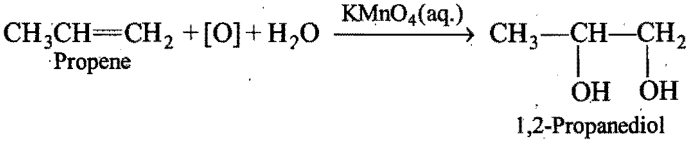
(vii) Ozonolysis : Dienes undergo ozonolysis to give three molecules. Buta-1,3-diene yields formaldehyde and glyoxal on ozonolysis.

$$\underset{\text{Buta-1,3-diene}}{H_2C{=}CHCH{=}CH_2} + 2O_3 \xrightarrow{Zn/H_2O} 2HCHO + OHCCHO$$

Problem 20. *How will you distinguish between:*

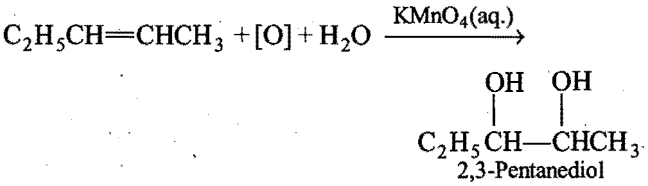
(*i*) *Cyclopropane and propene,*
(*ii*) *Cyclopentane and pent-2-ene,*
(*iii*) *Buta-1,3-diene and but-1-yne,*
(*iv*) *Buta-1, 3-diene and butane?*

Solution : (i) Propene decolourises dilute $KMnO_4$ solution while cyclopropane does not give this test.



$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + [O] + H_2O \xrightarrow{KMnO_4(aq.)} \underset{\text{1,2-Propanediol}}{CH_3{-}\underset{OH}{CH}{-}\underset{OH}{CH_2}}$$

(ii) Pent-2-ene decolourises the purple colour of $KMnO_4$ solution. It also decolourises red colour of bromine in CCl_4. These tests are not given by cyclopentane.



$$C_2H_5CH{=}CHCH_3 + [O] + H_2O \xrightarrow{KMnO_4(aq.)} \underset{\text{2,3-Pentanediol}}{C_2H_5\underset{OH}{CH}{-}\underset{OH}{CH}CH_3}$$

$$C_2H_5CH{=}CHCH_3 + Br_2 \xrightarrow{CCl_4} \underset{\text{2,3-Dibromopentane}}{C_2H_5CHBr{-}CHBrCH_3}$$

(iii) But-1-yne forms a white precipitate with ammoniacal silver nitrate solution, while this reaction is not observed with buta-1,3-diene.

$$CH_3CH_2C{\equiv}CH + Ag(NH_3)_2NO_3 \longrightarrow CH_3CH_2C{\equiv}C{-}Ag + NH_4NO_3 + NH_3$$

(iv) Buta-1,3-diene decolourises red colour of Br_2 in CCl_4 solution. It also decolourises purple colour of $KMnO_4$ solution. These tests are not observed with butane.

Problem 21. *How will you synthesise the following?*

(*i*) *Hexa-1,5-diene from propene.*
(*ii*) *Allene from propene.*
(*iii*) *1-Bromopropane from 1,3-dibromopropane.*
(*iv*) *Cyclohexene from cyclohexane.*
(*v*) *Buta-1,3-diene from but-1-ene*
(*vi*) *Hexachloroethane from calcium carbide.*

Solution :

(i) $$\underset{\text{Propene}}{CH_3CH{=}CH_2} \xrightarrow[600^\circ C]{Cl_2} \underset{\substack{\text{3-Chloroprop-1-ene}\\ \text{(Allyl chloride)}}}{CH_2ClCH{=}CH_2}$$

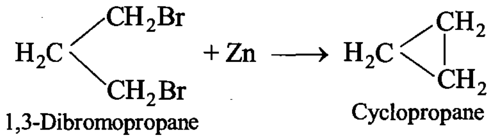
3-Chloropropene is treated with sodium in presence of ether, *i.e.*, undergoes Wurtz's reaction to form hexa-1,5-diene.

$$H_2C{=}CHCH_2\boxed{Cl + 2Na + Cl}CH_2CH{=}CH_2 \xrightarrow{\text{Ether}} \underset{\text{Hexa-1,5-diene}}{H_2C{=}CHCH_2CH_2CH{=}CH_2}$$

(ii) Propene is first treated with bromine at 500–600°C when 3-bromoprop-1-ene is formed which on treatment with alcoholic KOH yields allene (propadiene).

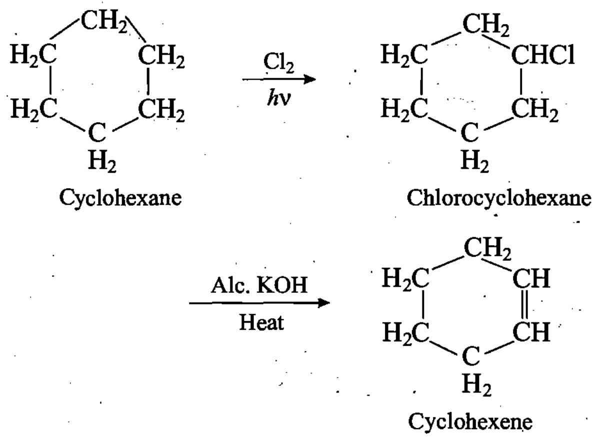
$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} \xrightarrow[500\text{–}600°C]{Br_2} \underset{\text{3-Bromoprop-1-ene}}{CH_2BrCH{=}CH_2} \xrightarrow{\text{Alc. KOH}} \underset{\text{Allene}}{H_2C{=}C{=}CH_2}$$

(iii) 1,3-Dibromopropane on heating with zinc forms cyclopropane which is reacted with conc. HBr to yield 1-bromopropane.



$$\xrightarrow{\text{Conc. HBr}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br}$$

(iv)



$$\text{(v)}\ \underset{\text{But-1-ene}}{CH_3CH_2CH{=}CH_2} \xrightarrow[500°C]{Br_2} CH_3CHBrCH{=}CH_2 \xrightarrow[\text{Heat}]{\text{Alc. KOH}} \underset{\text{Buta-1,3-diene}}{H_2C{=}CH{-}CH{=}CH_2}$$

$$\text{(vi)}\ CaC_2 \xrightarrow{H_2O} C_2H_2 \xrightarrow[Ni,\ 300°C]{H_2} C_2H_6 \xrightarrow[400°C]{Cl_2} C_2Cl_6$$

Problem 22. *Explain the following*:

(*i*) *Buta-*1,3-*diene gives* 1,2- *and* 1,4-*addition products.*

(*ii*) *Addition of* HBr *to* $H_2C{=}CHCH_2C{\equiv}CH$ *gives* $CH_3CHBrCH_2C{\equiv}CH$

(*iii*) *Alkenes in decreasing order of reactivity towards electrophilic addition*:

(*a*) $ClCH_2CH{=}CH_2$, (*b*) $(CH_3)_2C{=}CH_2$,
(*c*) $CH_3CH{=}CH_2$, (*d*) $H_2C{=}CHCl$

(*iv*) *Stereochemical structure of the reaction product of* Br_2 *with* (*a*) *cis-2-butene and* (*b*) *trans-2-butene.*

(*v*) *Why alkynes are generally less reactive than alkenes towards electrophilic reagents such as* H^+?

(*vi*) *The central carbon-carbon bond in buta-*1,3-*diene is shorter than that of n-butane.*

(*vii*) *Arrange following alkenes in decreasing order of stability towards acid-catalysed hydration.*

(*a*) 1-*phenyl*-1-*butene*; 1-*phenyl*-2-*butene*; 2-*phenyl*-2-*butene*
(*b*) 2-*methylpropene*; *cis*-2-*butene*; *trans*-2-*butene*
(*c*) 1-*hexene*, 2-*methyl*-1-*pentene*, 2-*hexene*.

Solution : (i) See mechanism on Page 345-346.

(ii) The addition occurs at double bond because isolated double bond is more reactive than an isolated triple bond in electrophilic additions.

(iii) Electron releasing alkyl groups make the pi-bond more electron rich and more reactive. While electron withdrawing halogen atoms make the pi-bond more electron poor and less reactive. The order is:

(b) Two *R* > (c) one *R* > (a) one *R* and a Cl > (d) Cl on a double bonded carbon.

(iv) 2,3-Dibromobutane (a) racemic (b) meso.

(v) The reaction of alkyne or alkene with electrophilic reagent proceeds through the formation of carbocation. Since the alkyl carbocation from the alkene group is more stable than the vinyl carbocation from alkyne group, the ΔH for its formation is less in case of alkene and hence alkene reacts faster than alkyne.

(vi) Buta-1,3-diene ($H_2C{=}CH{-}CH{=}CH_2$) has sp^2-sp^2 C—C bond length, while *n*-butane has sp^3-sp^3 C—C bond length. More is '*s*' character in hybridization, lesser is bond length.

(vii) (a) 2-phenyl-2-butene > 1-phenyl-2-butene > 1-phenyl-1-butene

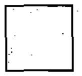
(b) 2-methylpropene > *trans*-2-butene > *cis*-2-butene

(c) 2-methyl-1-pentene > 2-hexene > 1-hexene.

Problem 23. *A hydrocarbon,* C_4H_8, *neither decolourised bromine in carbon tetrachloride nor reacted with* HBr. *When heated to* 200°C *with hydrogen in presence of a nickel catalyst, a new hydrocarbon,* C_4H_{10}, *was formed. What was the original hydrocarbon?*

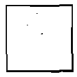
Solution : The hydrocarbon can have the following isomers:

$\underset{\substack{\text{But-1-ene}\\(A)}}{CH_3CH_2CH{=}CH_2}$, $\underset{\substack{\text{But-2-ene}\\(B)}}{CH_3CH{=}CHCH_3}$,



Cyclobutane
(*C*)

(*A*) and (*B*) are ruled out as the compound does not react with Br_2 and HBr. Thus, the compound is cyclobutane. Cyclobutane on reduction opens up the ring and forms *n*-butane.



Cyclobutane

$$+ H_2 \xrightarrow[200°C]{Ni} \underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3}$$

Problem 24. *(i) An organic compound,* C_4H_6, *on ozonolysis gives formaldehyde and glyoxal. What is this compound ?*

(ii) C_4H_6 *can represent various structures; identify:*

- *(a) Which reacts with ammoniacal* $AgNO_3$,
- *(b) Which does not react with ammoniacal* $AgNO_3$ *but by hot alkaline* $KMnO_4$ *gives* CH_3COOH,
- *(c) Which decolourises* Br_2 *water and by catalytic hydrogenation (using 1 mol) and subsequent reaction with alkaline* $KMnO_4$ *gives* CH_3COOH *and*
- *(d) Which by ozonolysis using* O_3/H_2O *gives succinic acid.*

Solution : (i) The formula suggests that either the compound is an alkyne or an alkadiene. The products of ozonolysis suggest that the compound is alkadiene. It may have the following structures.

$$\underset{\substack{\text{Buta-1,3-diene}\\(A)}}{H_2C{=}CH{-}CH{=}CH_2} \qquad \underset{\substack{\text{Buta-1,2-diene}\\(B)}}{CH_3{-}CH{=}C{=}CH_2}$$

Formaldehyde and glyoxal can be obtained from (*A*). Hence, the compound is buta-1,3-diene.

(ii) (a) C_4H_6 reacts with ammoniacal $AgNO_3$, so it is a terminal alkyne (—C≡C—H). For example,

$$CH_3CH_2{-}C{\equiv}CH \quad \text{(But-1-yne)}$$

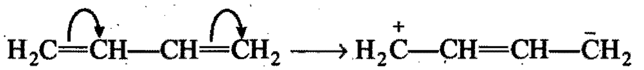
$$\text{(b)} \quad C_4H_6 \xrightarrow[\Delta]{\text{Alkaline } KMnO_4} CH_3COOH$$

Hence, it is $CH_3{-}C{\equiv}C{-}CH_3$ (But-2-yne)

$$\underset{\text{But-2-yne}}{CH_3{-}C{\equiv}C{-}CH_3} + 3[O] + H_2O \xrightarrow[\Delta]{\text{Alk. } KMnO_4} 2CH_3COOH$$

$$\text{(c)} \quad \underset{\substack{(H_2C{=}CH{-}CH{=}CH_2)\\ \text{Buta-1,3-diene}}}{C_4H_6 + H_2} \longrightarrow \underset{\substack{(CH_3CH{=}CHCH_3)\\ \text{But-2-ene}}}{C_4H_8} \xrightarrow[\Delta]{\text{Alk. } KMnO_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

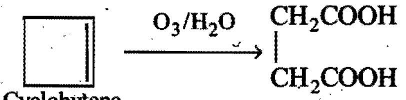
Explanation: Buta-1,3-diene is converted into but-2-ene by 1,4-addition.



$$\underset{\text{Buta-1,3-diene}}{H_2C{=}CH{-}CH{=}CH_2} \longrightarrow H_2\overset{+}{C}{-}CH{=}CH{-}\overset{-}{C}H_2$$

$$\xrightarrow[\text{1,4-addition}]{H_2} \underset{\text{But-2-ene}}{H_3C{-}CH{=}CH{-}CH_3}$$

(d)



Cyclobutene (C_4H_6)

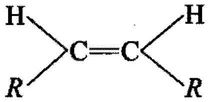
Succinic acid

Problem 25. *(a) Draw the stereochemical structure of the product in the following reaction.*

$$R{-}C{\equiv}C{-}R \xrightarrow[\textit{Lindlar's catalyst}]{H_2}$$

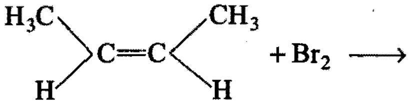
(b) W[illegible] *structures of the stereoisomers formed when cis-2-butene is reacted with bromine.*

Solution : (a) Only *cis*-form of the alkene is formed.

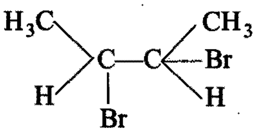


Cis-form

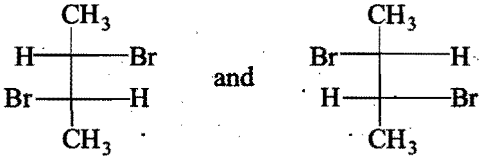
(b)



Cis-but-2-ene



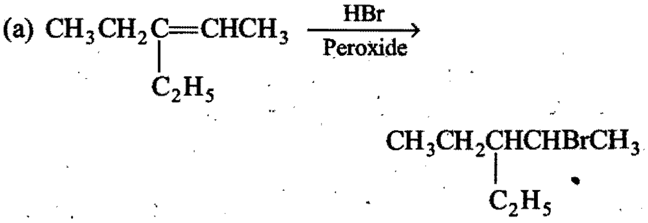
It exists in two optical isomers.



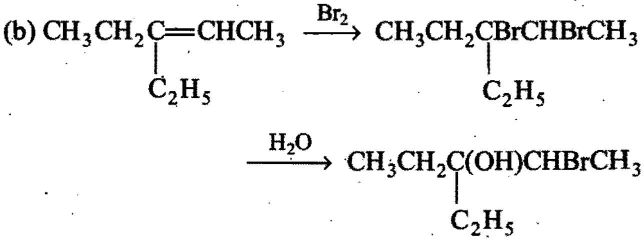
Problem 26. *Give the structures of the major products from 3-ethylpent-2-ene under each of the following conditions.*

- (*a*) HBr *in presence of peroxide,*
- (*b*) Br_2/H_2O,
- (*c*) $Hg(OAc)_2/H_2O$; $NaBH_4$.

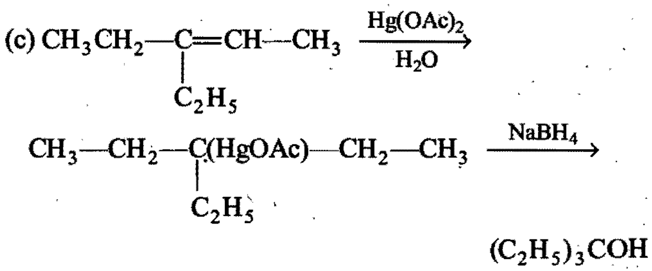
Solution :



$$\text{(a)} \quad CH_3CH_2\underset{C_2H_5}{\underset{|}{C}}{=}CHCH_3 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2\underset{C_2H_5}{\underset{|}{C}}HCHBrCH_3$$



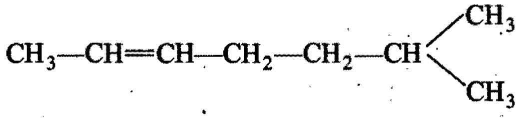
$$\text{(b)} \quad CH_3CH_2\underset{C_2H_5}{\underset{|}{C}}{=}CHCH_3 \xrightarrow{Br_2} CH_3CH_2\underset{C_2H_5}{\underset{|}{C}}BrCHBrCH_3 \xrightarrow{H_2O} CH_3CH_2\underset{C_2H_5}{\underset{|}{C}}(OH)CHBrCH_3$$



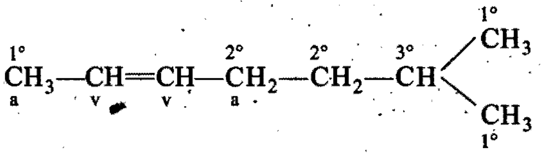
$$\text{(c)} \quad CH_3CH_2{-}\underset{C_2H_5}{\underset{|}{C}}{=}CH{-}CH_3 \xrightarrow[H_2O]{Hg(OAc)_2}$$

$$CH_3{-}CH_2{-}\underset{C_2H_5}{\underset{|}{C}}(HgOAc){-}CH_2{-}CH_3 \xrightarrow{NaBH_4} (C_2H_5)_3COH$$

Problem 27 *Indicate allylic, vinyl, 1°, 2°, 3° hydrogens in the following compound. Give the sequence of reactivity for free radical substitution.*



Solution :



a → allylic, v = vinylic, 1° → primary,
2° → secondary, 3° → tertiary

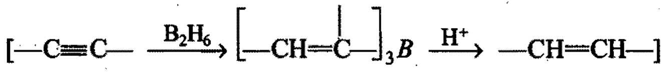
allylic (2°) > allylic (1°) > 3° > 2° > 1° > vinylic

Decreasing reactivity for free radical substitution

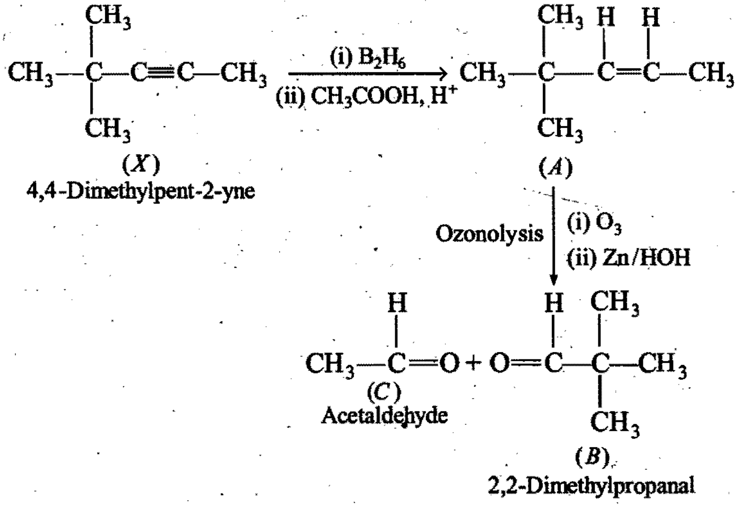
Problem 28 *Hydrocarbon* (X), C_7H_{12} *on reaction with boronhydride followed by treatment with* CH_3COOH *yields* (A). *On reductive ozonolysis* (A) *yields a mixture of two aldehydes,* (B) *and* (C). *Of these, only* (B) *can undergo Cannizzaro's reaction.* (A) *exists in two geometrical isomers* $(A\text{-}1)$ *and* $(A\text{-}2)$, *of which* $(A\text{-}2)$ *is more stable. Give structure of* (X), (A), (B), (C), $(A\text{-}1)$ *and* $(A\text{-}2)$ *with proper reasoning.*

[Roorkee 2000]

Solution : General formula of (X) indicates that it is an alkyne, which on monohydroboronation with B_2H_6, followed by protolysis with H^+ gives pure *cis*-alkene (A).


$$[\text{—C}\equiv\text{C—} \xrightarrow{B_2H_6} [\text{—CH}=\text{C—}]_3B \xrightarrow{H^+} \text{—CH}=\text{CH—}]$$

(A) on reductive ozonolysis gives two aldehydes (B) and (C). (B) undergoes Cannizzaro's reaction, hence, it should not contain any α-hydrogen (*i.e.*, at α-position, there should be quaternary carbon. Reactions may be given as:



(X) 4,4-Dimethylpent-2-yne

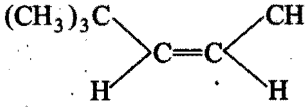
(A)

(C) Acetaldehyde

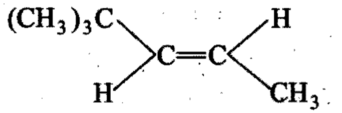
(B) 2,2-Dimethylpropanal

Only (B) gives Cannizzaro's reaction.

Alkene (A) exist in following two geometrical isomers $(A\text{-}1)$ and $(A\text{-}2)$, of which $(A\text{-}2)$ is more stable.



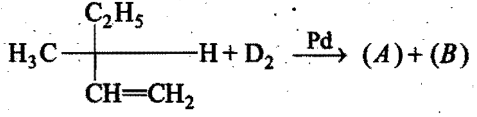
$(A\text{-}1)$ *Cis-*



$(A\text{-}2)$ *Trans-*

Problem 29. *Give structures/configuration of the products in the following reactions:*

(*a*)

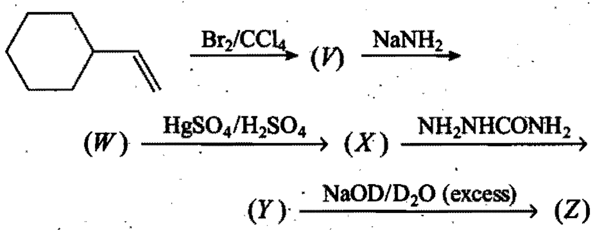


[Roorkee 2001]

(*b*) $2HC\equiv CH \xrightarrow[O_2]{Cu^{2+}} (C)$

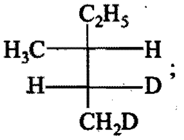
[Roorkee 2001]

(*c*)

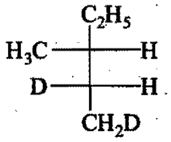


[IIT 2001]

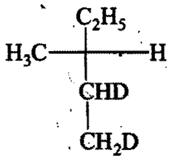
[**Hint :** (a) $[A]=$



$[B]=$

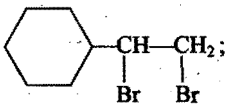


or

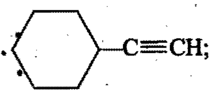


(b) $[C]=HC\equiv C—C\equiv CH$

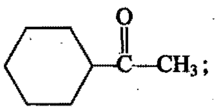
(c) $[V]=$



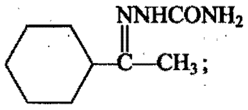
$[W]=$



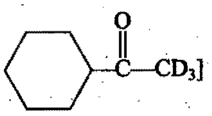
$[X]=$



$[Y]=$



$[Z]=$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IMPORTANT POINTS TO REMEMBER (SUMMARY)

ALKENES

☐ Unsaturated hydrocarbons with **one double bond** are called **alkenes** or **olefins** and are represented by the general formula C_nH_{2n}. Their functional group is $>C=C<$ and are isomeric with cycloalkanes. They are commonly named as **alkylenes.** Examples are:

$H_2C{=}CH_2$ (=), Ethylene or Ethene

$CH_3CH{=}CH_2$ (), Propylene or Propene

$CH_3CH_2CH{=}CH_2$ (), But-1-ene (α-Butylene)

$CH_3CH{=}CHCH_3$ () But-2-ene (β-Butylene)

☐ The double bond in alkenes consists of one sigma and one pi-bond. Each C-atom of a double bond is sp^2-hybridized. $>C=C<$ bond length (1.34 Å) is shorter than $\to C-C\leftarrow$ (1.54 Å) because the C-atoms in double bond are held more tightly.

☐ C=C are planar and H—C—C angle is 120° and H—C—H angle is 117.5 Å while C—H bond length is 1.09 Å.

☐ Heats of hydrogenation can be used to estimate the relative stability of alkenes. The **more substituted alkenes are more stable,** *i.e.,*

$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$$

General methods of preparation

☐ **By dehydration of alcohols:** In presence of conc. H_2SO_4 at 170°C or Al_2O_3 at 250°C or H_3PO_4 at 200°C or heating with P_2O_5 etc. The ease of dehydration is:

Tert. (3°) > Sec. (2°) > Primary (1°).

☐ **By dehydrohalogenation of alkyl halides:** On heating at high temperature with alcoholic KOH. Stronger bases like $NaNH_2$ or C_2H_5ONa or Et_3N can also be used for dehydrohalogenation. When two alkenes may be formed, the alkene which is the most substituted one predominates (Saytzeff's rule).

☐ The formation of less substituted alkene in an elimination reaction is called as a **Hofmann elimination** and that of more substituted alkene as a **Zaitsev elimination.** The ease of dehydrogenation is 3° > 2° > 1°.

☐ **By dehalogenation of dihaloalkanes (vic- and gem-):** On heating vic-dihalides with zinc dust and methanol (if sodium metal is used in place of zinc like Wurtz reaction), the gem-dihalides would give alkenes having double the number of carbon atoms. Dehalogenation by NaI in acetone takes place by E_2 mechanism.

☐ **By electrolysis of salts of dicarboxylic acids (Kolbe's method):** A concentrated aqueous solution of Na or K salt of saturated dicarboxylic acid on electrolysis gives an alkene.

☐ **By controlled partial hydrogenation of alkyne :** Hydrogenation of alkynes with Pd—$CaCO_3$ (Lindlar's catalyst) or a nickel boride (called P-2) catalyst yields *cis*-alkene. Sodamide (Na/liq. NH_3) yields predominantly *trans*-alkene (Birch reduction). Reduction with Na/C_2H_5OH gives *trans*-alkene. Hydroboration of alkynes (with B_2H_6) followed by protolysis (with H^+) gives almost pure *cis*-alkene.

☐ **By pyrolysis or cracking:** Petroleum is a complex mixture of hydrocarbons which on heating at high temperature (500–700°C) decomposes to produce lower alkenes and alkanes.

☐ **By heating quaternary ammonium compounds:** Lower alkenes are conveniently prepared by heating quaternary ammonium hydroxide with the elimination of trialkyl amine.

☐ **By Grignard reagents:** Alkenes can be obtained by reacting Grignard reagents with vinyl chloride.

☐ **By Wittig reaction:** Any aldehyde or ketone on treatment with $(C_6H_5)_3P{=}CH_2$, methylene triphenyl phosphorane (Wittig reagent) yields an alkene.

☐ **By Cope elimination reaction:** Tertiary amine oxide containing at least one β-hydrogen on heating at 150°C, decomposes to form an alkene and a derivative of hydroxylamine.

Physical properties

☐ Lower members (C_2–C_4) are gases, the next fourteen members are liquid while the higher members are solid. They are insoluble in water but soluble in non-polar solvents. The b.pts. increases with increasing chain length, while m.pts. of highly substituted alkenes are higher than straight chain alkenes. *Trans*-isomers are more stable than *cis*-isomers and *cis*-isomers show a dipole moment.

Chemical properties

☐ Alkenes are reactive due to the presence of double bond and the most important reactions of alkenes are the addition reactions. At low temperature in presence of polar solvents, addition proceeds by ionic mechanism whereas at high temperature in presence of light or non-polar solvents, the addition occurs by free radical mechanism.

☐ **Addition of hydrogen (Hydrogenation):** Alkene adds one mole of hydrogen under pressure and in presence of catalyst Ni (200–250°C) or finely divided Pt or Pd **(Sabatier-Senderen's reaction)** or Raney Ni at room temperature to give an alkane.

☐ This reaction is exothermic. The quantity of heat evolved when one mole of an unsaturated compound is hydrogenated is called the **heat of hydrogenation.** The lower the heat of hydrogenation of an alkene, the more is its stability. *Trans*-but-2-ene is more stable than *cis*-but-2-ene and but-1-ene.

- A terminal double bond may be reduced by Na/liq. NH_3 in presence of CH_3OH or C_2H_5OH to give alkane. This is called **Birch reduction.**
- The double bond is also reduced in excellent yield by $NaBH_4$-$PtCl_2$.
- **Addition of halogens:** Alkenes give addition products with Cl_2 and Br_2 in presence of an inert solvent, CCl_4, to form vicinal dihalides. Br_2 water is decolourised by unsaturated hydrocarbons (hence the **test of unsaturation**).
- The reaction with fluorine is explosive whereas when alkene is bubbled through alcoholic solution of iodine, a mixed halide is formed.
- Addition of halogens is usually predominantly *trans*, *i.e.*, the addition is stereoselective. With *trans*-but-2-ene, the product of Br_2 addition is optically inactive due to the formation of symmetric meso compounds.
- A more substituted alkene is more reactive towards Br_2 or Cl_2 than a less substituted alkene.

$$H_2C{=}CH_2 < RCH{=}CH_2 < RCH{=}CHR < R_2C{=}CH_2 < R_2C{=}CHR < R_2C{=}CR_2$$

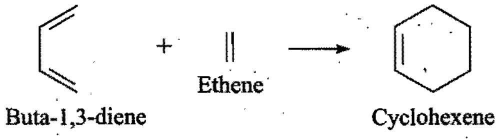
- **Addition of halogen acids:** Alkenes add one mole of HX to form alkyl halides. The order of reactivity is:

$$HI > HBr > HCl > HF.$$

- Addition of HX to symmetrical alkenes gives only one product and to unsymmetrical alkenes, the addition of HX can give two different products. Under normal conditions, the addition takes place in accordance with **Markownikoff's rule.** According to it, the negative part of the unsymmetrical reagent adds to that carbon atom of the unsymmetrical alkene containing less number of hydrogen atoms.
- It is an electrophile addition and is favoured by most stable carbocation intermediate. There may be 1,2-hydride or 1,2-methyl shift and stability order being $1° < 2° < 3°$.
- **Peroxide effect:** Kharasch observed that the addition of HBr only to unsymmetrical alkenes in the presence of organic peroxides, *i.e.*, benzoyl peroxide $(C_6H_5COO)_2$ follows anti-Markownikoff's addition and called as peroxide effect **(free radical mechanism).**

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br}$$

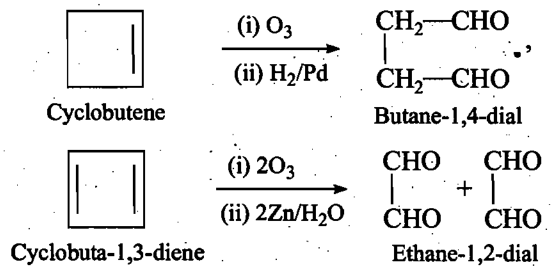
- **Addition of hypohalous acid (HO—*X*):** Alkenes form halohydrin with hypohalous acid (*i.e.*, Cl_2 or Br_2 in presence of water). In H—O—Cl or H—O—Br, the —O—Cl or —O—Br (rather than —O—H bond) is broken and the molecule is polarised in the manner $\overset{\delta-}{HO}{-}{-}{-}\overset{\delta+}{Cl}$ or $\overset{\delta-}{HO}{-}{-}{-}\overset{\delta+}{Br}$.
- In these halohydrin formation reactions, a halonium ion is formed as an intermediate which is attacked by water (nucleophile) in aqueous solution.
- **Addition of sulphuric acid:** Cold and concentrated H_2SO_4 readily adds to alkenes and forms alkyl hydrogen sulphate which on boiling with H_2O (hydrolysis) yields alcohol. So, this reaction is called **hydration of alkenes.**
- **Hydroboration oxidation:** It is **anti-Markownikoff's addition of water** (hydration) to a double bond. It involves addition of borane (B_2H_6) to double bond followed by hydrolysis to give alcohol.
- Another convenient hydroborating agent is borane-tetrahydrofuran (BH_3-THF) complex. Diglyme or ether can also be used in place of THF.
- **Addition of water:** Alkene adds up water molecule in presence of acid or catalyst BF_3 or Mn phosphate (catalytic amount) to yield alcohol in accordance with Markownikoff's rule.
- **Oxymercuration-demercuration:** With mercuric acetate (in THF) followed by reduction with $NaBH_4$/NaOH is also an example of hydration of alkene according to Markownikoff's rule. It is a better process than catalytic hydration by dil. H_2SO_4, because it avoids rearrangement.
- **Addition of nitrosyl chloride (Tilden's reagent):** NOCl or NOBr adds to C=C to yield halonitroso derivative.
- **Addition of alkanes:** Isoalkanes add to isoalkenes in presence of concentrated H_2SO_4 or HF to give branched chain alkanes **(alkylation of alkenes).**
- **Alkenylation of alkenes (Dimerisation):** Two molecules of isobutene (C_4H_8) add together in presence of concentrated H_2SO_4 or H_3PO_4 at about 80°C to give an alkene, C_8H_{16}, in two isomeric forms, a dimer of C_4H_8 and this is called **dimerisation.**
- **Diels-Alder reaction:** It is a diene-dienophile addition reaction and forms cyclic compounds.



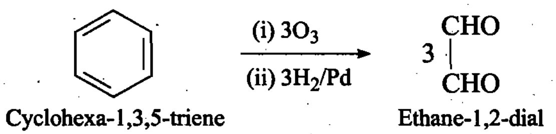
- **Addition of oxygen:** When mixed with air or oxidation with peroxy acids (CH_3COOOH, $C_6H_5CO_3H$ or CF_3CO_3H) or air passed through silver catalyst at high temperature (200–400°C), the lower alkenes form epoxides (cyclic ethers) which on hydrolysis give diols.
- **Addition of ozone:** When O_3 or ozonised oxygen is passed through a solution of alkene in an inert solvent, addition takes place across the double bond to form an ozonide. Ozonides are easily decomposed on warming with Zn/H_2O or reduction with H_2/Pd catalyst breaks $\rangle C{=}C\langle$ to produce two carbonyl compounds.
- An alkene of the type $RCH{=}CHR'$ gives two aldehydes (same or different).
- An alkene of the type $R_2C{=}CHR'$ gives one aldehyde and one ketone.
- An alkene of the type $R_2C{=}CR'_2$ gives two ketones (same or different).
- The two step process of forming the ozonide and then decomposing it to give a mixture of two carbonyl

compounds is known as **ozonolysis.** From the ozonolysis product, the position of the double bonds can be determined.

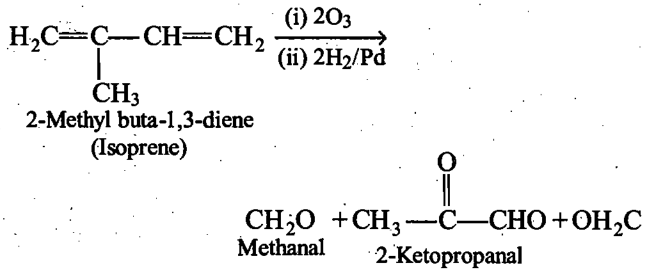
- ❑Ozonolysis of cycloalkenes gives only a single product containing two carbonyl compounds.



- ❑Cyclodienes on ozonolysis give two products each containing two carbonyl compounds.
- ❑Cyclotrienes on ozonolysis give three products each containing two carbonyl compounds.



- ❑Conjugated dienes on ozonolysis yield three products, *i.e.*, two monocarbonyl compounds and one dicarbonyl compound.



$$H_2C{=}\underset{\underset{CH_3}{|}}{C}{-}CH{=}CH_2 \xrightarrow[\text{(ii) }2H_2/Pd]{\text{(i) }2O_3} \underset{\text{Methanal}}{CH_2O} + \underset{\text{2-Ketopropanal}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CHO} + OH_2C$$

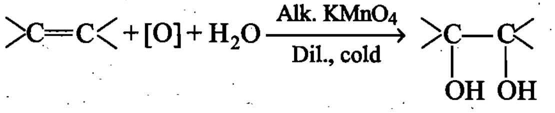
2-Methyl buta-1,3-diene (Isoprene)

- ❑A cumulated diene gives two monocarbonyl compounds and one mole of CO_2.

$$\underset{\text{Buta-1,2-diene}}{H_2C{=}C{=}CH{-}CH_3} \xrightarrow[\text{(ii) }2H_2/Pd]{\text{(i) }2O_3} \underset{\text{Methanal}}{CH_2O} + CO_2 + \underset{\text{Ethanal}}{OHCCH_3}$$

Oxidation reactions: Alkenes are readily oxidised. The oxidation products depend on the nature of oxidising agent used.

- ❑ **Oxidation or Hydroxylation with cold, dilute, alkaline KMnO₄ (Baeyer's reagent):** Glycols are formed.

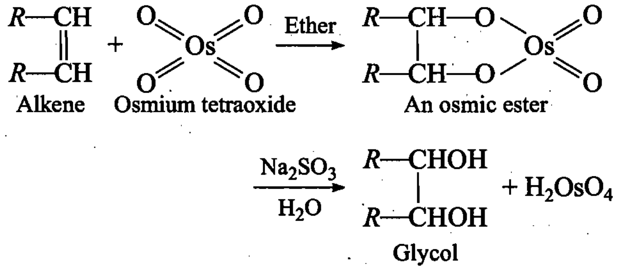


$$>C{=}C< + [O] + H_2O \xrightarrow[\text{Dil., cold}]{\text{Alk. KMnO}_4} >\underset{OH}{\underset{|}{C}}{-}\underset{OH}{\underset{|}{C}}<$$

This reaction is used for the detection of unsaturation and is called **Baeyer's test.**

- ❑Hydroxylation by $KMnO_4$ is always syn-addition.

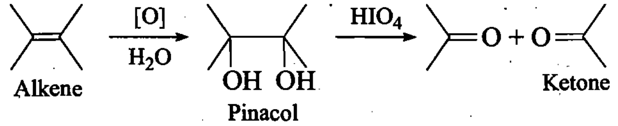
Hydroxylation using OsO_4:



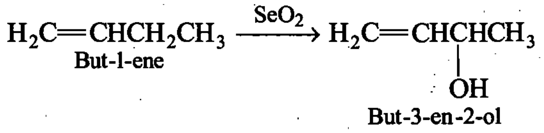
- ❑Hydroxylation can also be done with I_2/CH_3COOAg, peroxy acids (HCO_3H or a mixture of H_2O_2 and HCOOH).
- ❑ **Oxidation with acidic $KMnO_4$ or acidic $K_2Cr_2O_7$ (Strong oxidising agent):** They break the double bond and give ketones and carboxylic acids (because aldehydes formed cannot be isolated from $KMnO_4$ solution as they are easily oxidised to carboxylic acids).

$$\underset{\text{Alkene}}{R_2C{=}CHR'} \xrightarrow[\text{[O]}]{KMnO_4,\ \Delta} \underset{\text{Ketone}}{R_2C{=}O} + RCHO \xrightarrow{[O]} \underset{\text{Acid}}{RCOOH}$$

- ❑**Periodic acid** (HIO_4) or **lead tetra-acetate** [$(CH_3COO)_4Pb$] oxidises alkene into glycols and finally gives aldehydes or ketones depending upon the nature of alkene.

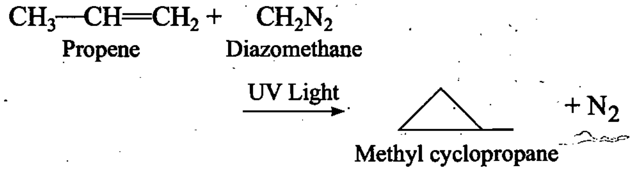


- ❑Oxidation of alkenes by SeO_2 affects the allylic position and not the double bond.



$$\underset{\text{But-1-ene}}{H_2C{=}CHCH_2CH_3} \xrightarrow{SeO_2} \underset{\text{But-3-en-2-ol}}{H_2C{=}CH\underset{OH}{\underset{|}{C}}HCH_3}$$

- ❑ **Combustion:** When burnt in air, alkenes are oxidised to CO_2 and H_2O. The reaction is exothermic, because heat is evolved.
- ❑ **Insertion of methylene (carbene):** Photolysis of diazomethane (CH_2N_2) and ketene ($CH_2{=}C{=}O$) gives methylene (carbene). This adds to alkene to yield cycloalkanes.

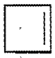
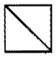


- ❑ **Polymerisation:** Two or more molecules of an alkene unite together to form a bigger molecule of higher molecular mass called **polyalkenes.**

Polyethene, polypropene and polybutene are "plastics" of industrial importance.

- ☐ **Substitution reaction (Halogenation):** NBS (N-bromo succinimide) is a reagent used for the specific purpose of brominating alkenes at the allylic position (*i.e.*, replacement of H atom of the alpha carbon atom with respect to double bond of alkyl group by the atom at about 500°C without breaking the double bond). This type of substitution is known as **allylic substitution.** It takes place in gas phase by free radical mechanism.

ALKYNES

- ☐ Unsaturated hydrocarbons with one triple bond are known as **alkynes** or **acetylenes** and represented by the general formula C_nH_{2n-2}. Their functional group is $-C\equiv C-$. Alkadienes $(H_2C=CH-CH=CH_2)$, cycloalkenes (C_4H_6)  and bicycloalkanes  are isomeric with alkynes containing same number of carbon atoms in their molecules.
- ☐ The triple bond in alkynes consists of one sigma and two pi- bonds. Each C-atom of the triple bond is *sp*-hybridised and $-C\equiv C-$ bond length (1.20 Å) is shorter as compared with $>C=C<$ (1.34 Å) and $\geq C-C\leq$ (1.54 Å).
- ☐ Monosubstituted acetylenes or 1-alkynes are called **terminal alkynes,** and the H atom attached to $C\equiv C$ is called acetylenic (acidic) hydrogen $(R-C\equiv C-H)$.

General methods of preparation

- ☐ **By dehydrohalogenation (-HX) of dihalides :** On heating dihalides (vic- and gem-) with alcoholic KOH or sodamide, $NaNH_2$ (in liquid NH_3) or solid KOH or KNH_2 etc.
- ☐ **By dehalogenation (-X) of tetrahalides :** On heating with Zn dust in alcohol.
- ☐ By heating iodoform with silver powder.
- ☐ By the electrolysis of Na/K salts of unsaturated dicarboxylic acids **(Kolbe's method).**
- ☐ By the action of water on calcium carbide **(Lab method).**
- ☐ By heating methane or natural gas at 1500°C in an electric arc **(Manufacture method).**
- ☐ By the controlled partial oxidation of methane at high temperature **(Manufacture method).**
- ☐ By the hydrolysis of magnesium carbide, propyne is formed.
- ☐ By passing an electric arc between carbon electrodes in an atmosphere of hydrogen at 2500°C **(Berthelot's synthesis).**
- ☐ **By reacting sodium alkynides with alkyl halides :** Higher alkynes are formed.

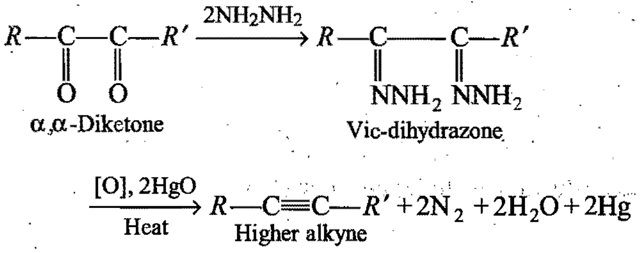
$$HC\equiv CH \xrightarrow[\text{or } NaNH_2]{Na/liq.\ NH_3} \underset{\text{Sod. alkynide}}{HC\equiv C-Na} \xrightarrow{XR} \underset{\text{1-Alkyne}}{HC\equiv C-R}$$

- ☐ **By reacting 1-alkynes with Grignard reagent followed by treatment with *R—X* :**

$$\underset{\text{Ethyne}}{HC\equiv C-H} \xrightarrow[(-CH_4)]{CH_3MgI} HC\equiv C-MgI \xrightarrow[(-MgI_2)]{CH_3I} \underset{\text{Propyne}}{HC\equiv C-CH_3}$$

$$\underset{\text{Propyne}}{CH_3-C\equiv CH} \xrightarrow[(-CH_4)]{CH_3MgI} CH_3-C\equiv C-MgI \xrightarrow[(-MgI_2)]{RI} \underset{\text{Higher alkyne}}{CH_3-C\equiv C-R}$$

- ☐ **By oxidation of *bis*-hydrazone of an α-diketone :**



$$\underset{\alpha,\alpha\text{-Diketone}}{R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R'} \xrightarrow{2NH_2NH_2} \underset{\text{Vic-dihydrazone}}{R-\underset{\underset{NNH_2}{\|}}{C}-\underset{\underset{NNH_2}{\|}}{C}-R'} \xrightarrow[\text{Heat}]{[O],\ 2HgO} \underset{\text{Higher alkyne}}{R-C\equiv C-R'} + 2N_2 + 2H_2O + 2Hg$$

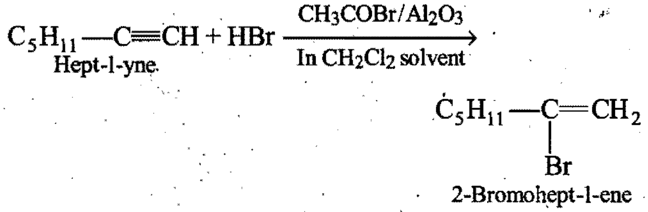
Physical properties

- ☐ Acetylene is a colourless gas with ether-like odour, b.pt. is –84°C. Acetylene (liquefied or when compressed) is explosive, burns with a luminous smoky flame, hence used for lighting purpose. Oxy-acetylene flame is used for cutting and welding of metals. Alkynes have linear structure and therefore, their molecules are rather more closely packed in space as compared to alkanes and alkenes.

Chemical properties

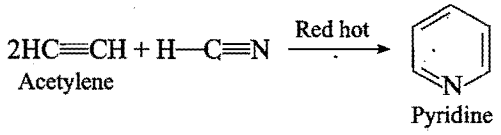
- ☐ **Acidic nature:** The H-atoms of ethyne are more acidic than those of ethene or ethane. The decreasing order of acidity is : $H-C\equiv C-H > H_2C=CH_2 > CH_3-CH_3$. The group $-C\equiv CH$ (1-alkynes) is acidic in nature due to more *s*-character (50%) of $C\equiv C$ which is *sp*-hybridised. Hence, proton release in $-C\equiv CH$ takes place more readily. On account of acidic nature, ethyne and all other terminal alkynes form salts with metal derivatives which are called **acetylides** or **alkynides.**
- ☐ **Formation of sodium acetylides:** Acetylene reacts with $NaNH_2$ or Na/liq. NH_3 forms sodium alkynides which is utilized for the preparation of higher alkynes with 1° alkyl halide (because 2° and 3° *R—X* give mainly alkenes).
- ☐ **Formation of copper acetylides:** Acetylene when passed through an ammoniacal cuprous chloride solution, a red precipitate of cuprous acetylide is formed.
- ☐ **Formation of silver acetylides:** Acetylene when passed through an ammoniacal solution of silver nitrate (Tollens' reagent), a white precipitate of silver acetylide is formed.
- ☐ **Addition of hydrogen (Hydrogenation):** Alkynes on treatment with hydrogen in presence of a catalyst (Ni, Pt or Pd) form alkenes and finally alkanes.

- Alkenes (*cis*-) can be obtained from alkynes by partial hydrogenation with Pd/$CaCO_3$ poisoned by quinoline or lead acetate **(Lindlar's catalyst).**
- $LiAlH_4$ or Na/liq. NH_3 converts alkynes to *trans* (*E*) alkenes.
- **Addition of halogens:** Alkynes add two molecules of halogens and decolourise Br_2 water **(test of unsaturation).** The reactivity order of halogens is as follows: $F > Cl > Br > I$. Liquid bromine yields tetrabromo derivative while Br_2/H_2O or Br_2/CCl_4 forms dibromo derivative. Iodine reacts slowly in alcohol to form di-iodo derivative (predominantly *trans*- isomer).
- Alkynes are less reactive than alkenes towards addition of halogens, because alkynes form less stable intermediate.
- Acetylene reacts with Cl_2 in the presence of catalyst $SbCl_5$ to give **westron** which on heating with $BaCl_2$ or lime or alc. KOH gives **westrosol.**
- **Addition of halogen acid (H*X*):** The decreasing order of reactivity is : $HI > HBr > HCl > HF$. Addition of one molecule of halogen acid gives vinyl halide which then adds another molecule of H*X* to form gem-dihalide. The addition follows Markownikoff's rule. In presence of peroxides, anti-Markownikoff product is obtained.
- When acetylene is passed into dilute HCl at 60–65°C in presence of mercuric ion (catalyst) only one molecule is added to give vinyl chloride (vinylation). Vinyl chloride ($CH_2{=}CH{-}Cl$) is the monomer of PVC.
- Addition of HBr to an alkyne can be facilitated by using acetyl bromide (CH_3COBr) and alumina (Al_2O_3) instead of aqueous HBr.



$$\underset{\text{Hept-1-yne}}{C_5H_{11}{-}C{\equiv}CH} + HBr \xrightarrow[\text{In } CH_2Cl_2 \text{ solvent}]{CH_3COBr/Al_2O_3} \underset{\text{2-Bromohept-1-ene}}{C_5H_{11}{-}\underset{\displaystyle Br}{\underset{|}{C}}{=}CH_2}$$

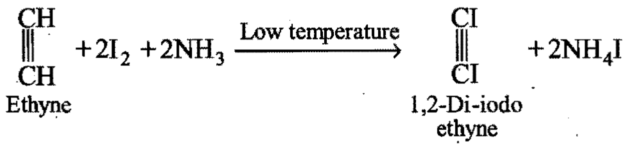
- **Addition of hypochlorous acid (HO—Cl):** It is chlorohydroxylation by chlorine water. Alkynes when passed into HO—Cl form dichloro aldehydes or ketones.
- **Addition of H_2SO_4 (conc.):** Acetylene gas, when passed through concentrated H_2SO_4, gets absorbed forming ethylidene hydrogen sulphate which on boiling with water gives acetaldehyde.
- **Addition of water (Hydration):** Alkynes add on one molecule of water when passed into dilute H_2SO_4 at 60°C in presence of $HgSO_4$ catalyst to form aldehydes or ketones through keto-enol tautomerism.
- **Addition of HCN:** Ethyne adds HCN in presence of $Ba(CN)_2$ or NaCN or CuCl/HCl or $CuCl_2/NH_3$ catalyst to form vinyl cyanide (acrylonitrile) which is a monomer for the polymer **polyacrylonitrile (PAN).**
- **Addition of CH_3COOH:** Ethyne adds two moles of acetic acid in presence of Hg^{2+} or BF_3 catalyst at 80°C to give ethylidene acetate which on heating gives acetaldehyde and acetic anhydride.
- **Addition of alcohol:** In presence of NaOH or KOH or mercury salt, acetylene reacts with alcohol to form alkyl vinyl ether (vinylation) which on hydrolysis gives acetaldehyde and alkanol.
- **Addition of O_3 and subsequent hydrolysis:** Acetylene and its homologues form ozonides with O_3 and these compounds are decomposed by water to form diketones which are then oxidised by H_2O_2 (formed in the reaction) to carboxylic acids.
- **Polymerisation:** Acetylene undergoes both cyclic and linear polymerisation.
- **Cyclic polymerisation:** When acetylene is passed through a red hot metallic tube at 600°C, it is polymerised to benzene. Propyne on heating trimerises to form mesitylene (1,3,5-trimethyl benzene).
- **Linear polymerisation:** When acetylene is passed into cuprous chloride solution dissolved in NH_4Cl, linear polymerisation occurs forming monovinyl acetylene and divinyl acetylene. Vinyl acetylene on reduction with H_2/Pt in presence of $BaSO_4$ forms buta-1,3-diene. Butadiene and vinyl cyanide form polymer **buna-N-synthetic rubber.** Vinyl acetylene reacts with HCl to give chloroprene (2-chloro-buta-1,3-diene) which polymerises to **neoprene** (synthetic rubber).
- **Addition of arsenic trichloride ($AsCl_3$):** Acetylene combines with $AsCl_3$ in presence of anhydrous $AlCl_3$ or Cu_2Cl_2 or $HgCl_2$ to form **Lewisite** (a poisonous gas).
- **Addition of carbonyl compounds** (Alkynylation of $>C{=}O$ compounds) : Terminal alkynes can add to $>C{=}O$ group in presence of C_2H_5ONa or Cu_2C_2 to form alkyndiol which is called **ethinylation.**
- **Carbonylation:** Acetylene adds to $(CO + H_2O)$ or $(CO + R{-}OH)$ in presence of catalyst nickel carbonyl, $Ni(CO)_4$, and forms α, β-unsaturated acid or ester.
- **Formation of heterocyclic compounds:** When acetylene is passed with sulphur over a heated tube at 300°C, it forms **thiophene.** Acetylene combines with NH_3 in red hot tube and forms pyrrole. With HCN in a red hot tube, acetylene produces pyridine.



- **Oxidation reactions:** Different oxidation products are obtained with different reagents.
- **Burning (combustion):** Acetylene burns with smoky flame in excess of air to give CO_2 and H_2O and large amount of heat is produced.
- **Oxidation with alkaline $KMnO_4$ solution:** Acetylene is finally converted into oxalic acid with cold, dilute

alkaline $KMnO_4$ (Baeyer's reagent) and pink colour of the solution is discharged. Higher alkynes under similar conditions give diketones. At higher temperature (110°C) the final products are carboxylic acids, CO_2 and ketones.

- ☐ **Oxidation with acidified $KMnO_4$:** Acetylene is converted into formic acid with acidic $KMnO_4$ on heating, while higher alkynes give *R*—COOH. Symmetrical alkynes give a single product while unsymmetrical alkynes give a mixture of two products.
- ☐ **Oxidation with chromic acid ($K_2Cr_2O_7 + H_2SO_4$):** Acetylene is converted into acetic acid and the orange colour changes to light green.
- ☐ **Oxidation with selenium dioxide (SeO_2):** Acetylene is oxidised to glyoxal with SeO_2 while propyne gives keto-propanal.
- ☐ **Substitution reactions:** When acetylene is passed through sodium hypochlorite (NaOCl) solution at 0°C in absence of light, hydrogen atoms are replaced by chlorine atoms with the formation of 1,2-dichloroethyne. With I_2 and NH_3 at low temperature, acetylene forms 1,2-di-iodo ethyne.



$$\underset{\text{Ethyne}}{\begin{matrix}CH\\|||\\CH\end{matrix}} + 2I_2 + 2NH_3 \xrightarrow{\text{Low temperature}} \underset{\text{1,2-Di-iodo ethyne}}{\begin{matrix}CI\\|||\\CI\end{matrix}} + 2NH_4I$$

- ☐ **Isomerisation :** On heating with alcoholic KOH or $NaNH_2$ in inert solvent, the triple bond of 1-alkyne is shifted towards the centre to form an isomer 2-alkyne. Similarly, on heating with sodamide (Na in liquid NH_3) the triple bond (2-butyne) shifts towards the end (1-butyne).
- ☐ **Oxidative-hydroboration:** Alkynes react with BH_3 (in THF) at 0°C to give an intermediate trivinyl borane which on oxidation with alkaline H_2O_2 gives an unsymmetrical alcohol that tautomerises to an aldehyde or ketone.
- ☐ **Degree of unsaturation:** The number of pairs of hydrogen atoms that a molecular formula lacks to be an alkane (C_nH_{2n+2}) is called degree of unsaturation and this value is called the index of hydrogen deficiency. The number of degree of unsaturation in a hydrocarbon is given by:

$$= \frac{2n_1 + 2 - n_2}{2},$$

where, n_1 is the number of carbon atoms and n_2 is the number of hydrogen atoms.

- ☐ **Tests of unsaturation:** The tests of unsaturation (detection of double or triple bonds) are generally performed by :

1. Baeyer's reagent: To an aqueous solution of the compound, a few drops of Baeyer's reagent (cold, dilute, alkaline $KMnO_4$ solution) is added. The decolourisation of pink colour indicates the presence of unsaturation.

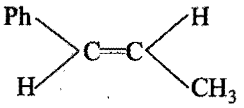
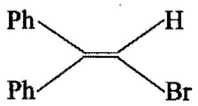
2. Br_2 water in CCl_4 or $CHCl_3$: The compound is dissolved in an inert solvent like CCl_4 or $CHCl_3$ and then a few drops of 5% bromine solution in CCl_4 are added to it. If the colour of bromine disappears, it indicates the presence of unsaturation.

- ☐ The presence of double and triple bonds are located by the identification of the products of ozonolysis.
- ☐ 1-Alkynes give a white precipitate when passed through ammoniacal $AgNO_3$ solution and also red precipitate when treated with ammoniacal cuprous chloride solution.

QUESTIONS

Very Short Answer Type

1. Fill in the blanks:
   (a) ...... is most acidic (Ethane, Ethene, Ethyne).
   (b) The compound having both *sp* and sp^2-hybridized carbon atoms is ...... (propene, propane, propadiene).
   (c) Acetylene is treated with excess of sodium in liquid ammonia. The product is reacted with excess of methyl iodide. The final product is ......
   (d) The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with ....
   (e) The monomer of polyvinyl chloride is ....
   (f) The addition of HBr on an unsymmetrical alkene takes place according to ...... rule.
   (g) $CH_3CH{=}CH_2 \xrightarrow[500°C]{Cl_2}$ ......
   (h) Kolbe's electrolysis of potassium succinate gives CO_2 and ....
   (i) Addition of water to acetylenic compounds is catalysed by ...... and ....
   (j) Unsaturation in alkenes can be tested with ...... reagent.
   (k) Methane is evolved when water is added to aluminium carbide. The gas evolved is ...... when water is added to calcium carbide.
   (l) The carbon atoms of ethene are ...... hybridized.
   (m) The carbon atoms of ethyne are ...... hybridized.
   (n) A white precipitate is obtained by passing acetylene through ammoniacal ...... solution.
   (o) Buta-1,3-diene with bromine in molar ratio generates predominately ....
   (p) The electrolysis of potassium fumarate gives ....
   (q) The position isomer of butene-1 is ....
   (r) The ozonolysis product of $CH_3CH{=}CHCH_3$ is ....
   (s) Lewisite and mustard gas are ...... in nature.
   (t) Alkyl halides undergo ...... reactions with alcoholic KOH and form ....
   (u) A compound of carbon and hydrogen used for welding purposes is ....
   (v) Carbon atoms in Ag_2C_2 (silver acetylide) are ...... hybridized.
   (w) Hydration of ethylene in presence of an acid produces ....
   (x) ...... is formed when ethylene is treated with alkaline $KMnO_4$.
   (y) S_2Cl_2 reacts with ...... to form mustard gas.
   (z) The kind of delocalization involving sigma bond orbitals is called ....

2. Fill in the blanks :
   (a) The structural formula of the compound which yields ethylene upon reaction with zinc is ....
   (b) The intermediate product in the preparation of ethylene from ethanol and sulphuric acid is ....
   (c) An olefinic '*X*' on ozonolysis gives CH_3COCH_3 and formaldehyde. The IUPAC name of the olefin is ......
   (d) Acetylene is practically insoluble in water but very soluble in ....
   (e) The 1% alkaline $KMnO_4$ solution is known as ....
   (f) Ethylene on treatment with chlorine water gives ....
   (g) Acetylene and formaldehyde interact in the presence of copper acetylide as a catalyst to form the organic compound ....
   (h) The H—C—H bond angle in ethylene is ....
   (i) Alkaline $KMnO_4$ oxidises acetylene to ....
   (j) Carbon-carbon distance is shortest in ...... (ethane, ethene, ethyne).
   (k) A hydrocarbon containing two double bonds is named as ....
   (l) Dichloroacetaldehyde is obtained by treating acetylene with ....
   (m) In alkenes and alkynes the electrophile adds across the ...... bond.
   (n) Trialkylborane on decomposition by CH_3COOH forms ....
   (o)  $\xrightarrow{HBr}$ ......
   [AIPMT 2008]
   (p) $H_2C{=}CH_2 \xrightarrow{H_2SO_4}$ ...... $\xrightarrow{H_2O}$ ......
   (q) $HC{\equiv}CH \xrightarrow{NaNH_2}$ ...... $\xrightarrow{CH_3Br}$ ......
   (r) $CH_3{-}CH{=}CH_2 \xrightarrow[Peroxide]{HBr}$ ...... $\xrightarrow{KOH\ (aq.)}$ ......
   (s) $H_2C{=}CH_2 \xrightarrow[CCl_4]{Br_2}$ ...... $\xrightarrow[KOH]{Alc.}$ ......
   (t) $HC{\equiv}CH \xrightarrow[CCl_4]{Br_2}$ ...... $\xrightarrow{Zn}$ ......
   (u)  $+ KNH_2 \longrightarrow$ ......
   (v) $HC{\equiv}CH \xrightarrow{NaNH_2}$ ...... $\xrightarrow{D_2O}$ ......
   (w) $HC{\equiv}CH \xrightarrow{2NaNH_2}$ ...... $\xrightarrow{D_2O}$ ......
   (x) $CH_3{-}C{\equiv}CH \xrightarrow{B_2H_6}$ ...... $\xrightarrow[H_2O_2]{NaOH}$ ......
   (y) $HC{\equiv}CH + CH_3OCH_2Cl \xrightarrow{AlCl_3}$ ......

(z) $(CH_3)_2C{=}CH_2 + CHCl_3 \xrightarrow{(CH_3)_3C{-}\bar{O}K^+} \ldots\ldots$

3. State whether the following statements are **True** or **False**:

(a) Moist ethylene can be dried by passing it through conc. H_2SO_4.

(b) 2-Methylpropene gives isobutyl bromide with HBr.

(c) Ethyne and its derivatives will give white precipitate with ammoniacal silver nitrate solution.

(d) The acidic nature of three types of hydrocarbons follows the order,

Alkanes < Alkenes < Alkynes.

(e) Peroxide effect is effective only in the addition of HBr and not HCl and HI.

(f) Acetylene is colourless, odourless gas.

(g) Vinyl acetate used in plastic industry can be prepared by the action of acetic acid on ethyne.

(h) Bromine water can be used to distinguish ethyne and ethene.

(i) Decolourisation of Baeyer's reagent is sure test of alkenes.

(j) The process of conversion of acetylene into benzene is polymerisation.

(k) The reaction of ethyl alcohol with acetylene is nucleophilic addition.

(l) Propyne is more acidic than acetylene.

(m) In Holme's signal of the ship, the torch contains CaC_2 and Al_4C_3.

(n) Propene with diborane forms an additive product which on reaction with H_2O_2 forms propanol.

(o) Propene can undergo addition as well as substitution with halogens depending upon the condition of the reaction.

(p) Propyl bromide on reaction with alc. KOH gives acetylene.

(q) $>C{=}C<$ bond length is more than $-C{\equiv}C-$ bond length.

(r) A carbon-carbon triple bond is considerably stronger than that of carbon-carbon double bond.

(s) Baeyer's reagent is acidified $KMnO_4$ solution.

(t) Addition of HBr to $(CH_3)_2C{=}CH_2$ in presence of benzoyl peroxide takes place according to anti-Markownikoff's rule.

(u) Ethene and Baeyer's reagent gives ethylene glycol.

(v) When propene is treated with Cl_2 at 500°C, substitution occurs in methyl group.

(w) Lewisite is formed by the reaction of acetylene and arsenic trichloride.

(x) But-2-yne forms white precipitate with Tollens' reagent.

(y) But-2-yne on ozonolysis forms formic acid and propionic acid.

(z) Acetylene when oxidised with selenium dioxide forms glyoxal.

4. Match the following:

[A]	(a) Dehydrohalogenation	(1) Poisonous gas
	(b) $nCH_2{=}CH_2 \rightarrow -\!\![CH_2{-}CH_2]\!\!-_n$	(2) Westron
	(c) Ozonolysis	(3) Alkaline potassium per-manganate
	(d) Mustard gas	(4) But-2-ene
	(e) Acetylene tetrachloride	(5) 2-Chlorovinyldichloro-arsenic
	(f) Baeyer's reagent	(6) Alcoholic KOH
	(g) Geometrical isomerism	(7) Structure of alkene
	(h) Lewisite	(8) Polymerisation
[B]	(a) C_nH_{2n}	(1) Formaldehyde
	(b) C_nH_{2n-2}	(2) Plastic
	(c) Alkyl halide + Alc. KOH	(3) Allene
	(d) Polythene	(4) Thiophene
	(e) $C_2H_4 + O_3/H_2O$	(5) Alkene
	(f) $H_2C{=}C{=}CH_2$	(6) Pyrrole
	(g) $C_2H_2 + S$	(7) Alkyne
	(h) $C_2H_2 + NH_3$	(8) Dehydrohalogenation

5. Complete the following equations:

(a) $H_2C{=}CH{-}CH_3 + HCl \longrightarrow (A)$

(b) $CH_3{-}CH{=}C(CH_3)_2 + O_3 \xrightarrow[H_2O]{Zn} (A) + (B)$

(c) $H_2C{=}CH_2 + O_3 \xrightarrow{H_2O} (A) \xrightarrow{NaOH(aq.)} (B) + (C)$

(d) $(CH_3)_3C{-}CH{=}CH_2 + HCl \longrightarrow (A)$

(e) $MeCH_2C{\equiv}CH \xrightarrow{NaNH_2} (A) \xrightarrow{Et.\,Br} (B)$

(f) $(A) \xrightarrow[H_2SO_4]{HgSO_4} CH_3CHO \xrightarrow{(CH_3CO)_2O} (B)$

(g) $HC{\equiv}CH \xrightarrow[(CH_3COO)_2Pb]{H_2,\,Pd(CaCO_3)} (A) \xrightarrow[CCl_4]{Br_2}$

$(B) \xrightarrow{(Alc.)\,KOH} (C)$

(h) $HC{\equiv}CH \xrightarrow[H_2SO_4]{HgSO_4,\,H_2O} (A) \xrightarrow[LiAlH_4]{H}$

$(B) \xrightarrow[170°C]{(Conc.)\,H_2SO_4} (C)$

(i) $CH_3CH_2CH_2OH \xrightarrow[170°C]{(Conc.)\,H_2SO_4} (A) \xrightarrow[500°C]{Cl_2} (B)$

(j) $CH_3CH{=}CH_2 \xrightarrow[500°C]{Br_2} (A) \xrightarrow[Heat]{(Alc.)\,KOH} (B)$

(k) $H_2C{=}CH_2 + CH_2N_2 \longrightarrow (A)$

(l) $CH_3CH{=}CH_2 + CH_2I_2 \longrightarrow (A)$

(m) $H_2C{=}CH{-}CH{=}CH_2 + H_2C{=}CH_2 \longrightarrow$

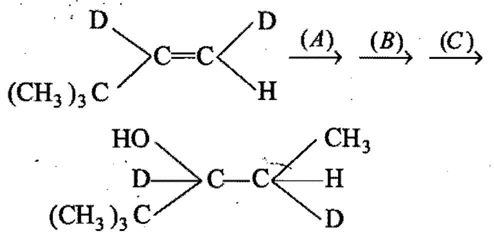
$(A) \xrightarrow[Pd]{H_2} (B)$

(n) $C_3H_7CH{=}CH_2 \xrightarrow[THF/H_2O]{Hg(OAc)_2} (A) \xrightarrow{NaBH_4/NaOH} (B)$

(o) $CH_3CH{=}CH_2 \xrightarrow{BH_3/THF} (A) \xrightarrow{CH_3COOH} (B)$

(p) $C_6H_5CH{=}CH_2 \xrightarrow{Br_2} (A) \xrightarrow[(ii)\;CH_3I]{(i)\;NaNH_2\;(3.0\,equiv.)} (B)$

(q) $C_6H_5CH_2CH(Cl)C_6H_5 \xrightarrow[\text{Heat}]{\text{(Alc.) KOH}} (A)$

(r) 

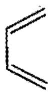
(s) $CH_3CH{=}CH_2 + BrCCl_3 \xrightarrow{\text{Peroxide}} (A)$

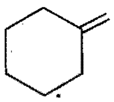
(t) $CH_3CH{=}C(CH_3)_2 + HCl \xrightarrow{\text{Peroxide}} (A)$

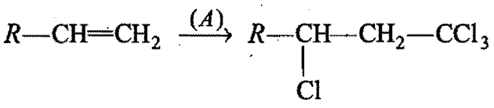
(u) $(CH_3)_2C{=}CH_2 + \text{isobutane} \xrightarrow[\text{273 K}]{\text{HF}} (A)$

(v) $CH_3CH_2CH{=}CH_2 \xrightarrow{CHCl_3} (A) \xrightarrow{\text{NaOH}} (B) \xrightarrow{\text{Dil. HCl}} (C)$

(w) $C_6H_5CH{=}CHCH_3 \xrightarrow[H_2O]{Br_2} (A)$

(x)  $+ CH_2{=}CHCl \longrightarrow (A)$

(y)  $\xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } BH_3,\ THF} (A)$

(z) 

$$R{-}CH{=}CH_2 \xrightarrow{(A)} R{-}\underset{\underset{Cl}{|}}{CH}{-}CH_2{-}CCl_3$$

[Roorkee 2001]

6. What is the final product when:

(a) Acetylene reacts with arsenic trichloride?

(b) Acetylene reacts with acetic acid in presence of mercuric salt ?

(c) Acetylene reacts with ethyl alcohol in presence of mercuric salt?

(d) Acetylene combines with ammonia at high temperature?

(e) Acetylene combines with nitrogen in presence of electric spark?

(f) Acetylene is heated with sulphur?

7. What happens when:

(a) Ethylene reacts with hypochlorous acid?

(b) Acetylene is passed through ammoniacal solution of silver nitrate?

(c) Acetylene is passed through a red hot metallic tube?

(d) Ethyl alcohol is heated at 170°C with excess of conc. H_2SO_4?

(e) Ethylene is treated with alkaline $KMnO_4$ solution?

(f) Propene is subjected to ozonolysis and subsequently treated with Zn/H_2O?

(g) Propene is treated with hydrogen bromide in the presence of a peroxide?

(h) Acetylene is passed through ammoniacal cuprous chloride solution?

(i) Acetylene is passed through dilute H_2SO_4 in presence of $HgSO_4$?

(j) Acetylene reacts with Baeyer's reagent?

8. Answer the following:

(a) If the bond order (number of bonds) between two carbon atoms increases what will happen to bond length and bond energy?

(b) What type of reactions usually occur in alkenes?

(c) What type of isomerism is exhibited by $CHBr{=}CHBr$?

(d) What type of $H_2C{=}C{=}CH_2$ diene is?

(e) Which type of mechanism is followed in Markownikoff's rule?

(f) Which type of mechanism is followed in anti-Markownikoff's rule?

(g) What reagent is used in the dehydrohalogenation of alkyl halides?

(h) Name two reagents which can be used to test unsaturation?

9. (a) Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.

(b) Write the structural formulae and IUPAC names for all the structural isomers of alkenes with molecular formula C_5H_{10}.

(c) Write the various types of isomerism shown by alkenes. Give one example of each.

10. Which of the following compounds will show *cis-trans* isomerism?

(i) $(CH_3)_2C{=}CH{-}C_2H_5$ (ii) $H_2C{=}CBr_2$

(iii) $C_6H_5CH{=}CH{-}CH_3$ (iv) $CH_3CH{=}CClCH_3$

11. Draw the *cis* and *trans* structures of hex-2-ene. Which isomer will have higher b.pt and why?

12. (a) How is ethene obtained from the following compounds in one step?

(i) Ethanol, (ii) Ethyl bromide, (iii) Ethyne, (iv) Ethylene bromide.

(b) How is ethyne obtained from the following compounds in one step?

(i) Ethylene bromide, (ii) Trichloromethane,

(iii) 1,1,2,2-Tetrabromoethane.

❖ Short Answer Type

13. How will you synthesise?

(a) Vinyl chloride from acetylene:

[**Hint:** $HC{\equiv}CH \xrightarrow{2HCl} CH_3CHCl_2 \xrightarrow{\text{(Alc.) KOH}} H_2C{=}CHCl$] or [$HC{\equiv}CH + HCl \xrightarrow{Hg^{2+}} H_2C{=}CH{-}Cl$]

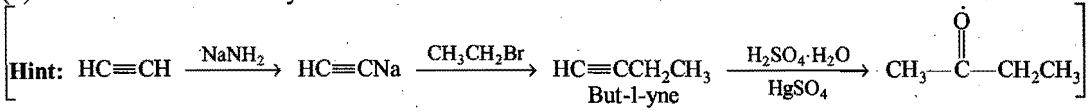
(b) But-1-yne from acetylene:

[**Hint:** $HC{\equiv}CH \xrightarrow{NaNH_2} HC{\equiv}CNa \xrightarrow{CH_3CH_2Br} HC{\equiv}C{-}CH_2CH_3$]

(c) But-2-yne from propyne:

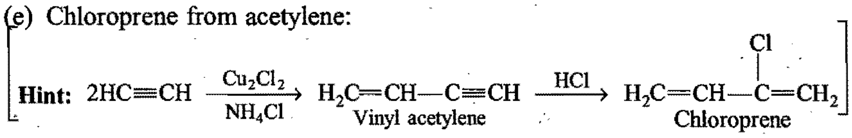
[**Hint:** $CH_3C{\equiv}CH \xrightarrow{NaNH_2} CH_3C{\equiv}CNa \xrightarrow{BrCH_3} CH_3C{\equiv}CCH_3$]

(d) Butan-2-one from acetylene:



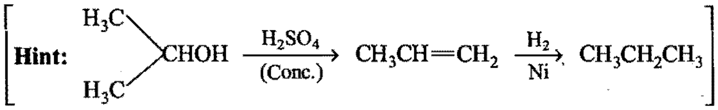
[**Hint:** $HC{\equiv}CH \xrightarrow{NaNH_2} HC{\equiv}CNa \xrightarrow{CH_3CH_2Br} \underset{\text{But-1-yne}}{HC{\equiv}CCH_2CH_3} \xrightarrow[HgSO_4]{H_2SO_4{\cdot}H_2O} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2CH_3$]

(e) Chloroprene from acetylene:

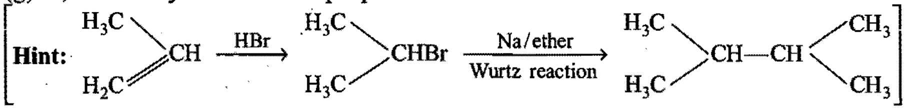


[**Hint:** $2HC{\equiv}CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{Vinyl acetylene}}{H_2C{=}CH{-}C{\equiv}CH} \xrightarrow{HCl} \underset{\text{Chloroprene}}{H_2C{=}CH{-}\overset{\overset{\displaystyle Cl}{|}}{C}{=}CH_2}$]

(f) Propane from isopropyl alcohol:



(g) 2,3-Dimethylbutane from propene:



(h) *n*-Hexane from propene:

[**Hint:** $CH_3CH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2CH_2Br \xrightarrow[\text{Wurtz reaction}]{\text{Na/ether}} CH_3(CH_2)_4CH_3$]

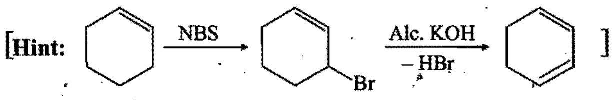
(i) Cyclohexene from cyclohexane:

[**Hint:** Cyclohexane $\xrightarrow[h\nu]{Cl_2}$ Chlorocyclohexane $\xrightarrow[KOH]{\text{Alc.}}$ Cyclohexene]

(j) Vinyl acetate from ethyl alcohol:

[**Hint:** $C_2H_5OH \xrightarrow[170^\circ C]{\text{(Conc.) } H_2SO_4} H_2C{=}CH_2 \xrightarrow{Br_2} CH_2Br{-}CH_2Br \xrightarrow{\text{(Alc.) KOH}} HC{\equiv}CH \xrightarrow[Hg^{2+}]{CH_3COOH} CH_3COOHC{=}CH_2$]

(k) Cyclohexa-1,3-diene from cyclohexene:



14. How will you obtain the following from propene?

(a) *n*-Propyl bromide,

[**Hint :** Reaction of HBr in presence of peroxide]

(b) *n*-Propyl alcohol,

[**Hint :** First convert into *n*-propyl bromide and then do hydrolysis with aq. NaOH or AgOH.]

(c) Isopropyl alcohol,

[**Hint :** First react with HBr to form isopropyl bromide and then do hydrolysis.]

(d) 1,2-Dichloropropane,

[**Hint :** Treat with Cl_2 in CCl_4]

(e) Acetylene;

[**Hint :** By ozonolysis propene is converted into acetaldehyde,

$$CH_3CHO \xrightarrow{PCl_5} CH_3CHCl_2 \xrightarrow{Alc.\ KOH} HC{\equiv}CH]$$

(f) Allene (Propadiene).

[**Hint:** $CH_3CH{=}CH_2 \xrightarrow[500°C]{Br_2} BrCH_2{-}CH{=}CH_2$

$$\xrightarrow[Heat]{Alc.\ KOH} H_2C{=}C{=}CH_2]$$

15. How will you differentiate the following?

(a) Ethylene and ethane
(b) Ethylene and acetylene
(c) Ethane and ethyne
(d) But-1-ene and but-1-yne
(e) But-2-yne and but-1-yne

[**Hint:** But-1-yne forms white ppt. with ammoniacal silver nitrate while but-2-yne does not as it has no acidic hydrogen.]

16. (a) A gaseous mixture consists ethane and ethylene. How are the individual members recovered?

[**Hint :** Pass mixture through conc. H_2SO_4. Ethylene is absorbed. The product on heating gives again C_2H_4.]

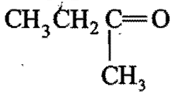
(b) A gaseous mixture consists of ethylene and acetylene. How both are separated from each other?

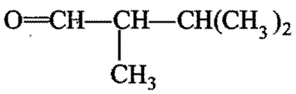
[**Hint :** Pass mixture through ammoniacal cuprous chloride solution. The acetylene forms red precipitate. It is filtered and treated with HNO_3 to recover acetylene. Cu_2C_2(red ppt.) + $2HNO_3 \rightarrow C_2H_2 + Cu_2(NO_3)_2$]

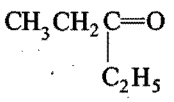
17. Explain the mechanism of the following reactions:

(a) Bromine on ethylene.
(b) HBr on ethylene.
(c) Dehydration of an alcohol.
(d) HBr on buta-1,3-diene.
(e) HCl on 3,3-dimethylbut-1-ene.

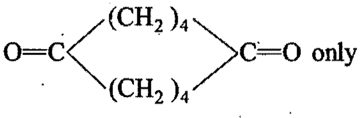
18. Deduce the structures of the compounds which yield the following products on reductive ozonolysis:

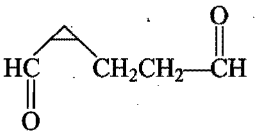
(a) CH_3CHO and $HCHO$
(b) $(CH_3)_2CO$ and $HCHO$
(c) $(CH_3)_2CO$ and CH_3CHO
(d) $(CH_3)_2CO$ only
(e)  $CH_3CH_2\underset{|\atop CH_3}{C}{=}O$ (two moles)

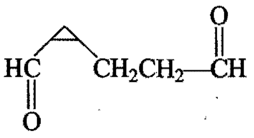
(f) HCHO and  $O{=}CH{-}\underset{|\atop CH_3}{CH}{-}CH(CH_3)_2$

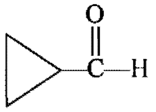
(g)  $CH_3CH_2\underset{|\atop C_2H_5}{C}{=}O$ and OHC—CHO and $OHCCH_2CH_3$

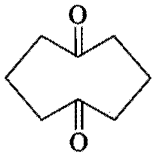
(h) OHC—$CH_2CH_2CH_2CHO$ only
(i) OHC—CH_2—CHO (two moles)

(j)  only

(k)  and OHC—CHO

(l)  only

(m) 

(n) 

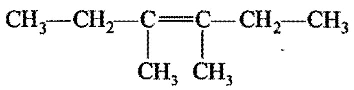
(o) $(CH_3)_2CO$ and CH_3CH_2CHO

[**Ans.** (a) $CH_3CH{=}CH_2$ (Propene)

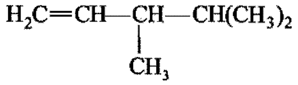
(b) $(CH_3)_2C{=}CH_2$ (2-Methylprop-1-ene)

(c) $(CH_3)_2C{=}CHCH_3$ (2-Methylbut-2-ene)

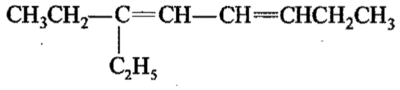
(d) $(CH_3)_2C{=}C(CH_3)_2$ (2,3-Dimethylbut-2-ene)

(e)  $CH_3{-}CH_2{-}\underset{|\atop CH_3}{C}{=}\underset{|\atop CH_3}{C}{-}CH_2{-}CH_3$

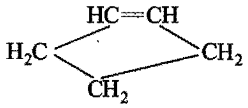
(3,4-Dimethylhex-3-ene)

(f)  $H_2C{=}CH{-}\underset{|\atop CH_3}{CH}{-}CH(CH_3)_2$

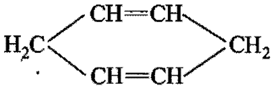
(3,4-Dimethylpent-1-ene)

(g)  $CH_3CH_2{-}\underset{|\atop C_2H_5}{C}{=}CH{-}CH{=}CHCH_2CH_3$

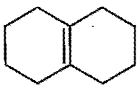
(3-Ethylocta-3,5-diene)

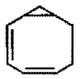
(h) 

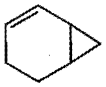
(Cyclopentene)

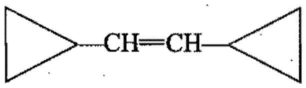
(i) 

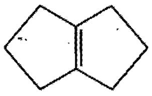
(Cyclohexa-1,4-diene)

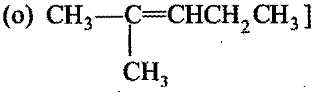
(j) 

(k) 

(l) 

(m) 

(n) 



(o) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=CHCH_2CH_3$]

2-Methyl pent-2-ene

19. Write short notes on:

(a) Markownikoff's rule
(b) Ozonolysis
(c) Polymerisation
(d) Anti-Markownikoff's rule or Peroxide effect
(e) Dehydrohalogenation
(f) Saytzeff's rule
(g) Baeyer's strain theory

20. Explain the following:

(a) Why alkenes are more reactive than alkanes?

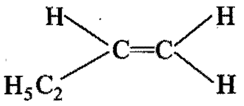
[**Ans.** π-bond is weaker than a sigma-bond and is easily broken. The π-electrons are less firmly bound to carbon nuclei.]

(b) Acetylene reacts with ammoniacal silver nitrate solution or ammoniacal cuprous chloride solution or sodamide to form an acetylide while ethylene does not.

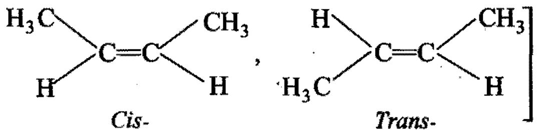
[**Ans.** Acetylene reacts to form acetylide because it contains acidic hydrogens.]

(c) But-2-ene shows geometrical isomerism but but-1-ene does not show.

[**Ans.** In but-1-ene, the carbon atom linked by double bond is attached with two hydrogen atoms (similar groups) and thus does not show geometrical isomerism.



But-1-ene



Cis- *Trans-*

But-2-ene

(d) Why has but-1-yne a larger dipole moment (0.80 D) than but-1-ene (0.30 D)?

[**Ans.** A $C—C_{sp}$ bond is more polarized than $C—C_{sp^2}$ bond because carbon with more *s*-character is more electronegative.]

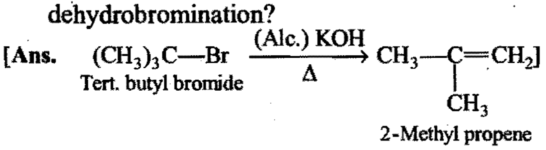
(e) Why alkynes are slightly more soluble in water than alkenes and alkanes?

[**Ans.** Alkynes are somewhat more polar in nature and thus, their solubility is slightly more in water.]

(f) Cyclopropane is more reactive than cyclobutane.

(g) Cyclopentane is inert like alkanes.

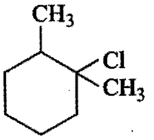
(h) Which isomer of C_4H_9Br yields only a single alkene on dehydrobromination?

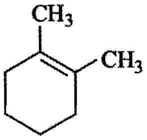


[**Ans.** $\underset{\text{Tert. butyl bromide}}{(CH_3)_3C—Br} \xrightarrow[\Delta]{\text{(Alc.) KOH}} CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$]

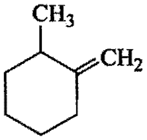
2-Methyl propene

(i) Write the products of dehydrochlorination of the following:

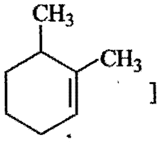




[**Ans.** (i) (Major) ;

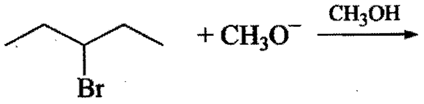


(ii) (Minor) and

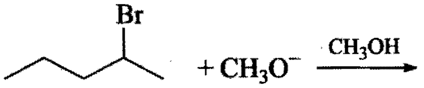


(iii) (Minor)]

(j) Which of the following reactions would provide a better synthesis of 2-pentene?

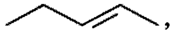


(i) $+ CH_3O^- \xrightarrow{CH_3OH}$

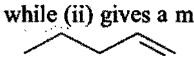


(ii) $+ CH_3O^- \xrightarrow{CH_3OH}$

[**Ans.** (i) is better because it gives only one product



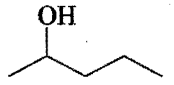
while (ii) gives a mixture of



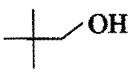
and

.]

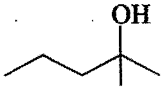
(k) Write the major products of dehydration of:



(i)

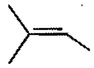


(ii)

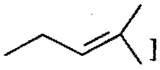


(iii)

[**Ans.** (i) *Trans*-but-2-ene



(ii) 2-Methyl but-2-ene



(iii) 2-Methyl pent-2-ene]

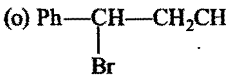
ANSWERS

1. (a) Ethyne; (b) propadiene; (c) but-2-yne

[**Hint :** (i) $CH\equiv CH \xrightarrow[NH_3(\text{liq.})]{2Na} NaC\equiv CNa$,

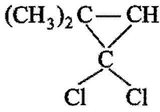
(ii) $NaC\equiv CNa \xrightarrow{2CH_3I} CH_3C\equiv CCH_3 + 2NaI$]; (d) acetylene [**Hint :** $C_2H_2 + HCl \longrightarrow CH_2=CHCl$]; (e) vinyl chloride; (f) Markownikoff's; (g) $ClCH_2CH=CH_2$; (h) ethene; (i) $HgSO_4$, H_2SO_4; (j) Baeyer's; (k) acetylene; (l) sp^2; (m) sp; (n) silver nitrate; (o) 3,4-dibromobut-1-ene (at low temperature) or 1,4-dibromobut-2-ene (at high temperature); (p) acetylene; (q) but-2-ene; (r) acetaldehyde; (s) poisonous; (t) elimination; (dehydrohalogenation), alkenes; (u) acetylene; (v) sp; (w) ethyl alcohol; (x) ethylene glycol; (y) $CH_2=CH_2$ (ethene); (z) hyperconjugation.

2. (a) CH_2BrCH_2Br; (b) $C_2H_5HSO_4$; (c) 2-methylpropene; (d) acetone; (e) Baeyer's reagent; (f) ethylene chlorohydrin; (g) $HOH_2CC\equiv CCH_2OH$ (But-2-yn-1,4-diol); (h) 120°; (i) oxalic acid; (j) ethyne; (k) alkadiene; (l) HOCl; (m) π; (n) alkane;



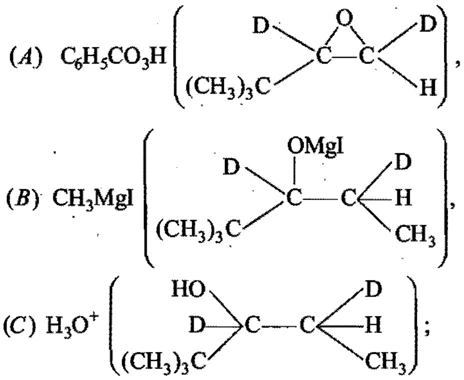
(o) $Ph—\underset{\displaystyle Br}{\underset{|}{C}H}—CH_2CH_3$; (p) $CH_3CH_2HSO_4$; CH_3CH_2OH;

(q) $CH\equiv CNa$, $CH_3—C\equiv CH$; (r) $CH_3CH_2CH_2Br$, $CH_3CH_2CH_2OH$; (s) $CH_2Br — CH_2Br$, $CH\equiv CH$; (t) $CHBr_2 — CHBr_2$, $CH\equiv CH$; (u) $Ph—C\equiv C—Ph$; (v) $HC\equiv C—Na$, $HC\equiv C—D$; (w) $Na—C\equiv C—Na$, $D—C\equiv C—D$; (x) $(CH_3—C=CH—)_3B$, CH_3CH_2CHO; (y) $CH_3OCH_2CH=CH_2$; (z)

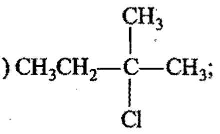


3. (a) False—Ethylene combines with H_2SO_4; (b) False—Tert. butyl bromide is formed; (c) False—Only $R—C\equiv CH$ derivatives give white ppt. but derivatives of the type $R—C\equiv C—R'$ do not give white ppt. with ammoniacal silver nitrate; (d) True; (e) True; (f) False—Acetylene is colourless with garlic odour gas; (g) True; (h) False—Both decolourise bromine water; (i) False—Reducing compounds can also decolourise Baeyer's reagent; (j) True; (k) True; (l) False—Propyne is less acidic than acetylene; (m) False—The torch contains CaC_2 and Ca_3P_2; (n) True; (o) True; (p) False—gives propene; (q) True; (r) True; (s) False—Baeyer's reagent is alkaline $KMnO_4$ solution; (t) True; (u) True; (v) True; (w) True; (x) False—It does not react with Tollens' reagent as it has no acidic hydrogen; (y) False—forms only acetic acid; (z) True.
4. [A] (a–6); (b–8); (c–7); (d–1); (e–2); (f–3); (g–4); (h–5).
[B] (a–5); (b–7); (c–8); (d–2); (e–1); (f–3); (g–4); (h–6).
5. (a) (*A*) $CH_3CHClCH_3$; (b) (*A*) CH_3CHO, (*B*) CH_3COCH_3; (c) (*A*) HCHO, (*B*) HCOONa, (*C*) CH_3OH. Formaldehyde undergoes Cannizzaro's reaction; (d) (*A*) 2-chloro-2,3-dimethyl butane; (e) (*A*) $Me—CH_2—C\equiv CNa$, (*B*) $MeCH_2C\equiv C\cdot Et$; (f) (*A*) $CH\equiv CH$, (*B*) $CH_3CH=CHCOOH$; (g) (*A*) C_2H_4, (*B*) CH_2BrCH_2Br, (*C*) C_2H_2; (h) (*A*) CH_3CHO, (*B*) CH_3CH_2OH, (*C*) C_2H_4; (i) (*A*) $CH_3—CH=CH_2$, (*B*) $CH_2Cl.CH=CH_2$; (j) (*A*) $CH_2BrCH=CH_2$, (*B*) $H_2C=C=CH_2$; (k) (*A*) cyclopropane; (l) (*A*) methylcyclopropane; (m) (*A*) cyclohexene, (*B*) cyclohexane; (n) (*A*) $C_3H_7CH(OH)CH_2 — HgOAc$, (*B*) $C_3H_7CH(OH)CH_3$; (o) (*A*) $(CH_3CH_2CH_2)_3B$, (*B*) $CH_3CH_2CH_3$; (p) (*A*) $C_6H_5CHBr—CH_2Br$, (*B*) $C_6H_5C\equiv CCH_3$; (q) (*A*) $C_6H_5CH=CHC_6H_5$ (*cis*- and *trans*-);

(r)

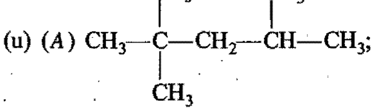


(s) (*A*) $CH_3CH(Br)—CH_2CCl_3$; (t)



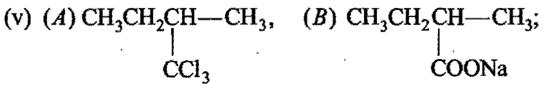
$(A)\ CH_3CH_2—\underset{Cl}{\overset{CH_3}{C}}—CH_3$;

(u)

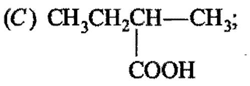


$(A)\ CH_3—\underset{CH_3}{\overset{CH_3}{C}}—CH_2—\overset{CH_3}{CH}—CH_3$;

(v)

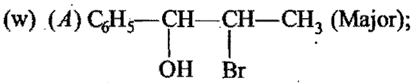


$(A)\ CH_3CH_2\underset{CCl_3}{CH}—CH_3$, $(B)\ CH_3CH_2\underset{COONa}{CH}—CH_3$;



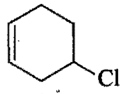
$(C)\ CH_3CH_2\underset{COOH}{CH}—CH_3$;

(w)

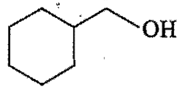


$(A)\ C_6H_5—\underset{OH}{CH}—\underset{Br}{CH}—CH_3$ (Major);

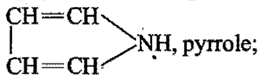
(x)



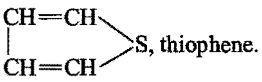
(y)



(z) CCl_4/peroxide
6. (a) Lewisite; (b) $CH_2=CHOOCCH_3$, vinyl acetate; (c) $C_2H_5O—CH=CH_2$, ethyl vinyl ether;
(d)

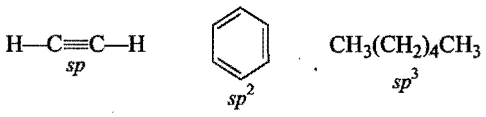


(e) HCN, hydrogen cyanide;
(f)



7. See properties of ethylene and acetylene.
8. (a) Bond length decreases and bond energy increases; (b) Electrophilic addition reactions; (c) Geometrical or *cis-trans* isomerism; (d) Cumulated; (e) Ionic mechanism; (f) Free radical mechanism; (g) Alcoholic potassium hydroxide; (h) Bromine and Baeyer's reagent.
9. (a) The decreasing order of acidic strength is:

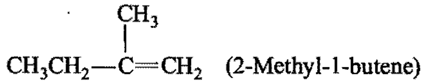
Ethyne > Benzene > *n*-Hexane



S-character 50% 33% 25%

The acidic character is linked with the percentage of *S*-character. Greater the *S*-character, more is the electronegativity of the carbon atom and more will be the acidic character.

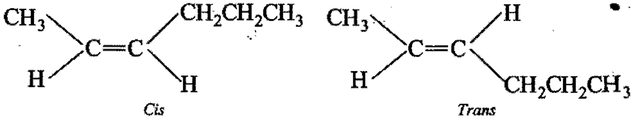
(b) $CH_3CH_2CH_2CH=CH_2$ (Pent-1-ene), $CH_3CH_2CH=CHCH_3$ (Pent-2-ene), $(CH_3)_2CHCH=CH_2$ (3-Methylbut-1-ene),



$CH_3CH_2—\overset{CH_3}{C}=CH_2$ (2-Methyl-1-butene)

$(CH_3)_2C=CHCH_3$ (2-Methyl-2-butene)

(c) Position isomerism—Example : but-1-ene and but-2-ene
Chain isomerism—Example : but-1-ene and 2-methylpropene
Geometrical isomerism—Example : *cis*- or *trans*-but-2-ene
Ring chain isomerism—Example : propene and cyclopropane.
10. (iii) and (iv) will show *cis-trans* isomerism.
11.



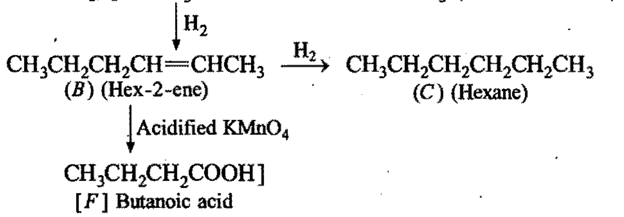
The *cis* form will have higher boiling point due to more polar nature leading to stronger intermolecular dipole-dipole interaction, thus requiring more heat energy to separate them.

PROBLEMS BASED ON STRUCTURE AND PROPERTIES

1. An organic compound [*A*] C_6H_{10}, on reduction first gives [*B*] C_6H_{12}, and finally [*C*] C_6H_{14}. [*A*] on ozonolysis followed by hydrolysis gives two aldehydes [*D*] C_2H_4O, and [*E*] $C_2H_2O_2$. Oxidation of [*B*] with acidified $KMnO_4$ gives acid [*F*] $C_4H_8O_2$. Determine the structures of the compounds [*A*] to [*F*] with proper reasoning.

[Hint: $C_6H_{10} \xrightarrow[\text{(ii) Hydrolysis}]{\text{(i) Ozonolysis}} \underset{(D)}{\underset{(CH_3CHO)}{C_2H_4O}} + \underset{(E)\ \text{(Glyoxal)}}{\underset{(OHC-CHO)}{C_2H_2O_2}}$

Thus, [*A*] is $CH_3CH{=}CH{-}CH{=}CHCH_3$ (Hexa-2,4-diene)



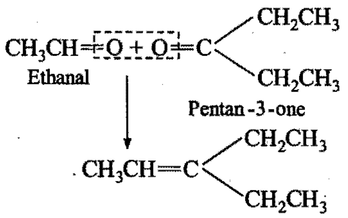
2. (*A*), (*B*) and (*C*) are isomeric heptenes. (*A*) on ozonolysis gives ethanal and pentanal, (*B*) on ozonolysis gives ethanal and pentan-3-one, while (*C*) on like treatment yields propanone and butanone. Give the structural formulae and IUPAC names of (*A*), (*B*) and (*C*).

[Hint: Compound (*A*) gives:

$\underset{\text{Ethanal}}{CH_3CH{=}O} + \underset{\text{Pentanal}}{O{=}CHCH_2CH_2CH_2CH_3}$

So, (*A*) is $\underset{\text{Hept-2-ene}}{\underset{(A)}{CH_3CH{=}CHCH_2CH_2CH_2CH_3}}$

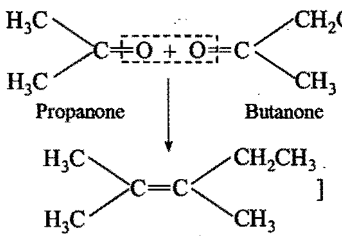
Compound (*B*) gives:



So, (*B*) is

(*B*)
3-Ethylpent-2-ene

Compound (*C*) gives:

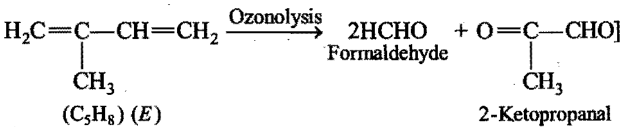


So, (*C*) is

(*C*)
2,3-Dimethylpent-2-ene

3. An organic compound (*E*) (C_5H_8) on hydrogenation gives compound (*F*) (C_5H_{12}). Compound (*E*) on ozonolysis gives formaldehyde and 2-keto-propanal. Deduce the structure of compound (*E*).

[Hint : C_5H_8 consists two double bonds as on hydrogenation, it is converted into C_5H_{12}.



$\underset{\text{2-Methyl buta-1,3-diene}}{\underset{(C_5H_8)\ (E)}{H_2C{=}C(CH_3){-}CH{=}CH_2}} \xrightarrow{\text{Ozonolysis}} \underset{\text{Formaldehyde}}{2HCHO} + \underset{\text{2-Ketopropanal}}{O{=}C(CH_3){-}CHO}$]

4. A hydrocarbon (*A*) adds one mole of hydrogen in presence of Pt catalyst to form *n*-hexane. When (*A*) is oxidized vigorously with $KMnO_4$, a single carboxylic acid containing three carbon atoms is isolated. Give the structure of (*A*) and explain.

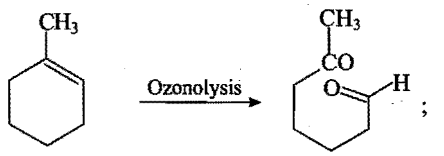
[Hint : $(A) \xrightarrow{+H_2(Pt)} CH_3CH_2CH_2CH_2CH_2CH_3$

$\xrightarrow{[O]\ KMnO_4} 2CH_3CH_2COOH$

So (*A*) is $CH_3CH_2CH = CHCH_2CH_3$ (Hex-3-ene)]

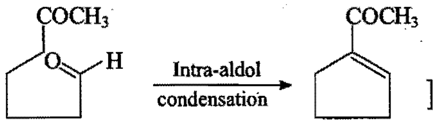
5. A hydrocarbon (*A*) of the formula C_7H_{12} on ozonolysis gives a compound (*B*) which undergo aldol condensation giving 1-acetylcyclopentene. Identify (*A*) and (*B*).

[Hint : Since, the ozonolysis of the hydrocarbon (*A*) gives only one compound (*B*), the compound (*A*) must be a cyclic alkene. Moreover since the number of C-atoms in the product obtained from the aldol condensation of (*B*) is the same as that of (*A*), the compound (*B*) must have gone intra aldol condensation. So, (*A*) and (*B*) are as follows:



(*A*) (*B*)

i.e.,



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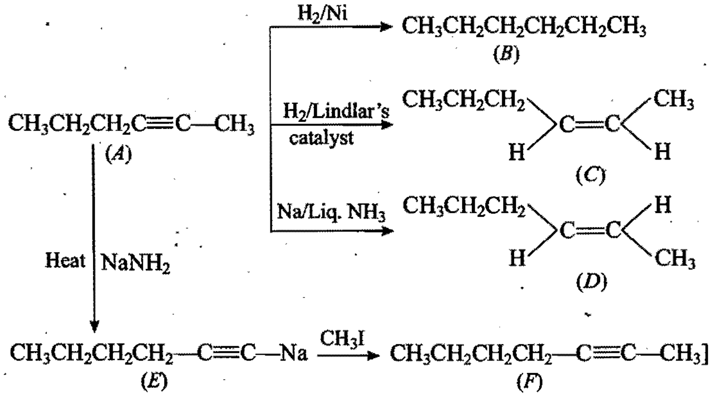
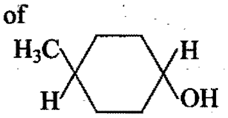
6. Hydrocarbon (*A*) C_6H_{10}, on treatment with H_2/Ni, H_2/Lindlar's catalyst and Na/liquid NH_3 forms three different reduction products (*B*), (*C*) and (*D*) respectively. (*A*) does not form any salt with ammoniacal $AgNO_3$ solution, but forms a salt (*E*) on heating with $NaNH_2$ in an inert solvent. Compound (*E*) reacts with CH_3I to give (*F*). Compound (*D*) on oxidative ozonolysis gives *n*-butanoic acid along with other product.

Give structures of (*A*) to (*F*) with proper reasoning.

[Hint :

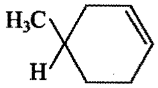


7. Dehydration of

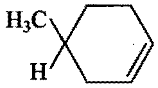


gives a compound which exists in two isomeric forms. Give the structure of both the isomers.

[Hint:



or



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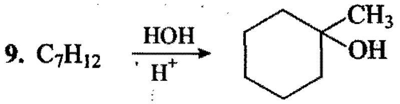
9.

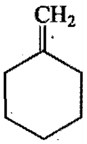


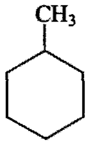
What are the possible isomers of formula C_7H_{12} which give above product?

[Hint : Degree of unsaturation $= \frac{14-12+2}{2} = 2$

Thus, the compound should have a ring and a double bond.

∴ Possible isomers will be





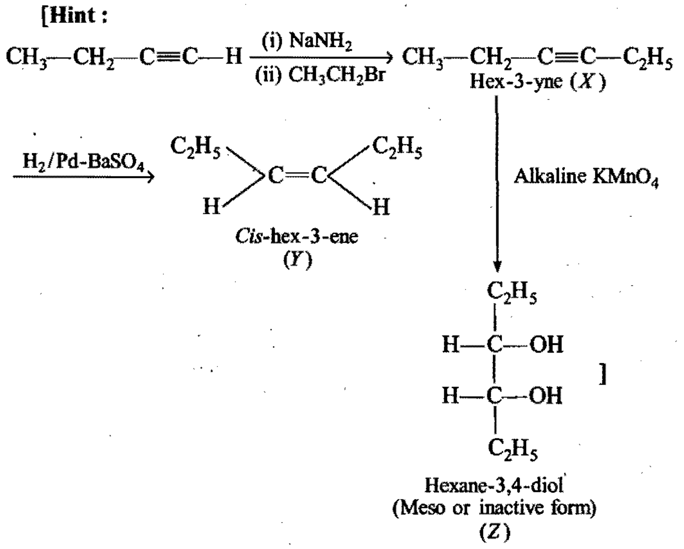
]

9. Identify (X), (Y) and (Z) in the following synthetic scheme and write their structures.

$$CH_3CH_2C{\equiv}CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} (X) \xrightarrow{H_2/Pd\text{-}BaSO_4} (Y) \xrightarrow{\text{Alkaline } KMnO_4} (Z)$$

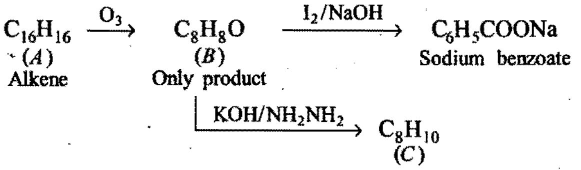
Is the compound (Z) optically active? Justify your answer. **[IIT 2002]**

[Hint :

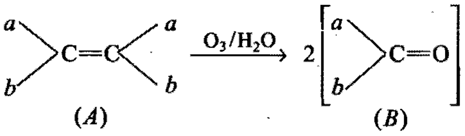


10. An alkene (A) $C_{16}H_{16}$, on ozonolysis gives one product (B) C_8H_8O. Compound (B) on reaction with NaOH/I_2 yields sodium benzoate. Compound (B) reacts with KOH/NH_2NH_2 yielding a hydrocarbon (C) C_8H_{10}. Write the structure of compounds (B) and (C). Based on this information two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation (H_2/Pd-C) gives a racemic mixture. **[IIT 2001]**

[Hint : The given reactions are as follows :

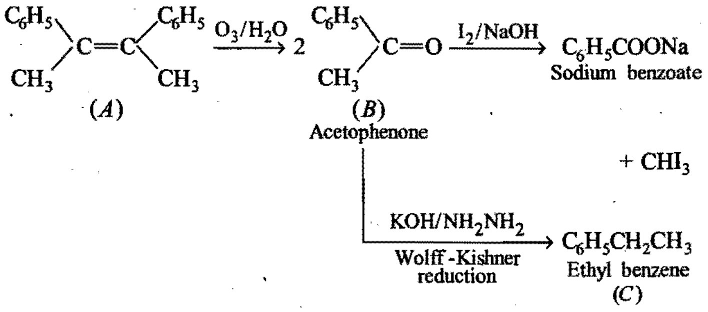


Since, (A) on ozonolysis gives only one product (B), the alkene must be a symmetrical one. This reaction may be written as,

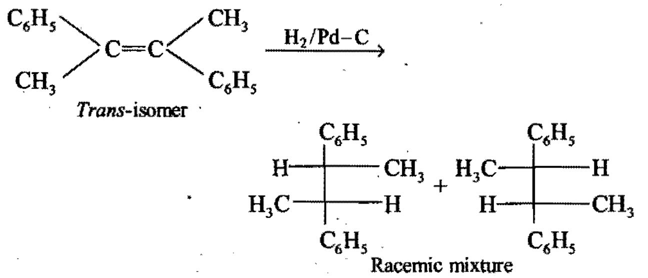


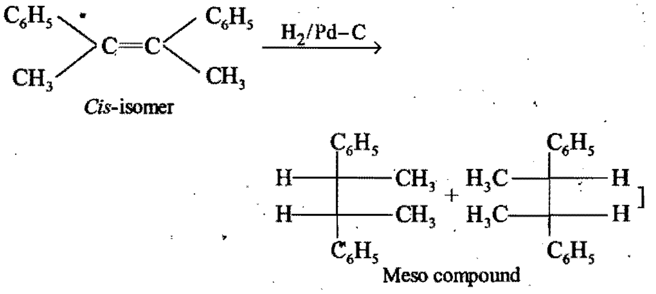
(where $a + b = C_7H_8$)

Further, (B) on treatment with I_2/NaOH (iodoform test) gives sodium benzoate, one of the group (a) and (b) may be identified with C_6H_5 and hence the other one may be CH_3 group. The given reactions are as follows:



The alkene (A) will have two isomers, *cis*- and *trans*. The catalytic hydrogenation (H_2/Pd—C) involves syn-addition of hydrogen. The *trans*-isomer gives racemic mixture while *cis*-isomer gives a meso compound.





OBJECTIVE QUESTIONS

SET I : This set contains the questions with single correct answer.

1. When ethyl iodide is treated with alcoholic potash, we get:
(a) ethyl alcohol ☐ (b) ethane ☐
(c) acetylene ☐ (d) ethylene ☐

2. Ethylene is produced by:
(a) dehydration of acetic acid ☐
(b) electrolysis of methyl alcohol ☐
(c) mixing acetic acid and calcium formate ☐
(d) passing C_2H_5OH vapours over hot Al_2O_3 ☐

3. A gas decolourises alkaline $KMnO_4$ solution but does not give precipitate with silver nitrate. It is:
(a) CH_4 ☐ (b) C_2H_6 ☐
(c) C_2H_4 ☐ (d) C_2H_2 ☐

4. Acetylene on treatment with dil. H_2SO_4 having $HgSO_4$ gives:
(a) acetaldehyde ☐ (b) acetic acid ☐
(c) ethanol ☐ (d) ethylene ☐

5. Which of the following reagents distinguish ethylene from acetylene? **[BHU 2006]**
(a) Ammoniacal cuprous chloride ☐
(b) Br_2 water ☐
(c) Alkaline $KMnO_4$ solution ☐
(d) Chlorine dissolved in CCl_4 ☐

6. Which of the following not only decolourises alkaline potassium permanganate but also gives red precipitate with ammoniacal cuprous chloride solution? **[EAMCET (Med.) 2006]**
(a) Ethane ☐ (b) Methane ☐
(c) Ethene ☐ (d) Acetylene ☐

7. The most reactive hydrocarbon is: **[JIPMER 2003]**
(a) ethene ☐ (b) ethyne ☐
(c) ethane ☐ (d) methane ☐

8. Aqueous solution of an organic compound '*A*' on electrolysis liberates acetylene and CO_2 at anode. '*A*' is: **[EAMCET (Engg.) 2007]**
(a) potassium citrate ☐ (b) potassium acetate ☐
(c) potassium succinate ☐ (d) potassium maleate ☐

9. Baeyer's reagent is:
(a) alkaline $KMnO_4$ solution ☐
(b) acidic $KMnO_4$ solution ☐
(c) neutral $KMnO_4$ solution ☐
(d) aqueous bromine solution ☐

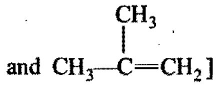
10. The negative part of the addendum adds on to the unsaturated carbon atom joined to the least number of hydrogen atoms. This statement is called: **[AFMC 2004]**
(a) Saytzeff rule ☐ (b) Kharasch effect ☐
(c) Markownikoff's rule ☐ (d) Anti-Saytzeff rule ☐

11. Products of the following reaction,
$Me_2C{=}CHCH_3 \xrightarrow[\text{(ii) }(CH_3)_2S]{\text{(i) }O_3}$? are: **[AMU (PMT) 2009]**
(a) $Me_2CO + CH_3CHO$ ☐
(b) $CH_3CHO + CH_3COOH$ ☐
(c) $Me_2CO + CH_3COOH$ ☐
(d) $2Me_2CO$ ☐

12. Ethyl alcohol is heated with conc. H_2SO_4 at 170°C. The product formed is: **[VITEEE 2008]**
(a) CH_3COOCH_3 ☐ (b) C_2H_6 ☐
(c) C_2H_4 ☐ (d) C_2H_2 ☐

13. The maximum number of isomers for an alkene with molecular formula C_4H_8 is:
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 5 ☐

[**Hint:** $CH_3CH_2CH{=}CH_2$, $CH_3CH{=}CHCH_3$ (*cis-* and *trans-*)



and $CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2$]

14. When ethylene is passed through alkaline $KMnO_4$ solution, we get:
(a) ethanol ☐ (b) glycol ☐
(c) oxalic acid ☐ (d) acetaldehyde ☐

15. But-2-ene can be obtained by reacting:
(a) 1,2-dibromopropane with zinc ☐
(b) ethyl bromide with sodium ☐
(c) ethylidene bromide with zinc ☐
(d) *n*-butyl alcohol with alcoholic KOH ☐

16. On electrolysis of potassium succinate solution, the hydrocarbon obtained is: **[JIPMER 2004]**
(a) ethene ☐ (b) ethane ☐
(c) ethyne ☐ (d) all of these ☐

17. Ethylene reacts with sulphur monochloride to form:
(a) ethyl chloride ☐ (b) ethylene chloride ☐
(c) mustard gas ☐ (d) ethylidene chloride ☐

18. Ethylene reacts with air under pressure in presence of silver catalyst at 250°C to form:
(a) ethylene glycol ☐ (b) formaldehyde ☐
(c) acetaldehyde ☐ (d) epoxide ☐

19. 1,2-dibromopropane on reaction with alc. KOH yields:
(a) acetylene ☐ (b) propylene ☐
(c) propyne ☐ (d) none ☐

20. ...... is obtained when iodoform is heated with Ag powder.
(a) CH_4 ☐ (b) C_2H_4 ☐
(c) C_2H_6 ☐ (d) C_2H_2 ☐

21. Benzene is a polymer of:
(a) methane ☐ (b) acetylene ☐
(c) ethane ☐ (d) ethylene ☐

22. Acetylene on ozonolysis gives:
(a) glycol ☐
(b) glyoxal and formic acid ☐

(c) formaldehyde ☐
(d) none of the above ☐

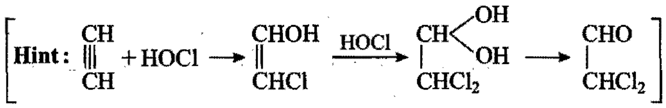
23. Chromic acid oxidises acetylene into:
(a) oxalic acid ☐ (b) acetic acid ☐
(c) acetaldehyde ☐ (d) $CO_2 + H_2O$ ☐

24. The end product of the following sequence is:

$$CaO + C \xrightarrow{Heat} A \xrightarrow{H_2O} B \xrightarrow[HgSO_4]{H_2SO_4} C$$

(a) ethanol ☐
(b) ethyl hydrogen sulphate ☐
(c) acetaldehyde ☐
(d) ethylene glycol ☐

25. Addition of HOCl to ethyne gives:
(a) ethyl chloride ☐ (b) vinyl chloride ☐
(c) dichloroacetaldehyde ☐ (d) ethylidene chloride ☐



$$\left[\textbf{Hint:}\ \begin{matrix}CH\\ |||\\ CH\end{matrix} + HOCl \longrightarrow \begin{matrix}CHOH\\ \|\\ CHCl\end{matrix} \xrightarrow{HOCl} \begin{matrix}CH\!<^{OH}_{OH}\\ |\\ CHCl_2\end{matrix} \longrightarrow \begin{matrix}CHO\\ |\\ CHCl_2\end{matrix}\right]$$

26. When acetylene is reacted with HCl in presence of $HgCl_2$, the product obtained is:
(a) methyl chloride ☐ (b) vinyl chloride ☐
(c) formaldehyde ☐ (d) acetaldehyde ☐

27. When propyne is treated with aqueous H_2SO_4 in presence of $HgSO_4$, the major product is: **[PMT (Kerala) 2010]**
(a) propanone ☐ (b) 2-propanol ☐
(c) ethanal ☐ (d) ethyne ☐
(e) propane ☐

28. The bond between carbon atom (1) and carbon atom (2) in the compound,

$$N\equiv\overset{1}{C}-\overset{2}{C}H=CH_2$$

involves the hybrids as:
(a) sp and sp^2 ☐ (b) sp^2 and sp^2 ☐
(c) sp and sp ☐ (d) sp^3 and sp ☐

29. Which of the following displaces hydrogen on reaction with sodium in liquid ammonia?
(a) C_2H_2 ☐ (b) CH_4 ☐
(c) C_2H_6 ☐ (d) C_2H_4 ☐

30. When 1,1,2,2-tetrabromoalkane is heated with zinc powder in alcohol, which is formed?
(a) Alkyne ☐ (b) Alkene ☐
(c) Alkane ☐ (d) None of these ☐

31. The end product of the following sequence of operations is:

$$CaC_2 \xrightarrow{H_2O} (A) \xrightarrow[HgSO_4]{H_2SO_4} (B) \xrightarrow[LiAlH_4]{H} (C)$$

(a) methyl alcohol ☐ (b) ethyl alcohol ☐
(c) acetaldehyde ☐ (d) ethylene ☐

32. The name of the poisonous gas formed by the interaction of acetylene and arsenic trichloride is:
(a) phosgene ☐ (b) lewisite ☐
(c) mustard gas ☐ (d) westron ☐

33. Acetylene when treated with Cl_2 in CCl_4 forms:
(a) mustard gas ☐ (b) lewisite ☐
(c) westrosol ☐ (d) westron ☐

34. Acetylene is not used to prepare:
(a) westron ☐ (b) westrosol ☐
(c) lewisite ☐ (d) mustard gas ☐

35. Acetylene is prepared industrially by passing electric discharge through graphite electrodes in the atmosphere of:
(a) air ☐ (b) H_2 ☐
(c) N_2 ☐ (d) CO_2 ☐

36. When a mixture of acetylene and nitrogen is subjected to electric discharge, the product obtained is:
(a) ether ☐ (b) ethyl amine ☐
(c) HCN. ☐ (d) ammonia ☐

37. A metallic carbide on treatment with water gives a colourless gas which burns readily in air and gives a precipitate with ammoniacal silver nitrate solution. The gas evolved is:
(a) CH_4 ☐ (b) C_2H_6 ☐
(c) C_2H_4 ☐ (d) C_2H_2 ☐

38. Which one has of the red colour?
(a) C_2Na_2 ☐ (b) C_2Ag_2 ☐
(c) Cu_2C_2 ☐ (d) $CH_3C\equiv CNa$ ☐

39. The gas, which is used for artificial ripening of fruits, is:
(a) CH_4 ☐ (b) C_2H_4 ☐
(c) C_2H_6 ☐ (d) none ☐

40. The gas, which is used for welding purposes is:
(a) CH_4 ☐ (b) C_2H_6 ☐
(c) C_2H_4 ☐ (d) C_2H_2 ☐

41. Propane can be distinguished from propylene with:
(a) sodium ☐ (b) bromine water ☐
(c) ammoniacal $AgNO_3$ ☐ (d) $NaHSO_3$ ☐

42. Reaction of HBr with propene in the presence of peroxide gives: **[CBSE (Med.) 2004]**
(a) isopropyl bromide ☐ (b) allyl bromide ☐
(c) *n*-propyl bromide ☐ (d) 3-bromopropane ☐

43. The compound which is insoluble in cold H_2SO_4 is:
(a) *n*-butane ☐ (b) 1-butene ☐
(c) 2-butene ☐ (d) ethyl acetate ☐

44. Which one of the following molecules is linear?
(a) $HC\equiv CH$ ☐ (b) $H_2C=CH_2$ ☐
(c) CH_3-CH_3 ☐ (d) $H-O-H$ ☐

45. In the laboratory by dehydration of ethyl alcohol, ethylene was obtained in 50% yield. The ethylene so obtained reacted with bromine to give ethylene dibromide in 80% yield. If the amount of ethyl alcohol was 0.5 mole then ethylene dibromide produced would be:
(a) 0.8 mole ☐ (b) 0.4 mole ☐
(c) 0.2 mole ☐ (d) 0.1 mole ☐

46. Conjugated double bond is present in:
(a) propylene ☐ (b) isobutylene ☐
(c) butylene ☐ (d) butadiene ☐

47. When alcoholic solution of ethylene dibromide is heated with granulated zinc, the compound formed is:
(a) ethylene ☐ (b) ethyne ☐
(c) cyclobutane ☐ (d) butane ☐

48. In the reaction given below, X is:

Neo-pentylalcohol $\xrightarrow{H_2SO_4} X$ **[DPMT 2009]**

(a) 2-methylpentane ☐ (b) Neo-pentane ☐
(c) 2-methylpent-2-ene ☐ (d) 2-methylbut-2-ene ☐

49. Which of the following will have least hindered rotation about carbon-carbon bond?
(a) Ethylene ☐ (b) Acetylene ☐
(c) Ethane ☐ (d) Hexachloroethane ☐
[**Hint :** Hexachloroethane has less rotation than ethane because of greater size of chlorine than hydrogen.]

50. The olefin which on ozonolysis gives CH_3CH_2CHO and CH_3CHO is:
(a) 1-butene ☐ (b) 2-butene ☐
(c) 1-pentene ☐ (d) 2-pentene ☐

51. Dilute aqueous $KMnO_4$ at room temperature reacts with $R—CH═CHR$ to give:
(a) $R—CHO$ ☐ (b) $RCOOH$ ☐
(c) $R—CHOHCHOHR$ ☐ (d) $CO_2 + H_2O$ ☐

52. Lindlar's catalyst is:
(a) Pt in ethanol ☐ (b) $Pd + BaSO_4$ ☐
(c) Ni in ethanol ☐ (d) Na in liquid NH_3 ☐

53. Which of the following molecules is not linear?
(a) $H_2C═CH_2$ ☐ (b) CO_2 ☐
(c) $BeCl_2$ ☐ (d) $HC≡CH$ ☐

54. Butyne on reaction with hot alkaline $KMnO_4$ gives:
(a) $CH_3CH_2CH_2COOH$ ☐
(b) CH_3CH_2COOH ☐
(c) $CH_3CH_2COOH + CO_2$ ☐
(d) $CH_3CH_2COOH + HCOOH$ ☐

55. When C_2H_2, CH_4 and C_2H_4 passes through a test tube which have ammoniacal Cu_2Cl_2, find out which gas comes out unaffected from test tube? **[BCECE (Med.) 2008]**
(a) C_2H_2 and CH_4 ☐ (b) C_2H_2 and C_2H_4 ☐
(c) C_2H_2 ☐ (d) C_2H_4 and CH_4 ☐

56. When propene is treated with chlorine at 500°C, allyl chloride is formed as the main product. The mechanism of the reaction is:
(a) free radical addition ☐
(b) free radical substitution ☐
(c) electrophilic addition ☐
(d) electrophilic substitution ☐

57. The general formula of the product formed when 1,1,1-trichloroethane is heated with metallic silver is:
(a) C_nH_{2n+2} ☐ (b) C_nH_{2n} ☐
(c) C_nH_{2n-2} ☐ (d) C_nH_{2n+1} ☐

58. To prepare 2-butyne from 2,2,3,3-tetrachlorobutane, use is made of:
(a) zinc ☐ (b) sodamide ☐
(c) alc. KOH ☐ (d) aq. KOH ☐

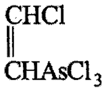
59. Indicate the organic structure for the product expected when 2-methylpropene is heated with acetyl chloride in presence of anhydrous zinc chloride:
(a) $(CH_3)_2CClCH_2OCCH_3$ ☐
(b) $(CH_3)_2CHCH_2OCCH_3$ ☐
(c) $CH_3COCH(CH_3)_2$ ☐
(d) none of the above ☐

60. Reactions of alkenes with ...... are explosive in nature:
(a) Cl_2 ☐ (b) I_2 ☐
(c) F_2 ☐ (d) Br_2 ☐

61. Catalyst used in dimerisation of acetylene to prepare chloroprene is:
(a) $HgSO_4 + H_2SO_4$ ☐ (b) Cu_2Cl_2 ☐
(c) $Cu_2Cl_2 + NH_4OH$ ☐ (d) $Cu_2Cl_2 + NH_4Cl$ ☐

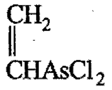
62. Ammoniacal silver nitrate forms a white precipitate easily with: **[UPSEE (Engg.) 2008]**
(a) $CH_3CH═CH_2$ ☐ (b) $CH_3—C≡CH$ ☐
(c) $CH_3—C≡C—CH_3$ ☐ (d) $H_2C═CH_2$ ☐

63. Structural formula for lewisite is:

(a) 
$$\begin{matrix}CHCl\\ \|\\ CHAsCl_3\end{matrix}$$
☐

(b) 
$$\begin{matrix}CHCl\\ \|\\ CHAsCl\end{matrix}$$
☐

(c) 
$$\begin{matrix}CHCl\\ \|\\ CHAsCl_2\end{matrix}$$
☐

(d) 
$$\begin{matrix}CH_2\\ \|\\ CHAsCl_2\end{matrix}$$
☐

64. An olefin may be converted into alcohol by:
(a) B_2H_6 and H_2O_2 ☐ (b) $LiAlH_4$ ☐
(c) alkaline $KMnO_4$ ☐ (d) HOCl ☐

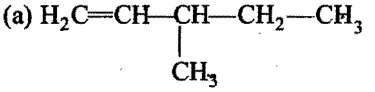
65. Propene is more reactive than ethene towards HBr because:
(a) propene can more readily undergo a free radical chain reaction ☐
(b) propene gives rise to more stable carbonium ion ☐
(c) the double bond in case of propene is unstable ☐
(d) the methyl group attached to double bond withdraws electrons and facilitates the attack ☐

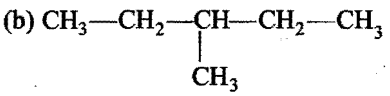
66. Acetylene when passed through cuprous chloride in presence of ammonium chloride forms:
(a) benzene ☐ (b) vinyl acetylene ☐
(c) allyl chloride ☐ (d) allene ☐

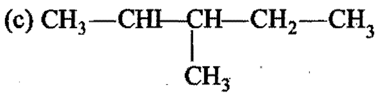
67. Which of the following alkynes is most acidic?
(a) $CH_3—C≡CH$ ☐ (b) $CH_3—C≡C—CH_3$ ☐
(c) $CH_3—CH_2—C≡CH$ ☐ (d) $HC≡CH$ ☐

68. Acetylenic hydrogens are acidic because:
(a) sigma electron density of C—H bond in acetylene is nearer to carbon which has 50% *s*-character ☐
(b) acetylene has only one hydrogen on each carbon ☐
(c) acetylene contains least number of hydrogens among the possible hydrocarbons having two carbons ☐
(d) acetylene resembles acetic acid ☐

69. Sample of 2,3-dibromo-3-methylpentane is heated with zinc dust. The resulting product is isolated and heated with HI in the presence of phosphorus. Indicate which is the structure that represents the final product in the reaction:

(a)  $H_2C{=}CH—CH(CH_3)—CH_2—CH_3$ ☐

(b)  $CH_3—CH_2—CH(CH_3)—CH_2—CH_3$ ☐

(c)  $CH_3—CH_2—CH(CH_3)—CH_2—CH_3$ ☐

(d) none of the above ☐

70. Which of the following reactions will yield 2,2-dibromo-propane? **[CPMT 2004; AIEEE 2007]**
(a) $H_2C{=}CHBr + HBr$ ☐
(b) $CH_3C{\equiv}CCH_3 + 2HBr$ ☐
(c) $CH_3C{\equiv}CH + 2HBr$ ☐
(d) $CH_3CH{=}CHBr + HBr$ ☐

71. How many grams of bromine will react with 21 grams of C_3H_6?
(a) 320 ☐ (b) 240 ☐
(c) 160 ☐ (d) 80 ☐

72. Which of the following will be the final product when C_2H_2 reacts with HCl?
(a) $H_2C{=}CHCl$ ☐ (b) $CH_3—CH_2Cl$ ☐
(c) $CH_3—CHCl_2$ ☐ (d) $CHCl{=}CHCl$ ☐

73. The reaction, $(CH_3)_3C—OH \xrightarrow[\text{Heat}]{H_2SO_4} (CH_3)_2C{=}CH_2$, is an example of:
(a) sulphonation ☐ (b) decomposition ☐
(c) dehydration ☐ (d) alkylation ☐

74. Propene $CH_3—CH{=}CH_2$ can be converted into propanol-1 by oxidation. Indicate which set of reagents amongst the following is ideal to bring the above conversion?
(a) O_3/Zn dust ☐
(b) B_2H_6 and alkaline H_2O_2 ☐
(c) Alkaline $KMnO_4$ ☐
(d) OsO_4 followed by $NaHSO_3$/alcohol ☐

75. $H_2C{=}CH_2 + HOCl \longrightarrow \ldots\ldots + \ldots\ldots \longrightarrow$ ethylene chlorohydrin. Fill in the blanks in the above reaction with:
(a) $CH_2OH—\overset{-}{C}H_2 + \overset{+}{Cl}$ ☐ (b) $CH_2Cl—\overset{-}{C}H_2 + \overset{+}{O}H$ ☐
(c) $CH_2OH—\overset{+}{C}H_2 + \overset{-}{Cl}$ ☐ (d) $CH_2Cl—\overset{+}{C}H_2 + \overset{-}{O}H$ ☐

76. Acetylene is used as an anaesthetic under the name of:
(a) narcylene ☐ (b) pyrene ☐
(c) neopyrene ☐ (d) pyroline ☐

77. Which one will form thiophene when heated with sulphur or H_2S?
(a) CH_4 ☐ (b) C_2H_6 ☐
(c) C_2H_4 ☐ (d) C_2H_2 ☐

78. To which class cyclopentane does belong?
(a) Aromatic ☐ (b) Heterocyclic ☐
(c) Alicyclic ☐ (d) Unsaturated aliphatic ☐

79. The compound 1,2-butadiene has:
(a) only *sp*-hybridized carbon atoms ☐
(b) only sp^2-hybridized carbon atoms ☐
(c) both *sp*- and sp^2-hybridized carbon atoms ☐
(d) sp-sp^2- and sp^3-hybridized carbon atoms ☐

80. A compound with molecular formula C_4H_6 may contain:
(a) a double bond ☐
(b) two double bonds or a triple bond ☐
(c) a triple bond ☐
(d) all single bonds ☐

81. Cyclopentene on treatment with alkaline $KMnO_4$ gives:
(a) cyclopentanol ☐
(b) *trans*-1,2-cyclopentanediol ☐
(c) *cis*-1,2-cyclopentanediol ☐
(d) mixture of (b) and (c) ☐

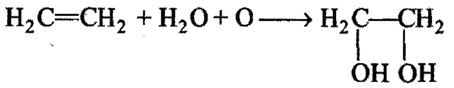
82. A hydrocarbon of formula C_6H_{10}, absorbs only one molecule of H_2 upon catalytic hydrogenation. Upon ozonolysis the hydrocarbon yields, $OHC—CH_2—CH_2—CH_2—CH_2—CHO$, the compound is:
(a) cyclohexene ☐ (b) cyclohexane ☐
(c) benzene ☐ (d) cyclobutane ☐

83. Diels-Alder reaction is used to synthesise a ring of:
(a) four carbon atoms ☐ (b) five carbon atoms ☐
(c) three carbon atoms ☐ (d) six carbon atoms ☐

84. Terminal (α, ω) dihalides on heating with zinc or sodium forms:
(a) alkenes ☐ (b) alkynes ☐
(c) alkanes ☐ (d) cycloalkanes ☐

85. The theory of strainless ring was explained by:
(a) Baeyer ☐ (b) Sachse and Mohr ☐
(c) Kekule ☐ (d) Erlenmeyer ☐

86. Which of the following reagents will you choose for the given reaction? **[PET (Rajasthan 2008)]**

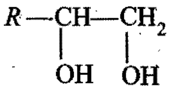


$$H_2C{=}CH_2 + H_2O + O \longrightarrow H_2C(OH)—CH_2(OH)$$

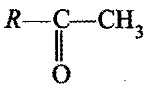
(a) Dil. $KMnO_4$, 273K ☐
(b) Alkaline $KMnO_4$, high temperature ☐
(c) Acid and $K_2Cr_2O_7$ at room temperature ☐
(d) Acid and $KMnO_4$ at room temperature ☐

87. In the presence of platinum catalyst, hydrocarbon (*A*) adds hydrogen to form *n*-hexane. When hydrogen bromide is added to (*A*) instead of hydrogen, only a single bromo compound is formed. Which of the following is (*A*)?
(a) $H_2C{=}CH—CH_2—CH_2—CH_2—CH_3$ ☐
(b) $CH_3—CH{=}CH—CH_2—CH_2—CH_3$ ☐
(c) $CH_3—CH_2—CH{=}CH—CH_2—CH_3$ ☐
(d) $CH_3—CH_2—CH_2—CH{=}CH—CH_3$ ☐

88. Alkene $RCH{=}CH_2$ reacts readily with B_2H_6 and the product on oxidation with alkaline H_2O_2 produces:

(a) 

$R{-}\underset{OH}{CH}{-}\underset{OH}{CH_2}$ ☐ (b) $R{-}CH_2{-}CHO$ ☐

(c) RCH_2CH_2OH ☐ (d) 

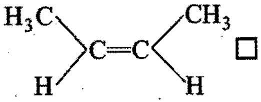
$R{-}\underset{O}{\overset{\|}{C}}{-}CH_3$ ☐

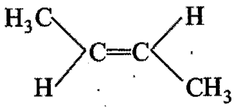
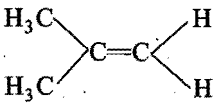
89. The intermediate during the addition of HCl to propene in the presence of peroxide is:

(a) $CH_3\dot{C}HCH_2Cl$ ☐ (b) $CH_3\overset{+}{C}HCH_3$ ☐

(c) $CH_3CH_2\dot{C}H_2$ ☐ (d) $CH_3CH_2\overset{+}{C}H_2$ ☐

90. The compound which reacts with HBr obeying Markownikoff's rule is:

(a) $H_2C{=}CH_2$ ☐ (b)  ☐

(c)  ☐ (d)  ☐

91. The number and type of bonds between two carbon atoms in CaC_2 are:

(a) one sigma and one pi (π) bond ☐

(b) one sigma and two pi (π) bonds ☐

(c) one sigma and one and a half pi (π) bonds ☐

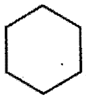
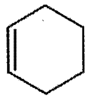
(d) one sigma bond ☐

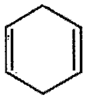
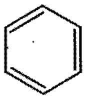
92. Cyclohexadiene contains how many degrees of unsaturation?

(a) 1 ☐ (b) 2 ☐

(c) 3 ☐ (d) 6 ☐

93. Acetylene contains same degrees of unsaturation as:

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

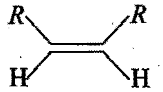
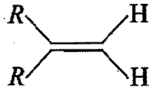
94. Four degrees of unsaturation are present in which of the compounds given below?

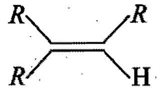
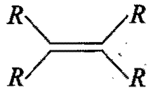
(a) But-1-yne ☐ (b) But-2-yne ☐

(c) Buta-1,3-diene ☐ (d) Toluene ☐

95. Which one of the following alkenes will react faster with H_2 under catalytic hydrogenation condition?

[IIT 2000; CBSE (Med.) 2005]

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

96. Propyne and propene can be distinguished by:

[IIT 2000; DCE 2005]

(a) conc. H_2SO_4 ☐ (b) Br_2 in CCl_4 ☐

(c) $AgNO_3$ in ammonia ☐ (d) dil. $KMnO_4$ ☐

97. An alkyne combines with a conjugated diene to give an unconjugated cycloalkadiene. The most likely title of this reaction is: **[JEE (Orissa) 2008]**

(a) Schotten-Baumann reaction ☐

(b) Hofmann-bromamide reaction ☐

(c) Diels-Alder reaction ☐

(d) Pinacol-Pinacolone rearrangement ☐

98. When cyclohexane is poured on water, it floats because cyclohexane is:

(a) in boat form ☐ (b) in chair form ☐

(c) in crown form ☐ (d) less dense than water ☐

99. The cylindrical shape of an alkyne is due to the fact that it has:

(a) three sigma C—C bonds ☐

(b) two sigma and one pi C—C bond ☐

(c) three pi C—C bonds ☐

(d) one sigma and two pi C—C bonds ☐

100. During debromination of meso-2,3-dibromobutane, the major product formed is:

(a) *n*-butane ☐ (b) 1-butene ☐

(c) *cis*-2-butene ☐ (d) *trans*-2-butene ☐

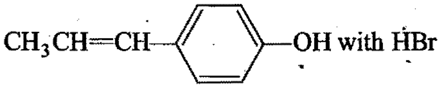
101. Addition of bromine to buta-1,3-diene gives:

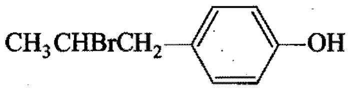
(a) 1,2-addition product only ☐

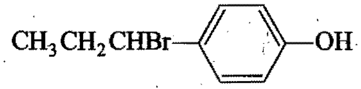
(b) 1,4-addition product only ☐

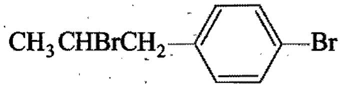
(c) both 1,2 and 1,4-addition products ☐

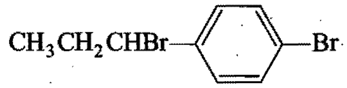
(d) no reaction ☐

102. The reaction of  with HBr gives:

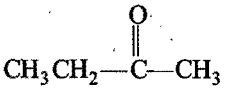
(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

103. The product(s) obtained *via* oxymercuration ($HgSO_4$ + H_2SO_4) of 1-butyne would be:

(a) 

$CH_3CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3$ ☐

(b) $CH_3CH_2CH_2CHO$ ☐

(c) $CH_3CH_2CHO + HCHO$ ☐

(d) $CH_3CH_2COOH + HCOOH$ ☐

104. The reaction of propene with HOCl proceeds via the addition of: **[IIT (S) 2001]**

(a) H^+ in the first step ☐

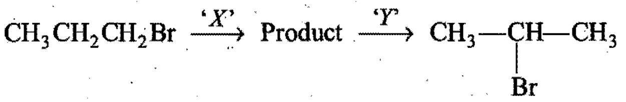
(b) Cl^+ in the first step ☐

(c) OH^- in the first step ☐

(d) Cl^+ and ^-OH in the single step ☐

105. Which of these will not react with acetylene? **[AIEEE 2002]**
(a) NaOH ☐ (b) Ammoniacal $AgNO_3$ ☐
(c) Na ☐ (d) HCl ☐

106. Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations: **[IIT (S) 2002]**



$$CH_3CH_2CH_2Br \xrightarrow{\text{'}X\text{'}} \text{Product} \xrightarrow{\text{'}Y\text{'}} CH_3-\underset{\substack{|\\ Br}}{CH}-CH_3$$

(a) X = dilute aqueous NaOH, 20°C
Y = HBr/acetic acid, 20°C ☐
(b) X = conc. alcoholic NaOH, 80°C
Y = HBr/acetic acid, 20°C ☐
(c) X = dilute aqueous NaOH, 20°C
$Y = Br_2/CHCl_3, 0°C$ ☐
(d) X = conc. alcoholic NaOH, 80°C
$Y = Br_2/CHCl_3, 0°C$ ☐

107. In presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff's addition to alkenes because : **[IIT (S) 2001]**
(a) both are highly ionic ☐
(b) one is oxidising and other is reducing ☐
(c) one of the steps is endothermic in both the cases ☐
(d) all the steps are exothermic in both the cases ☐

108. In the preparation of alkene from alcohol using Al_2O_3, which is effective factor? **[CBSE (Med.) 2001]**
(a) Porosity of Al_2O_3 ☐
(b) Temperature ☐
(c) Concentration ☐
(d) Surface area of Al_2O_3 ☐

109. Consider the following statements; a hydrocarbon of molecular formula C_5H_{10} is a;
(I) mono substituted alkene
(II) disubstituted alkene
(III) trisubstituted alkene
Which of the following statements are correct? **[SCRA 2001]**
(a) I, II and III ☐ (b) I and II ☐
(c) II and III ☐ (d) I and III ☐

110. Identify a reagent from the following list, which can easily distinguish between 1-butyne and 2-butyne: **[IIT (S) 2002]**
(a) bromine, CCl_4 ☐
(b) H_2, Lindlar's catalyst ☐
(c) dil. H_2SO_4, $HgSO_4$ ☐
(d) ammoniacal Cu_2Cl_2 solution ☐

111. But-1-ene may be converted to butane by a reaction with: **[AIEEE 2003]**
(a) Zn-HCl ☐ (b) Sn-HCl ☐
(c) Zn-Hg ☐ (d) Pd/H_2 ☐

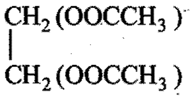
112. Correct statement about 1,3-dibutene: **[UPSEAT 2003]**
(a) conjugated double bonds are present ☐
(b) reacts with HBr ☐
(c) forms polymers ☐
(d) all of the above ☐

113. Acetylene reacts with HCN in the presence of $Ba(CN)_2$ to yield: **[UPSEAT 2004]**
(a) 1,1-dicyanoethane ☐ (b) 1,2-dicyanoethane ☐
(c) vinyl cyanide ☐ (d) none of these ☐

114. Which one of the following has the minimum boiling point? **[AIEEE 2004]**
(a) *n*-Butane ☐ (b) 1-Butyne ☐
(c) 1-Butene ☐ (d) Isobutene ☐

115. Which of the following alkenes will give an optically active alcohol when treated with H_2O/H_2SO_4? **[CPMT 2004]**
(a) 1-Butene ☐ (b) Ethene ☐
(c) Propene ☐ (d) 2-Methyl propene ☐

116. CH_3COOH is reacted with $HC{\equiv}CH$ in presence of Hg^{2+}, the product is: **[DPMT 2004; BHU 2005]**

(a) 

$$\begin{matrix} CH_2(OOCCH_3) \\ | \\ CH_2(OOCCH_3) \end{matrix}$$ ☐

(b) $CH_3CH_2(OOC-CH_3)$ ☐
(c) $CH_3CH(OOC-CH_3)_2$ ☐
(d) none of the above ☐

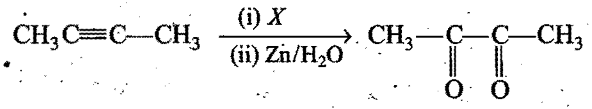
117. The product of acid catalysed hydration of 2-phenyl propene is: **[IIT 2004]**
(a) 3-phenyl-2-propanol ☐ (b) 1-phenyl-2-propanol ☐
(c) 2-phenyl-2-propanol ☐ (d) 2-phenyl-1-propanol ☐

118. Which of the following used for the conversion of 2-hexyne into *trans*-2-hexene? **[IIT 2004]**
(a) $H_2/Pd/BaSO_4$ ☐ (b) H_2, PtO_2 ☐
(c) $NaBH_4$ ☐ (d) $Li\text{-}NH_3/C_2H_5OH$ ☐

119. Which of the following gives propyne on hydrolysis? **[AIIMS 2005]**
(a) Al_4C_3 ☐ (b) Mg_2C_3 ☐
(c) B_4C ☐ (d) La_4C_3 ☐

120. When 2-butyne is treated with $Pd-BaSO_4$; the product formed will be: **[DCE 2005; JEE (Orissa) 2006]**
(a) *cis*-2-butene ☐ (b) *trans*-2-butene ☐
(c) 1-butene ☐ (d) 2-hydroxy butane ☐

121. In the reaction,



$$CH_3C{\equiv}C-CH_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) }X} CH_3-\underset{\substack{\|\\ O}}{C}-\underset{\substack{\|\\ O}}{C}-CH_3$$

X is : **[DCE 2005]**
(a) HNO_3 ☐ (b) O_2 ☐
(c) O_3 ☐ (d) $KMnO_4$ ☐

122. Reaction of one molecule of HBr with one molecule of 1,3-butadiene at 40°C gives predominantly: **[AIEEE 2005]**
(a) 3-bromobutene under kinetically controlled conditions ☐
(b) 1-bromo-2-butene under thermodynamically controlled conditions ☐
(c) 3-bromobutene under thermodynamically controlled conditions ☐

(d) 1-bromo-2-butene under kinetically controlled conditions ☐

123. Which of the reagents on reaction with cyclohexanol gives best yield of cyclohexene? **[IIT 2005]**

(a) Conc. H_3PO_4 ☐

(b) Conc. HCl ☐

(c) Conc. HBr ☐

(d) Conc. HCl with $ZnCl_2$ ☐

124. Acid catalysed hydration of alkenes except ethene leads to the formation of: **[AIEEE 2005; JCECE (Med.) 2008]**

(a) primary alcohol ☐

(b) secondary or tertiary alcohol ☐

(c) mixture of primary and secondary alcohols ☐

(d) mixture of secondary and tertiary alcohols ☐

125. Elimination of bromine from 2-bromobutane results in the formation of: **[AIEEE 2005]**

(a) equimolar mixture of 1- and 2-butene ☐

(b) predominantly-2-butene ☐

(c) predominantly-1-butene ☐

(d) predominantly-2-butyne ☐

126. The only alcohol that can be prepared by the indirect hydration of alkene is: **[AFMC 2005]**

(a) ethyl alcohol ☐ (b) propyl alcohol ☐

(c) isobutyl alcohol ☐ (d) methyl alcohol ☐

127. 3-phenyl propene on reaction with HBr gives (as a major product): **[AIIMS 2005]**

(a) $C_6H_5CH_2CH(Br)CH_3$ ☐

(b) $C_6H_5CH(Br)CH_2CH_3$ ☐

(c) $C_6H_5CH_2CH_2CH_2Br$ ☐

(d) $C_6H_5CH(Br)CH{=}CH_2$ ☐

128. $HC{\equiv}CH \xrightarrow[H_2SO_4]{HgSO_4} (A) \xrightarrow[HOH]{CH_3MgBr} (B) \xrightarrow{P/Br_2} (C)$

In this reaction, the final product (C) is: **[DPMT 2005]**

(a) $CH_3CH(Br)CH_3$ ☐ (b) $CH_3CH_2CH_2Br$ ☐

(c) $CH_2{=}CHBr$ ☐ (d) $BrHC{=}CH{-}CH_3$ ☐

129. One mole of an unsaturated hydrocarbon on ozonolysis gives one mole each of CH_3CHO, HCHO and OHC—CHO. The hydrocarbon is: **[PMT (Kerala) 2006]**

(a) $CH_3CH_2{-}C{\equiv}C{-}CH_3$ ☐

(b) $HC{\equiv}C{-}CH_2CH_2CH_3$ ☐

(c) $CH_3CH{=}CHCH{=}CH_2$ ☐

(d) $H_2C{=}CH{-}CH_2{-}CH{=}CH_2$ ☐

(e) $H_2C{=}C{=}CHCH_2CH_3$ ☐

130. Addition of Br_2 to Z-but-2-ene gives: **[PMT (Kerala) 2006]**

(a) (R,R)-2,3-dibromobutane only ☐

(b) (S,S)-2,3-dibromobutane only ☐

(c) (R,S)-2,3-dibromobutane only ☐

(d) (R,S)-1,2-dibromobutane ☐

(e) a mixture of (R,R) and (S,S)-2,3-dibromo butanes (50% : 50%) ☐

131. The Markownikoff's rule is best applicable to the reaction between: **[PET (Kerala) 2006]**

(a) $C_2H_4 + HCl$ ☐ (b) $C_3H_6 + Br_2$ ☐

(c) $C_3H_6 + HBr$ ☐ (d) $C_3H_8 + Cl_2$ ☐

(e) $C_2H_4 + I_2$ ☐

132. An alkene on reductive ozonolysis gives two molecules of $CH_2(CHO)_2$. The alkene is: **[PET (Kerala) 2006]**

(a) 2,4-hexadiene ☐

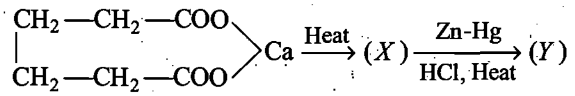
(b) 1,3-cyclohexadiene ☐

(c) 1,4-cyclohexadiene ☐

(d) 1-methyl-1,3-cyclopentadiene ☐

(e) 1,2-dimethyl cyclopropene ☐

133. Identify the product (Y) in the following reaction sequence: **[CET (Karnataka) 2006]**



$$\begin{matrix} CH_2{-}CH_2{-}COO \\ | \\ CH_2{-}CH_2{-}COO \end{matrix} \Big\rangle Ca \xrightarrow{Heat} (X) \xrightarrow[HCl,\ Heat]{Zn\text{-}Hg} (Y)$$

(a) cyclobutane ☐ (b) cyclopentane ☐

(c) pentane ☐ (d) cyclopentanone ☐

134. Which cycloalkane has the lowest heat of combustion per $-CH_2$ group? **[CET (Karnataka) 2006]**

(a) Cyclopropane ☐ (b) Cyclobutane ☐

(c) Cyclopentane ☐ (d) Cyclohexane ☐

135. HBr reacts with $H_2C{=}CH{-}OCH_3$ under anhydrous conditions at room temperature to give: **[AIEEE 2006]**

(a) CH_3CHO and CH_3Br ☐

(b) $BrCH_2CHO$ and CH_3OH ☐

(c) $BrCH_2{-}CH_2{-}OCH_3$ ☐

(d) $H_3C{-}CHBr{-}OCH_3$ ☐

136. Reaction of *trans*-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces: **[AIEEE 2006]**

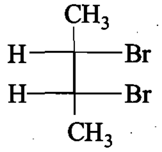
(a) 4-phenyl cyclopentene ☐

(b) 2-phenyl cyclopentene ☐

(c) 1-phenyl cyclopentene ☐

(d) 3-phenyl cyclopentene ☐

137. *Trans*-2-butene + Br_2 gives: **[CET (Gujarat) 2006]**

(a) 

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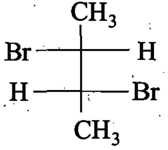
(b) 

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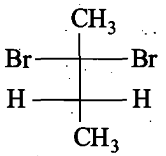
(c) 

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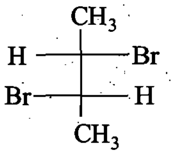
(d) 

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138. Reaction of acetylene and propylene with $HgSO_4$ in presence of H_2SO_4 produces respectively: **[BHU 2006]**

(a) acetone and acetaldehyde ☐

(b) acetaldehyde and acetone ☐

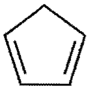
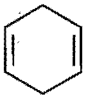
(c) propanaldehyde and acetone ☐

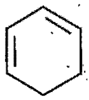
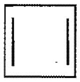
(d) acetone and propanaldehyde ☐

139. Which of the following reagents, when heated with ethyl chloride, forms ethylene? **[EAMCET (Engg.) 2006; AFMC 2008]**

(a) Aqueous KOH ☐ (b) Zn/HCl ☐
(c) Alcoholic KOH ☐ (d) HI ☐

140. Ozonolysis products of an olefin are OHC—CHO and OHC—CH_2—CH_2—CHO, the olefin is: **[DCE 2006; AMU (Engg.) 2007]**

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

141. What is formed when calcium carbide reacts with heavy water? **[DCE 2006]**

(a) C_2D_2 ☐ (b) CaD_2 ☐
(c) CaD_2O ☐ (d) CD_2 ☐

142. A molecule (*X*) has (i) four sigma bonds formed by the overlap of sp^2 and *s* orbitals; (ii) one sigma bond formed by sp^2 and sp^2-orbitals and (iii) one π-bond formed by p_z and p_z orbitals. Which of the following is *X*? **[EAMCET (Engg.) 2006]**

(a) C_2H_6 ☐ (b) C_2H_3Cl ☐
(c) $C_2H_2Cl_2$ ☐ (d) C_2H_4 ☐

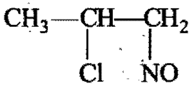
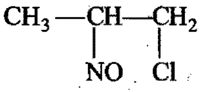
143. $RCH{=}CH_2 \xrightarrow[C_2H_5OH]{Na/NH_3(l)} RCH_2CH_3$

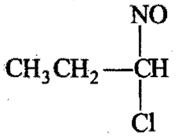
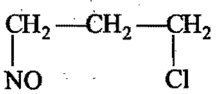
This reaction is called as: **[BVP 2006]**

(a) Fischer-Siper reaction ☐
(b) Clemmensen reduction ☐
(c) Birch reduction ☐
(d) Arndt-Eistert synthesis ☐

144. $CH_3CH{=}CH_2 + NOCl \longrightarrow P$

Identify the adduct: **[IIT 2006]**

(a)  $CH_3-CH(Cl)-CH_2(NO)$ ☐ (b)  $CH_3-CH(NO)-CH_2(Cl)$ ☐

(c)  $CH_3CH_2-CH(NO)(Cl)$ ☐ (d)  $CH_2(NO)-CH_2-CH_2(Cl)$ ☐

145. Identify '*B*' in the following reaction:

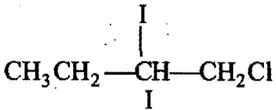
$$H_2C{=}CH_2 + HCl \xrightarrow{\text{Anhyd. }AlCl_3} (A) + 2H \xrightarrow[C_2H_5OH]{Zn\text{-}Cu} (B) + HCl$$

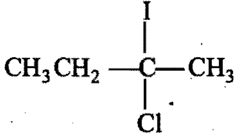
[EAMCET (Engg.) 2007]

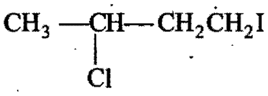
(a) CH_4 ☐ (b) C_2H_6 ☐
(c) C_2H_5Cl ☐ (d) C_2H_5OH ☐

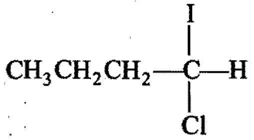
146. Predict the product '*C*' obtained in the following reaction of 1-butyne: **[CBSE (Med.) 2007]**

$$CH_3CH_2C{\equiv}CH + HCl \longrightarrow (B) \xrightarrow{HI} (C)$$

(a)  $CH_3CH_2-CH(I)-CH_2Cl$ ☐

(b)  $CH_3CH_2-C(I)(Cl)-CH_3$ ☐

(c)  $CH_3-CH(Cl)-CH_2CH_2I$ ☐

(d)  $CH_3CH_2CH_2-C(I)(Cl)-H$ ☐

147. $CaC_2 + H_2O \longrightarrow (X) \xrightarrow{O_3/H_2O} HCOOH$, (*X*) is: **[DCE (Engg.) 2007]**

(a) C_2H_4 ☐ (b) C_2H_2 ☐
(c) C_2H_6 ☐ (d) $Ca(OH)_2$ ☐

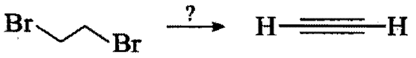
148. In the reactions

$$(B) \xleftarrow[H_2]{\text{Lindlar catalyst}} R-C{\equiv}C-R \xrightarrow{Na/NH_3} (A)$$

(*A*) and (*B*) are geometrical isomers. Then: **[EAMCET (Med.) 2007; DCE 2008]**

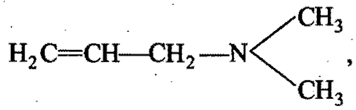
(a) *A* is *cis* and *B* is *trans* ☐ (b) *A* is *trans* and *B* is *cis* ☐
(c) *A* and *B* are *cis* ☐ (d) *A* and *B* are *trans* ☐

149. The reagent(s) for the following conversion, is/are: **[IIT 2007]**



(a) alcoholic KOH ☐
(b) alcoholic KOH followed by $NaNH_2$ ☐
(c) aqueous KOH followed by $NaNH_2$ ☐
(d) Zn/CH_3OH ☐

150. The compound



$H_2C{=}CH-CH_2-N(CH_3)_2$, is an: **[DPMT (Med.) 2007]**

(a) alkyne, 3° amine ☐ (b) alkene, 2° amine ☐
(c) alkene, 3° amine ☐ (d) alkyne, 2° amine ☐

151. Identify the product/(s) in the following reaction:

$$3CH_3CH{=}CH_2 \xrightarrow{BH_3} (X) \xrightarrow{H_2O_2/OH^-} \text{Product(s)} + H_3BO_3$$

[PET (Kerala) 2007]

(a) $CH_3CH_2CH_2OH$ ☐ (b) $CH_3CHOHCH_3$ ☐
(c) CH_3CH_2CHO ☐ (d) $CH_3CH_2OH + CH_3OH$ ☐
(e) $CH_3CHO + CH_3OH$ ☐

152. A hydrocarbon of molecular formula, C_6H_{10} reacts with sodamide and the same on ozonolysis followed by hydrogen

peroxide oxidation gives two molecules of carboxylic acids, one being optically active. Then the hydrocarbon may be:
[PMT (Kerala) 2007; Punjab CET (Engg.) 2008]
(a) 1-hexyne ☐ (b) 2-hexyne ☐
(c) 3-hexyne ☐ (d) 3-methyl-1-pentyne ☐
(e) 3,3-dimethyl-1-butyne ☐

153. The hydrocarbon which does not decolourise alkaline $KMnO_4$ solution and also does not give any precipitate with ammoniacal silver nitrate is: **[AIIMS 2007]**
(a) benzene ☐ (b) acetylene ☐
(c) propyne ☐ (d) 1-butyne ☐

154. Which of the following is the most stable alkene?
[AFMC 2007; Ludhiana CMC (Med.) 2008]
(a) $R_2C{=}CR_2$ ☐ (b) $RCH{=}CHR$ ☐
(c) $RCH{=}CH_2$ ☐ (d) $H_2C{=}CH_2$ ☐

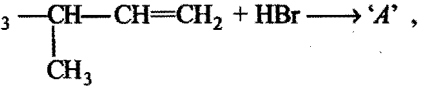
155. Which of the following compounds yields acetone on ozonolysis followed by hydrolysis? **[BHU (Mains) 2008]**
(a) 2-Methyl-2-butene ☐ (b) 3-Methyl-1-butene ☐
(c) Cyclopentane ☐ (d) 2-Methyl-1-butene ☐

156. The angle strain in cyclobutane is:
[CET (Karnataka) 2008]
(a) 19°22′ ☐ (b) 9°44′ ☐
(c) 24°44′ ☐ (d) 29°16′ ☐

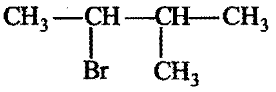
157. A mixture of 1-chlorobutane and 2-chlorobutane when treated with alcoholic KOH gives: **[GGSIP (Engg.) 2008]**
(a) 1-butene ☐
(b) 2-butene ☐
(c) isobutylene ☐
(d) mixture of 1-butene + 2 butene ☐

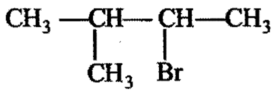
158. Acetylene and HCHO react in presence of copper acetylide catalyst to form: **[DCE 2008; PMET (Med.) 2008]**
(a) 1-butyne-1,4-diol ☐ (b) 2-butyne-1,2-diol ☐
(c) 2-butyne-1,4-diol ☐ (d) none of these ☐

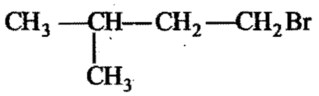
159. The major product formed when a 3,3-dimethyl butan-2-ol is heated with concentrated sulphuric acid is:
[IIT 1996; Punjab CET (Engg.) 2008]
(a) 2,3-dimethyl-2-butene ☐
(b) 2,3-dimethyl-1-butene ☐
(c) 3,3-dimethyl-1-butene ☐
(d) *cis*- and *trans*-isomers of 2,3-dimethyl-1-butene ☐

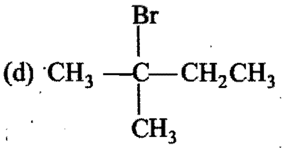
160. 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH{=}CH_2 + HBr \longrightarrow$ 'A',

'A' (predominantly) is: **[CBSE (Med.) 2008]**

(a) 
$CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3$ ☐

(b) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_3$ ☐

(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2-CH_2Br$ ☐

(d) 
$CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2CH_3$ ☐

161. The hydrocarbon which can react with sodium in liquid ammonia is: **[AIEEE 2008]**
(a) $CH_3CH_2C{\equiv}C-CH_2CH_3$ ☐
(b) $CH_3CH{=}CHCH_3$ ☐
(c) $CH_3CH_2C{\equiv}CH$ ☐
(d) $CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3$ ☐

162. Oxidation of 1-butene with hot $KMnO_4$ solution produces:
[UGET (Med.) 2008]
(a) $CH_3CH_2COOH + HCOOH$ ☐
(b) $CH_3CH_2COOH + CO_2$ ☐
(c) $CH_3COOH + CO_2$ ☐
(d) $(CH_3)_2C{=}O + CO_2$ ☐

163. From which one of the following, both ethylene and acetylene could be prepared in a single step reaction?
[PMT (Kerala) 2008]
(a) CH_3CH_2OH ☐ (b) $Br-CH_2-CH_2-Br$ ☐
(c) CH_3CH_2Br ☐ (d) $Br-CH_2-CH_2-OH$ ☐
(e) CH_3COOH ☐

164. A compound 'X' on ozonolysis followed by reduction gives an aldehyde, C_2H_4O and 2-butanone. Compound 'X' is:
[UPSEE (Engg.) 2008]
(a) 3-methyl pent-2-ene ☐ (b) 3-methyl pent-3-ene ☐
(c) 3-methyl hex-3-ene ☐ (d) 3-ethyl pent-3-ene ☐

165. The number of possible alkynes with molecular formula C_5H_8 is: **[UPSEE (Engg.) 2008]**
(a) 6 ☐ (b) 5 ☐
(c) 4 ☐ (d) 3 ☐

166. Hydration of which one of the following yields a ketone?
[CET (J&K) 2009]
(a) Propyne ☐ (b) Ethene ☐
(c) Propene ☐ (d) Ethyne ☐

167. One molecule of alkene 'X' on ozonolysis gave one mole of acetone. The IUPAC name of 'X' is:
[EAMCET (Engg.) 2009]
(a) 2-methyl-1-butene ☐ (b) 2-methyl-2-butene ☐
(c) 2-butene ☐ (d) 1-butene ☐

168. The order of reactivity of the alkenes,
$$\underset{\text{I}}{(CH_3)_2C{=}CH_2},\quad \underset{\text{II}}{CH_3CH{=}CH_2},\quad \underset{\text{III}}{H_2C{=}CH_2}$$
when subjected to acid catalyzed hydration is:
[AMU (PMT) 2009, 10]
(a) I > II > III ☐ (b) I > III > II ☐
(c) III > II > I ☐ (d) II > I > III ☐

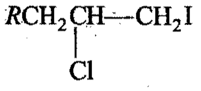
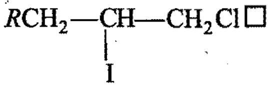
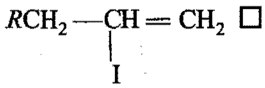
169. Identify the alkyne in the following sequence of reactions:
$$\text{Alkyne} \xrightarrow[\text{Lindlar's catalyst}]{H_2} (A) \xrightarrow{\text{Ozonolysis}} \underset{\text{Only}}{(B)} \xleftarrow[\text{Process}]{\text{Wacker}} H_2C{=}CH_2$$
[EAMCET (Engg.) 2009]

(a) $H_3C—C{\equiv}C—CH_3$ ☐
(b) $H_3C—CH_2—C{\equiv}CH$ ☐
(c) $H_2C{=}CH—C{\equiv}CH$ ☐
(d) $HC{\equiv}C—CH_2—C{\equiv}CH$ ☐

170. In the following reaction,

$$RCH_2CH{=}CH_2 + ICl \longrightarrow (A)$$

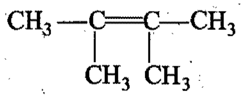
Markownikoff's product (*A*) is: **[AMU (Engg.) 2009]**

(a) 
$RCH_2\underset{\displaystyle Cl}{\underset{|}{C}H}—CH_2I$ ☐
(b) 
$RCH_2—\underset{\displaystyle I}{\underset{|}{C}H}—CH_2Cl$ ☐
(c) 
$RCH_2—\underset{\displaystyle I}{\underset{|}{C}H}{=}CH_2$ ☐
(d) $RCH{=}CHCH_2I$ ☐

171. The addition of HBr to 2-pentene gives: **[JEE (WB) 2009]**

(a) 2-bromopentane only ☐
(b) 3-bromopentane only ☐
(c) 2-bromopentane and 3-bromopentane ☐
(d) 1-bromopentane and 3-bromopentane ☐

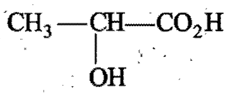
172. Which of the following has lowest boiling point? **[AFMC 2009]**

(a) $CH_3CH_2CH{=}CHCH_3$ ☐
(b) $CH_3CH_2CH_2CH_2CH_3$ ☐
(c) $H_2C{=}CH—CH_2CH{=}CH_2$ ☐
(d) 
$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}{=}\underset{\displaystyle CH_3}{\underset{|}{C}}—CH_3$ ☐

173. One per cent composition of an organic compound A is carbon = 85.71% and hydrogen = 14.29%. Its vapour density is 14. Consider the following reaction sequence:

$$A \xrightarrow{Cl_2/H_2O} B \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) KCN/EtOH}} C\text{ ; Identify C.}$$

[EAMCET (Engg.) 2009]

(a) 
$CH_3—\underset{\displaystyle OH}{\underset{|}{C}H}—CO_2H$ ☐
(b) $HO—CH_2—CH_2—CO_2H$ ☐
(c) $HO—CH_2—CO_2H$ ☐
(d) $CH_3CH_2—CO_2H$ ☐

174. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44*u*. The alkene is : **[AIEEE 2010]**

(a) ethene ☐ (b) propene ☐
(c) 1-butene ☐ (d) 2-butene ☐

175. The decreasing order of acidic character among ethane (I), ethene (II), ethyne (III) and propyne (IV) is : **[PET (Kerala) 2010]**

(a) I > II > III > IV ☐ (b) II > III > I > IV ☐
(c) III > IV > II > I ☐ (d) IV > III > II > I ☐
(e) III > IV > I > II ☐

176. The alkene that will give the same product with HBr in the absence as well as in the presence of peroxide is : **[PET (Kerala) 2010]**

(a) 2-butene ☐ (b) 1-butene ☐
(c) propene ☐ (d) 1-hexene ☐
(e) 2-methylpropene ☐

177. Among the given compounds, one which can be distinguished by $AgNO_3$ is : **[AFMC 2010]**

(a) ethane ☐ (b) ethylene ☐
(c) acetylene ☐ (d) diethyl ether ☐

178. In the following reaction, the product '*R*' is :

$$CaC_2 \xrightarrow{H_2O} P \xrightarrow[\text{tube}]{\text{hot iron}} Q \xrightarrow[AlCl_3]{CH_3Cl} R$$

[AFMC 2010]

(a) benzene ☐ (b) ethylbenzene ☐
(c) toluene ☐ (d) *n*-propyl benzene ☐

179. Name the reagent used to bring about the following transformation; but-2-ene to ethanal: **[AMU (Med.) 2010]**

(a) $K_2Cr_2O_7$ in acidic medium ☐
(b) CrO_2Cl_2/H_3O^+ ☐
(c) PCC ☐
(d) O_3/H_2O-Zn dust ☐

180. The major product formed when 2-bromobutane is treated with alcoholic KOH is : **[PMT (Kerala) 2010]**

(a) 2-butanol ☐ (b) *trans*-2-butene ☐
(c) 1-butanol ☐ (d) 1-butene ☐
(e) iso-butyl alcohol ☐

181. Identify the product in the reaction

$$Ph—C{\equiv}C—Me \xrightarrow{H_3O^+,\ Hg^{2+}} ?$$

[DUMET 2010]

(a) $PhCH_2CH_2CHO$ ☐ (b) $PhCOCH_2CH_3$ ☐
(c) $PhCH_2COCH_3$ ☐ (d) $PhCOCOMe$ ☐

182. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromo alkane and alkyne respectively are : **[IIT 2010]**

(a) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$ ☐
(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C{\equiv}CH$ ☐
(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C{\equiv}CH$ ☐
(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$ ☐

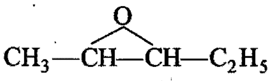
Set II : This set contains the questions with two or more correct answers.

183. Which of the following reagents can be used to distinguish between propene and propyne?

(a) Schiff's reagent ☐ (b) Lucas reagent ☐
(c) Grignard reagent ☐ (d) Ammoniacal $AgNO_3$ ☐

184. The reaction,

$$CH_3—CH{=}CH—C_2H_5 \xrightarrow{C_6H_5COOOH}$$


$$CH_3—\overset{\displaystyle O}{CH—CH}—C_2H_5$$
is called:

(a) hydroxylation ☐
(b) ozonolysis ☐
(c) Prileschaiev's reaction ☐
(d) epoxidation ☐

185. The reagent used for the following reaction is/are:

$$CH_3—CH{=}CH—C_2H_5 \longrightarrow CH_3CHO + C_2H_5CHO$$

(a) O_3 and Zn/steam ☐ (b) Baeyer's reagent ☐
(c) $KMnO_4/H_2SO_4$ ☐ (d) Lemieux reagent ☐

186. Which of the following on reductive ozonolysis give only glyoxal?
(a) Ethylene ☐ (b) Benzene ☐
(c) Toluene ☐ (d) Acetylene ☐

187. Aqueous solution of which of the following compounds is electrolysed, when acetylene gas is obtained ?
(a) Sodium fumerate ☐ (b) Sodium maleate ☐
(c) Sodium acetate ☐ (d) Calcium carbide ☐

188. Anti-Markownikoff's addition of HBr is/are observed in :
(a) propene ☐ (b) but-1-ene ☐
(c) but-2-ene ☐ (d) pent-3-ene ☐

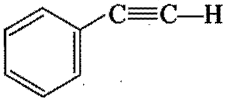
189. What product(s) results when two moles of hydrogen chloride react with 4-methyl-2-pentyne?
(a) 3,3-Dichloro-4-methyl pentane ☐
(b) 2-Chloro-4-methyl pentene ☐
(c) 2,2-Dichloro-4-methyl pentane ☐
(d) 3-Chloro-4-methyl pentene ☐

190. Which is/are correct statements about oxymercuration demercuration?
(a) The rearrangement takes place ☐
(b) In the first step $(OAc)_2Hg$ and H_2O are added to the double bond ☐
(c) In the second step $NaBH_4$ reduces—Hg $(OAc)_2$ group to hydrogen ☐
(d) The net reaction is addition of water according to Markownikoff's rule ☐

191. Hexa-2,4-diene on ozonolysis by using O_3/CCl_4 followed by Zn/H_2O gives :
(a) acetaldehyde ☐ (b) glyoxal ☐
(c) formaldehyde ☐ (d) propanaldehyde ☐

192. Alkenes can be prepared by:
(a) dehydrohalogenation of alkyl halide ☐
(b) Sabatier-Sanderen's reduction of alkynes ☐
(c) dehydration of alcohols with conc. H_2SO_4 at 443K ☐
(d) treatment of 3° alkyl halide at 573K ☐

193. The compound(s) which will give propylene on dehydration with conc. H_2SO_4 at 440 K is/are :
(a) isobutyl alcohol ☐ (b) *n*-propyl alcohol ☐
(c) isopropyl alcohol ☐ (d) *n*-butyl alcohol ☐

194. Which of the following alkynes show acidic character?
(a) $H—C{\equiv}C—H$ ☐ (b) $CH_3—C{\equiv}C—H$ ☐
(c)  ☐ (d) $CH_3—C{\equiv}C—CH_3$ ☐

195. Presence of unsaturation in organic compounds can be tested with:
(a) Br_2 water ☐ (b) Baeyer's reagent ☐
(c) Tollens' reagent ☐ (d) Grignard reagent ☐

ASSERTION-REASON TYPE QUESTIONS

The questions given below consist **Assertion (A)** and **Reason (R)**. Use the following keys to select the appropriate answer :
(a) If both (A) and (R) are correct and (R) is correct explanation of (A)
(b) If both (A) and (R) are correct but (R) is not correct explanation of (A)
(c) If (A) is correct but (R) is incorrect
(d) If (A) is incorrect but (R) is correct
(e) Both (A) and (R) are incorrect.

1. (A) Addition of HBr to 1-butene gives two optical isomers.
(R) The product contains one asymmetric carbon.

2. (A) Dimethyl sulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds.
(R) It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. **[IIT (S) 2001]**

3. (A) Addition of HCl to propene in presence of peroxide gives 1-chloropropane.
(R) The reaction occurs by carbonium ion intermediate.

4. (A) Addition of HBr to 1-butene in presence of peroxide produces 1-bromobutane.
(R) It involves the formation of primary radical. **[IIT (S) 2000]**

5. (A) Reduction of but-2-yne by Na/liq. NH_3 gives '*trans*' but-2-ene.
(R) It is an example of 'anti' addition.

6. (A) Propene is more reactive than ethene towards electrophilic addition reactions.
(R) Electron density of double bond increases due to hyperconjugation of methyl group.

7. (A) 1-chlorobutane on heating with alcoholic KOH undergoes dehydrohalogenation to yield but-1-ene.
(R) It is elimination reaction involving carbonium ion intermediate.

8. (A) Moist ethylene can be dried by passing it through concentrated H_2SO_4.
(R) Addition of sulphuric acid takes place on alkene.

9. (A) Acidity of C—H bond lies in following sequence:
$$HC{\equiv}CH > CH_2{=}CH_2 > CH_3—CH_3$$
(R) Percentage character of '*s*' orbital in these compounds lie in following sequence.
$$H—C{\equiv}CH > CH_2{=}CH_2 > CH_3—CH_3$$

10. (A) Addition of bromine to *trans*-but-2-ene yields meso-2,3-dibromo butane.
(R) Bromine addition to an alkene is an electrophilic addition. **[IIT (S) 2001]**

11. (A) 1,3-Butadiene is the monomer for natural rubber.
(R) Natural rubber is formed through anionic addition polymerization. **[AIIMS 2006]**

12. (A) Addition of HBr on 2-butene gives two isomeric products.
(R) Addition of HBr on 2-butene follows Markownikoff's rule. [AIIMS 2006]

13. (A) C—H bond in ethyne is shorter than C—H bonds in ethene.
(R) Carbon atom in ethene is *sp* hybridised while it is sp^2 in ethyne. [AIIMS 2007]

ANSWERS

OBJECTIVE QUESTIONS

1. (d)	2. (d)	3. (c)	4. (a)	5. (a)	6. (d)	7. (a)	8. (d)	9. (a)	10. (c)
11. (a)	12. (c)	13. (c)	14. (b)	15. (c)	16. (a)	17. (c)	18. (d)	19. (c)	20. (d)
21. (b)	22. (b)	23. (b)	24. (c)	25. (c)	26. (b)	27. (a)	28. (a)	29. (a)	30. (a)
31. (b)	32. (b)	33. (d)	34. (d)	35. (b)	36. (c)	37. (d)	38. (c)	39. (b)	40. (d)
41. (b)	42. (c)	43. (a)	44. (a)	45. (c)	46. (d)	47. (a)	48. (d)	49. (c)	50. (d)
51. (c)	52. (b)	53. (a)	54. (d)	55. (d)	56. (b)	57. (c)	58. (a)	59. (a)	60. (c)
61. (d)	62. (b)	63. (c)	64. (a)	65. (b)	66. (b)	67. (d)	68. (a)	69. (b)	70. (c)
71. (d)	72. (c)	73. (c)	74. (b)	75. (d)	76. (a)	77. (d)	78. (c)	79. (d)	80. (b)
81. (c)	82. (a)	83. (d)	84. (d)	85. (b)	86. (a)	87. (c)	88. (c)	89. (b)	90. (d)
91. (b)	92. (c)	93. (b)	94. (d)	95. (a)	96. (c)	97. (c)	98. (d)	99. (d)	100. (d)
101. (c)	102. (b)	103. (a)	104. (b)	105. (a)	106. (b)	107. (c)	108. (d)	109. (a)	110. (d)
111. (d)	112. (d)	113. (c)	114. (d)	115. (a)	116. (c)	117. (c)	118. (d)	119. (b)	120. (a)
121. (c)	122. (b)	123. (a)	124. (b)	125. (b)	126. (a)	127. (b)	128. (a)	129. (c)	130. (e)
131. (c)	132. (c)	133. (b)	134. (d)	135. (d)	136. (d)	137. (a)	138. (b)	139. (c)	140. (c)
141. (a)	142. (d)	143. (c)	144. (a)	145. (b)	146. (b)	147. (b)	148. (b)	149. (b)	150. (c)
151. (a)	152. (d)	153. (a)	154. (a)	155. (a)	156. (b)	157. (d)	158. (c)	159. (a)	160. (d)
161. (c)	162. (b)	163. (b)	164. (a)	165. (d)	166. (a)	167. (b)	168. (c)	169. (a)	170. (a)
171. (c)	172. (d)	173. (b)	174. (d)	175. (c)	176. (a)	177. (c)	178. (c)	179. (d)	180. (b)
181. (b)	182. (d)	183. (c,d)	184. (c,d)	185. (a,d)	186. (b,d)	187. (a,d)	188. (a,b,d)	189. (a,c)	190. (b,c,d)
191. (a,b)	192. (a,c,d)	193. (b,c)	194. (a,b,c)	195. (a,b)					

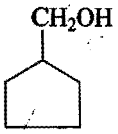
ASSERTION-REASON TYPE QUESTIONS

1. (a)	2. (a)	3. (d)	4. (c)	5. (a)	6. (a)	7. (a)	8. (d)	9. (a)	10. (b)
11. (e)	12. (e)	13. (c)							

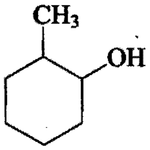
BRAIN STORMING PROBLEMS

1. Write down the products when following compounds are dehydrated :

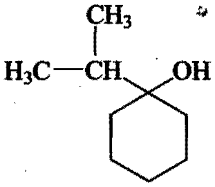
(a)



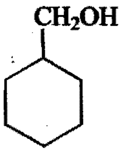
(b)



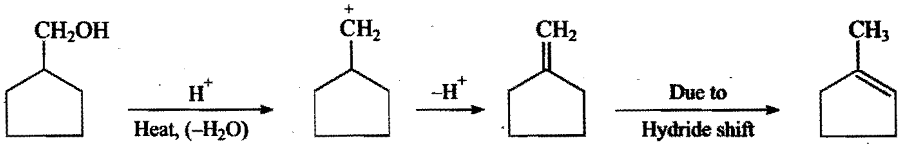
(c)



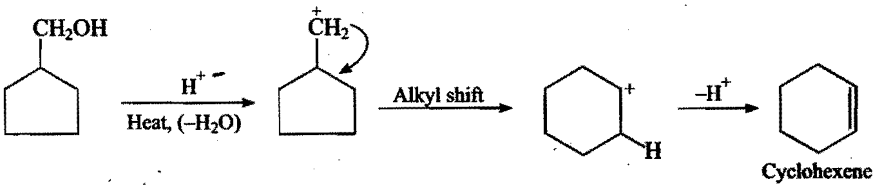
(d)



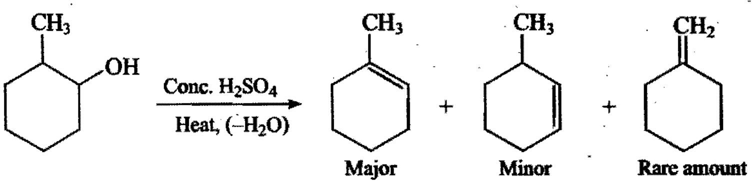
[Hint: (a) (i)



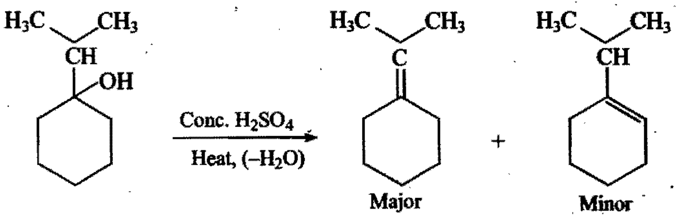
(ii)



(b)

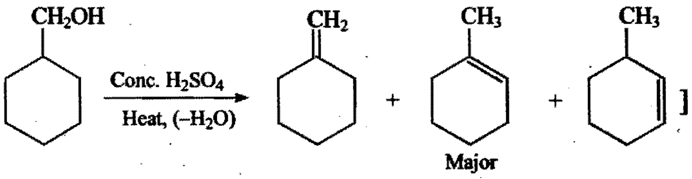


(c)



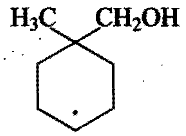
(These products are according to Saytzeff 's rule)

(d)

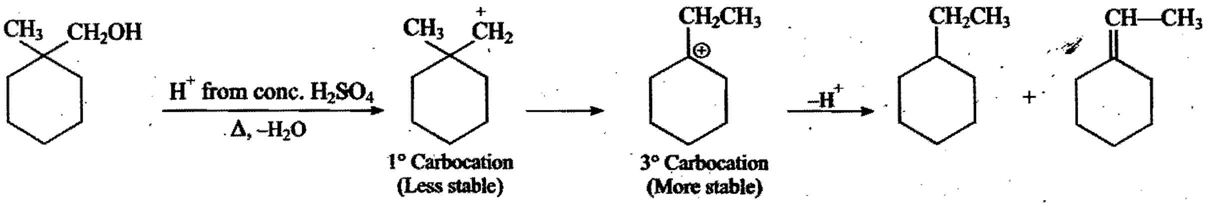


]

2. Write down dehydration products of the following compound:

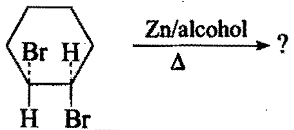


[Hint:

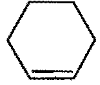


]

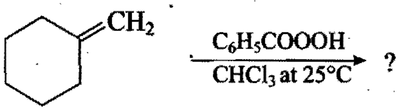
3. Complete the following reactions:

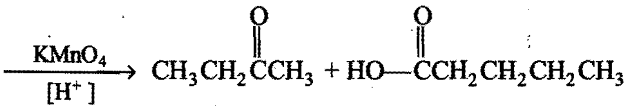
(i) 

(ii) $(CH_3)_3C{-}Cl \xrightarrow[\Delta]{CH_3COO^-} ?$

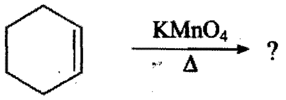
[Ans. (i)  (ii) $(CH_3)_2C{=}CH_2$]

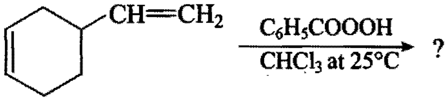
4. Complete the following reactions:

(i) 

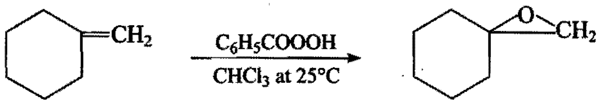
(ii) 

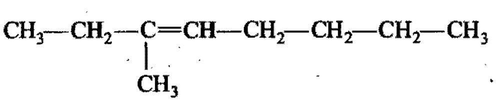
$? \xrightarrow[[H^+]]{KMnO_4} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3 + HO{-}\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$

(iii) 

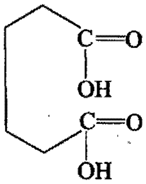
(iv) 

[Hint : (i) Formation of epoxide takes place.

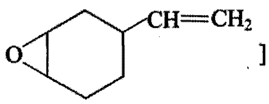


(ii) 

$CH_3{-}CH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

(iii) 

(iv) Since, C=C bond in ring is more substituted than that in open chain, epoxide will be formed at the unsaturation of ring.

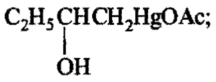
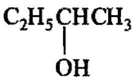


]

5. Give the structures of (A) and (B) in the following reaction:

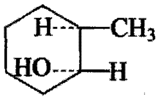
$$C_2H_5{-}CH{=}CH_2 \xrightarrow[THF/H_2O]{Hg(OAc)_2} (A) \xrightarrow{NaBH_4/NaOH} (B)$$

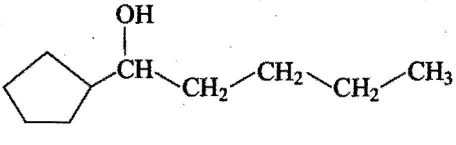
According to which rule, above addition takes place?

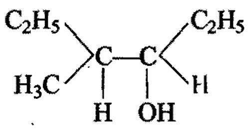
[Hint : (A) ⟶  $C_2H_5\underset{OH}{\underset{|}{C}}HCH_2HgOAc$; ($B$) ⟶  $C_2H_5\underset{OH}{\underset{|}{C}}HCH_3$

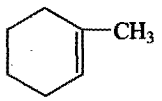
The reaction is according to Markownikoff's rule and is better acid catalyzed hydration as it avoids rearrangement.]

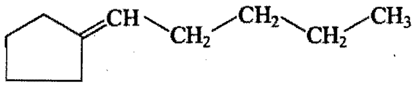
6. Give the structures of compounds which give following products on hydroboration-oxidation:

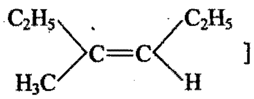
(i) 

(ii) 

(iii) 

[Hint: (i) 

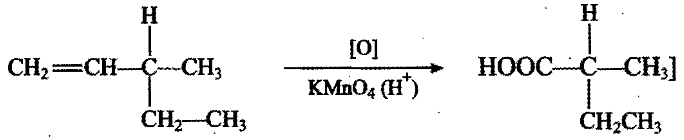
(ii) 

(iii) 

]

7. An unsaturated compound C_6H_{12} (A) decolourises Br_2 water and on oxidation by acidified $KMnO_4$ gives optically active carboxylic acid C_4H_9COOH (B). Give the structure of (A) and (B).

[Hint : Compound is unsaturated because it is decolourising Br_2 water. On oxidation it gives a carboxylic acid with one carbon atom less than alkene; it shows that compound is terminal alkene. Thus, structure of terminal alkene with chiral carbon can be given as:



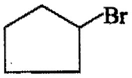
$$CH_2{=}CH-\overset{H}{\underset{CH_2-CH_3}{C}}-CH_3 \xrightarrow[KMnO_4\,(H^+)]{[O]} HOOC-\overset{H}{\underset{CH_2CH_3}{C}}-CH_3]$$

(*A*) Optically active (*B*)

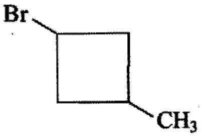
8. A compound C_5H_9Br (*A*) does not decolourise Baeyer's reagent or Br_2 water. (*A*) on treatment with alcoholic KOH forms (*B*) C_5H_8 which reacts with Baeyer's reagent and Br_2 water. Ozonolysis of (*B*) forms (*C*) $C_5H_8O_2$. Identify (*A*), (*B*), (*C*) and explain reactions.

[**Hint :** C_5H_9Br is not decolourising Baeyer's reagent or Br_2 water hence, it should be cyclic compound. Possible structure for (*A*) can be given as:

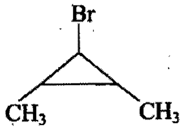
(i)



(ii)

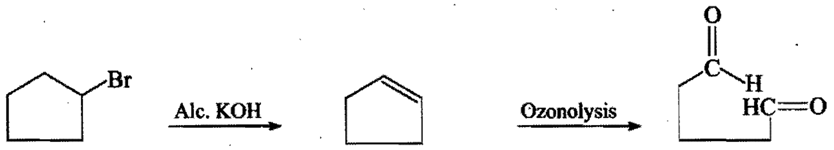


(iii)



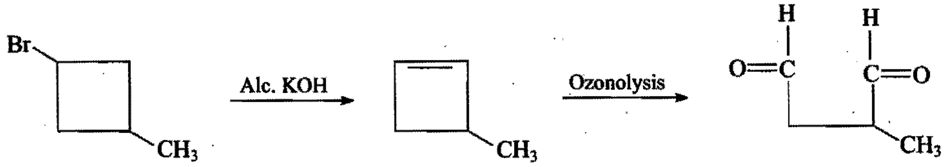
Reactions involved may be given for above compounds as:

(i)



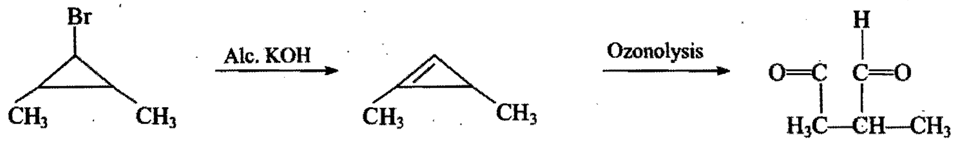
(*A*) (*B*) (*C*)

(ii)



(*A*) (*B*) (*C*)

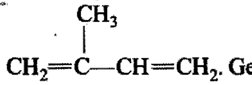
(iii)



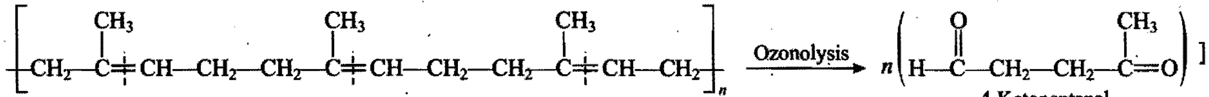
(*A*) (*B*) (*C*)

9. Give the structure of polyisoprene (natural rubber). Write down the ozonolysis of polyisoprene.

[**Ans.** Monomer of natural rubber is isoprene



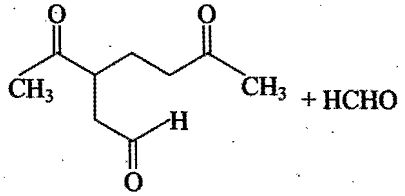
$CH_2{=}\overset{CH_3}{C}-CH{=}CH_2$. General structure of polyisoprene will be :



$$\left[-CH_2-\overset{CH_3}{C}{=}CH-CH_2-CH_2-\overset{CH_3}{C}{=}CH-CH_2-CH_2-\overset{CH_3}{C}{=}CH-CH_2-\right]_n \xrightarrow{\text{Ozonolysis}} n\left(H-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{CH_3}{C}{=}O\right)\ ]$$

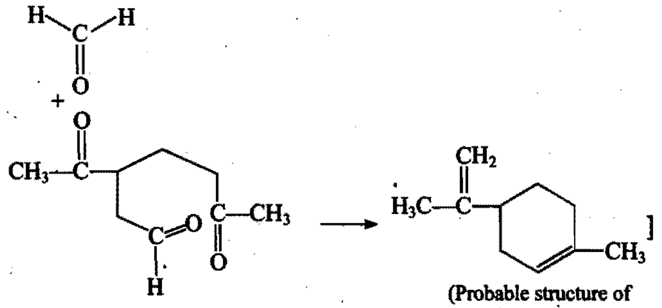
Natural rubber 4-Ketopentanal

10. Limonene ($C_{10}H_{16}$) is a naturally occurring hydrocarbon. It absorbs 2 molecules of hydrogen for each molecule during hydrogenation. On ozonolysis followed by zinc dust and steam hydrolysis, it gives one mole of formaldehyde and one mole of tricarbonyl compound of following structure.



Give probable structure of limonene if it has a six membered ring.

[**Hint :** Compound has a six membered ring. Therefore, its structure will be cyclic unsaturated. There will be two double bonds in the limonene because it absorbs two molecules of H_2.



(Ozonolysis products)

(Probable structure of limonene)

11. Hydrocarbon (A) $(C = 87.2\%)$ on hydrogenation forms (B) $(C = 84.1\%)$. Ozonolysis of (A) forms acetic acid, acetone and pyruvic acid $\left(CH_3-\overset{\overset{O}{\|}}{C}-COOH\right)$. What are (A) and (B) ?

[**Hint :** Percentage composition shows that (A) and (B) has empirical formula (A) C_4H_7 and (B) C_4H_9.

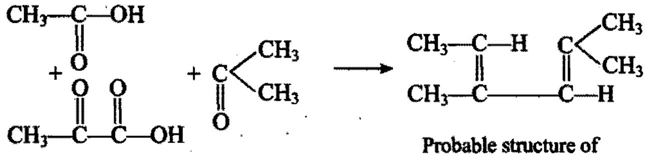
$$\text{Compound } (A) \xrightarrow{\text{Ozonolysis}} CH_3-\overset{\overset{O}{\|}}{C}-OH + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$$

Thus, compound (A) should have eight carbons.

$\therefore$ Molecular formula of (A) will be C_8H_{14} and that of (B) will be C_8H_{18}.

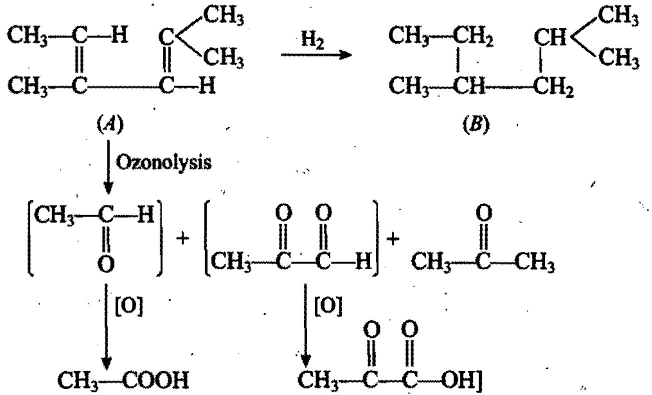
Degree of unsaturation in compound $(A) = \frac{2n_1 - n_2 + 2}{2} = \frac{2 \times 8 - 14 + 2}{2} = 2$

Thus, compound (A) should have two double bonds. On the basis of ozonolysis products structure of (A) can be guessed as,

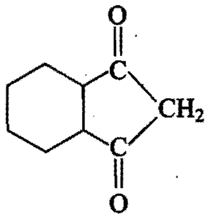


Probable structure of (A)

Reactions may be summarized as:

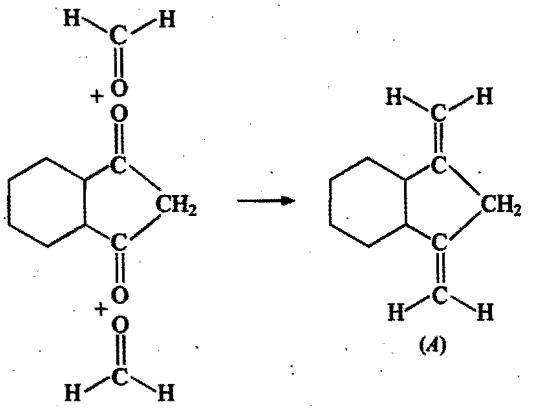


12. $C_{11}H_{16}$ (A) reacts with two equivalent of H_2 and on reductive ozonolysis gives two equivalents formaldehyde and (B) of following structure:

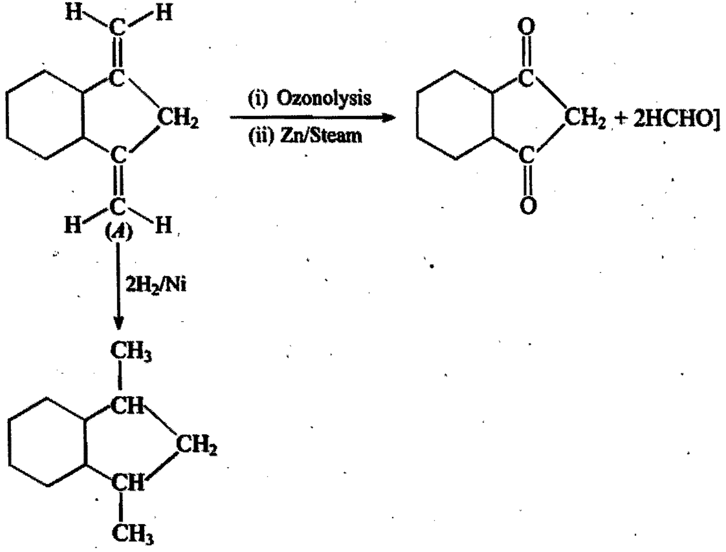


Identify structure of (A).

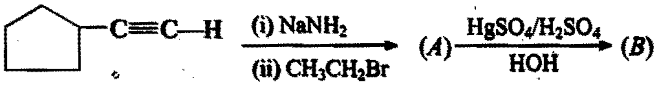
[**Hint :** Structure of compound (A) can be guessed as,



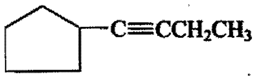
Involved reaction may be given as,



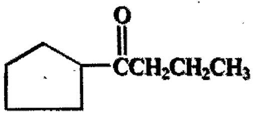
13. Complete the following reaction :



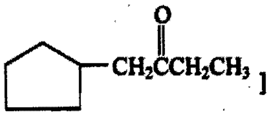
[Hint : (*A*)



(*B*)

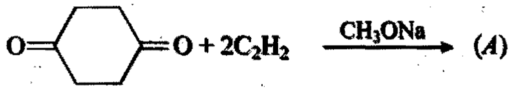


or

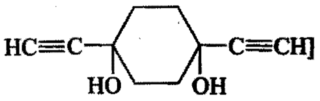


]

14. Identify the product in the following reaction:



[Hint : (*A*)



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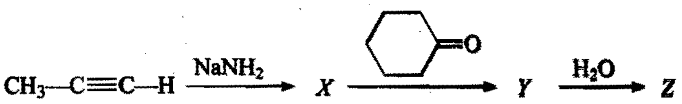
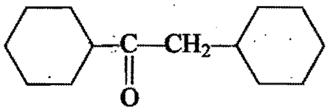
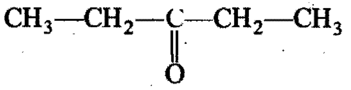
15. (a) Identify the unknown products among the following:



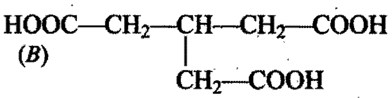
(b) Give the formula of alkynes which gives following carbonyl compounds on hydration :

(i) 

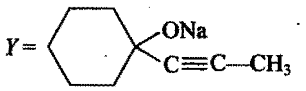
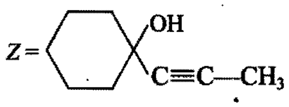
(ii) 

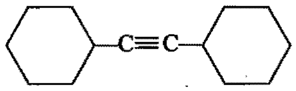
$CH_3—CH_2—\underset{\underset{O}{\|}}{C}—CH_2—CH_3$

(c) Deduce the structural formula of a compound, $C_{10}H_{10}$ (*A*) that gives (*B*) on oxidation :



$$\underset{(B)}{HOOC—CH_2—\underset{\underset{CH_2—COOH}{|}}{CH}—CH_2—COOH}$$

[Hint : (a) $X = CH_3—C{\equiv}\bar{C}Na^+$, $Y =$  , $Z =$ 

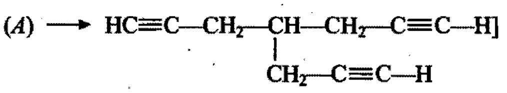
(b) (i) 

(ii) $CH_3—C{\equiv}C—CH_2—CH_3$

(c) Degree of unsaturation $= \dfrac{2n_1 - n_2 + 2}{2} = \dfrac{20 - 10 + 2}{2} = 6$

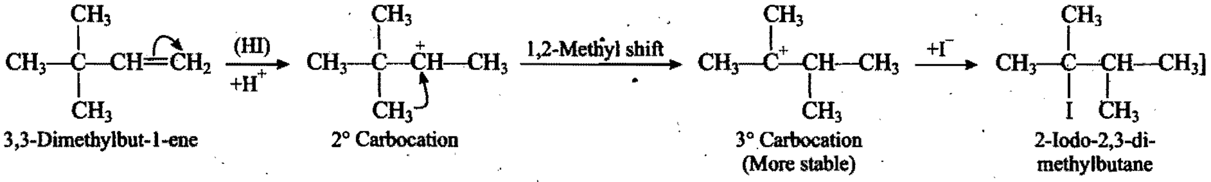
Thus, there may be 6π bonds. Presence of three carboxylic acids confirm that there are three triple bonds in '*A*'.

∴

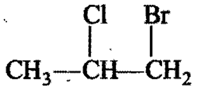


$$(A) \longrightarrow HC{\equiv}C—CH_2—\underset{\underset{CH_2—C{\equiv}C—H}{|}}{CH}—CH_2—C{\equiv}C—H]$$

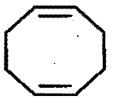
16. Explain why the addition of HI to 3,3-dimethylbut-1-ene gives 2-iodo-2,3-dimethylbutane as the major product and not the 1-iodo-3,3-dimethyl-butane. **[Roorkee 2001]**

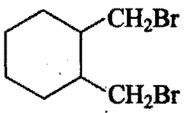
[Hint: 

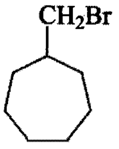
17. In which case the product formed is in accordance of anti Markownikoff's rule?
(a) $CH_3—CH{=}CH_2 \xrightarrow{\text{HCl Peroxide}}$ ☐
(b) $CH_3—CH{=}CH—CH_3 \xrightarrow[\text{Peroxide}]{\text{HBr}}$ ☐
(c) $(CH_3)_2C{=}CH_2 \xrightarrow{\text{NOCl}}$ ☐
(d) $(CH_3)_2C{=}CH_2 \xrightarrow{\text{HBr/Peroxide}}$ ☐

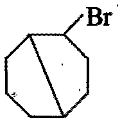
18. In which of the following cases, the correct product is not written?
(a) $CH_3—CH{=}CH_2 \xrightarrow{\text{BrCl}}$  $CH_3—\overset{\overset{Cl}{|}}{CH}—\overset{\overset{Br}{|}}{CH_2}$ ☐
(b) $(CH_3)_2CH{=}CH_2 \xrightarrow[H_2O]{Cl_2} (CH_3)_2CH(OH)CH_2Cl$ ☐
(c) $(CH_3)_3C—CH{=}CH_2 \xrightarrow{\text{Hydroboration}} (CH_3)_3C—CH_2CH_2OH$ ☐
(d) $CCl_3CH{=}CH_2 \xrightarrow{\text{HCl}} CCl_3—CH_2—CH_2—Cl$ ☐

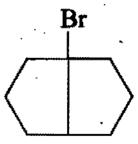
19. *Cis*-2-butene on reaction with Baeyer's reagent gives:
(a) meso-geminal diol ☐ (b) racemic-vicinal diol ☐
(c) meso-vicinal diol ☐ (d) none of these ☐

20.  , on reaction with HBr and peroxide gives:

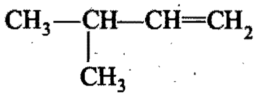
(a)  ☐

(b)  ☐

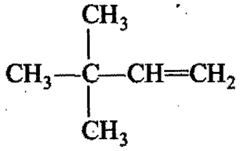
(c)  ☐

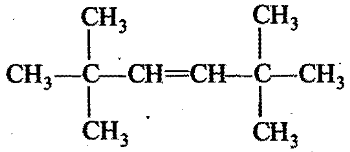
(d)  ☐

21. A hydrocarbon has the formula C_3H_4. To find out whether it contains two double bond or a triple bond, the following test is preferred:
(a) passed through ammoniacal $AgNO_3$ ☐
(b) treated with Fehling's solution ☐
(c) treated with Baeyer's reagent ☐
(d) treated with Br_2 water ☐

22. Which among the following alkenes will be oxidised by SeO_2 ?
(a) $CH_2{=}CH_2$ ☐
(b)  ☐

$CH_3—\underset{\underset{CH_3}{|}}{CH}—CH{=}CH_2$

(c) 
$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH{=}CH_2$ ☐

(d) 
$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH{=}CH-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$ ☐

[Hint : Only $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH{=}CH_2$ has hydrogen at α-carbon.]

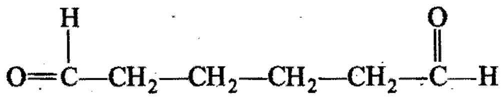
23. Match List-I with List-II and select the correct answer from the codes given below the lists:

List-I Reaction	List-II Product
A. $CH_3CH{=}CH_2 \xrightarrow[\text{(ii) HCOOH}]{\text{(i) } BH_3\text{-THF}}$	1. *n*-propylamine
B. $CH_3CH{=}CH_2 \xrightarrow[\text{(ii) } AgNO_3]{\text{(i) } BH_3\text{-THF}}$	2. *n*-propylbromide
C. $CH_3CH{=}CH_2 \xrightarrow[\text{(ii) } NH_4Cl\text{, HOH}]{\text{(i) } BH_3\text{-THF}}$	3. *n*-hexane
D. $CH_3CH{=}CH_2 \xrightarrow[\text{(ii) } Br_2]{\text{(i) } BH_3\text{-THF}}$	4. *n*-propane

Codes:

	A	B	C	D
(a)	1	2	3	4
(b)	2	1	4	3
(c)	3	4	2	1
(d)	4	3	1	2

24. A hydrocarbon of formula C_6H_{10} absorbs only one molecule of H_2 upon catalytic hydrogenation. Upon ozonolysis, the hydrocarbon yields a compound of the following structure,


$O{=}\overset{H}{\overset{|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$

The hydrocarbon is:

(a) cyclohexane ☐ (b) cyclohexyne ☐

(c) cyclohexene ☐ (d) cyclobutane ☐

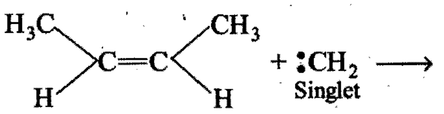
25. Match List-I with List-II and select the correct answer using the codes given below the lists:

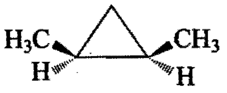
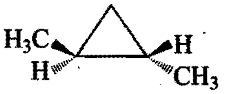
List-I Reaction	List-II Reagent
A. $CH_3-CH{=}CH_2 \longrightarrow CH_3-CHBr-CH_3$	1. HBr
B. $CH_3-CH{=}CH_2 \longrightarrow CH_3-CH_2-CH_2Br$	2. NBS
C. $CH_3-CH{=}CH_2 \longrightarrow BrCH_2-CH{=}CH_2$	3. Br_2/CCl_4
D. $CH_3-CH{=}CH_2 \longrightarrow CH_3-CHBr-CH_2Br$	4. HBr (peroxide)

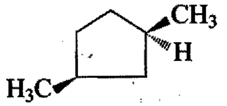
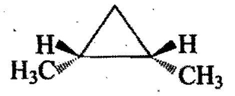
Codes:

	A	B	C	D
(a)	2	1	3	4
(b)	3	2	4	1
(c)	1	4	2	3
(d)	4	3	1	2

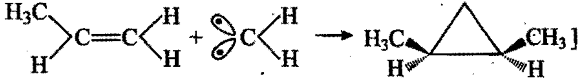
26. The major product formed in the following reaction is:



(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

[Hint : The reaction may be given as:


]

27. Alkyne (A) on catalytic hydration gives only one ketone while alkyne (B) gives only aldehyde. (A) and (B) may be:

(a) pent-2-yne, acetylene ☐ (b) oct-3-yne, propyne ☐

(c) pent-2-yne, but-1-yne ☐ (d) but-1-yne, propyne ☐

28. The catalyst used in the manufacture of polythene by Zeigler-Natta method is:

(a) $TiCl_4, (C_6H_5)_3Al$ ☐ (b) $TiCl_4, (CH_3)_3Al$ ☐

(c) TiO_2 ☐ (d) Titanium metal ☐

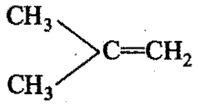
29. Intermediate in hydration of alkene is:

(a) free radical ☐ (b) carbene ☐

(c) carbonium ion ☐ (d) carbanion ☐

30. Order of reactivity of given four alkenes for hydrogenation reaction will be:

I. $CH_2{=}CH_2$ II. $CH_3-CH{=}CH_2$

III.  IV. $CH_3-CH{=}CH-CH_3$

(a) III > IV > II > I ☐ (b) I > II > IV > III ☐

(c) I > II > III > IV ☐ (d) II > I > III > IV ☐

31. In the given reaction,

$$CH_3-C{\equiv}C-CH_3 \xrightarrow{Na/NH_3(\text{liq.})} X$$

Compound (X) will be:

(a) butane ☐ (b) *trans*-2-butene ☐

(c) *cis*-2-butene ☐ (d) 1-butene ☐

32. 3,5-dimethyl cyclopentene, on ozonolysis, yields:

(a) only an aldehyde ☐

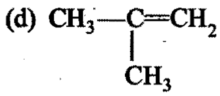
(b) only a ketone ☐

(c) an aldehyde and a ketone ☐

(d) a dialdehyde ☐

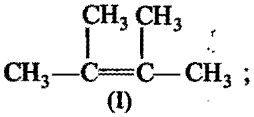
33. A compound C_4H_8 decolourizes a $KMnO_4$ solution. How many structures are possible for this compound?
(a) 3 ☐ (b) 4 ☐
(c) 2 ☐ (d) 5 ☐

34. An organic compound decolourises Br_2 in CCl_4 and can be reduced catalytically. Also, it gives a precipitate with ammoniacal cuprous chloride. The compound will be:
(a) $CH_3-CH=CH-CH_3$ ☐
(b) $CH_3CH_2C\equiv CH$ ☐
(c) $CH_3-CH=CH_2$ ☐
(d) ☐



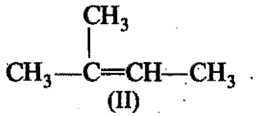
$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$

35. The relative stability of the compounds,



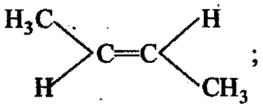
$CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3$;

(I)



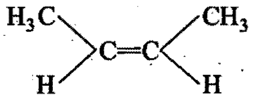
$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3$

(II)



;

(III)



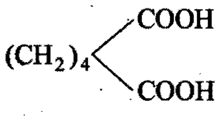
(IV)

$CH_3-CH=CH_2$; $H_2C=CH_2$
(V) (VI)

is of the order:
(a) I > II > III > IV > V > VI ☐
(b) VI > V > IV > III > II > I ☐
(c) I > III > V > II > IV > VI ☐
(d) II > I > IV > III > V > VI ☐

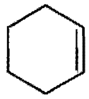
36. Alkenes can be converted to carbonyl compound in one step by:
(a) Wacker process ☐
(b) Oxymercuration-demercuration ☐
(c) Hydroboration oxidation ☐
(d) Wittig reaction ☐

37. Unknown compound (A) on oxidation with hot basic $KMnO_4$ gives only one compound whose structure is given below,

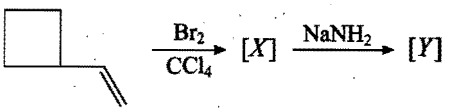


$(CH_2)_4\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array}$

Compound (A) will be:
(a) $CH_3-C\equiv C-(CH_2)_4-C\equiv C-CH_3$ ☐
(b) $CH_3-CH=CH-(CH_2)_4-CH=CH_2$ ☐
(c) $CH_3-CH=CH-(CH_2)_4-CH=CH-CH_3$ ☐
(d) ☐



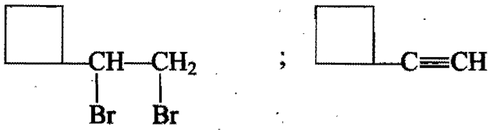
38.



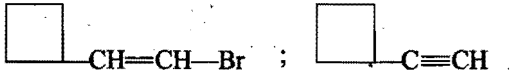
$\xrightarrow[CCl_4]{Br_2} [X] \xrightarrow{NaNH_2} [Y]$

Compounds [X] and [Y] are respectively:

(a) ☐

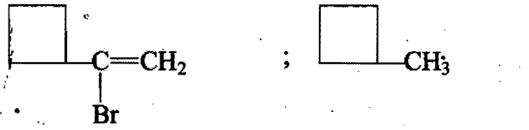


(b) ☐



(c) ☐

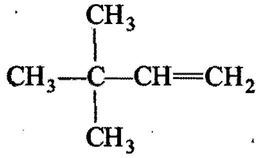
(d) ☐



39. The number of structural and configurational isomers of a bromocompound, C_5H_9Br formed on addition of HBr to 2-pentyne respectively are:
(a) 4 and 3 ☐ (b) 2 and 4 ☐
(c) 4 and 2 ☐ (d) 2 and 7 ☐

40. $H_2C=CH-C\equiv CH$ on reaction with one mole DBr gives:
(a) $CH_2=CH-CBr=CHD$ ☐
(b) $CH_2(Br)-CHDC\equiv CH$ ☐
(c) $DCH_2-CHBrC\equiv CH$ ☐
(d) $CH_2=CH-CD=CHBr$ ☐

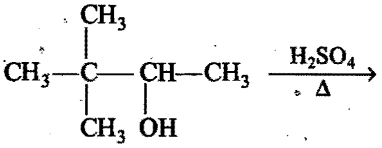
41. Which of the following reactions are expected to give



$CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH=CH_2$

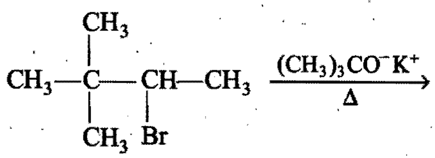
in yields of more than 50%?

(a) ☐



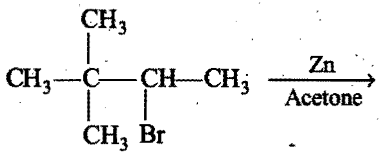
$CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[\Delta]{H_2SO_4}$

(b) ☐



$CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[\Delta]{(CH_3)_3CO^-K^+}$

(c) ☐



$CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[Acetone]{Zn}$

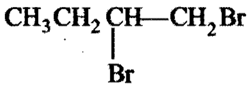
(d) None of the above ☐

42. Addition polymerisation can be brought about by:
(a) free radicals ☐ (b) cations ☐
(c) anions ☐ (d) none of these ☐

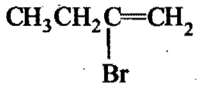
43. Which of the following contains acidic hydrogen?
(a) Ethene ☐ (b) Ethane ☐
(c) Ethyne ☐ (d) But-1-yne ☐

44. Which are the possible intermediates in the following reaction?

$$CH_3CH_2CH{=}CH_2 \xrightarrow[2.\ NaNH_2\ (110\text{–}160°C)]{1.\ Br_2/CCl_4} CH_3CH_2C{\equiv}CH$$

(a) 
$CH_3CH_2CH(Br){-}CH_2Br$ ☐

(b) $CH_3CH_2CH{=}CHBr$ ☐

(c) 
$CH_3CH_2C(Br){=}CH_2$ ☐

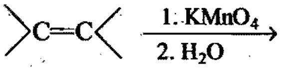
(d) None of the above ☐

45. Which of the following statements are not correct for alkanes?
(a) All C—H and C—C bonds have a length of 1.112 Å and 1.54 Å respectively ☐
(b) All bond angles are tetrahedral, having a value of 109.5° ☐
(c) The C—C chain is linear and not zig-zag ☐
(d) All alkanes exhibit isomerism ☐

46. What are the products obtained by the ozonolysis of $RCH{=}CR_1R_2$?
(a) $RCHO$ ☐ (b) R_1R_2CO ☐
(c) R_2CO ☐ (d) $RCH_2CH_2R_1$ ☐

47. Which of the following will reach with sodium metal?
(a) Ethyne ☐ (b) But-1-yne ☐
(c) But-2-yne ☐ (d) Ethane ☐

48. Which of the following will give *cis*-diols?

(a) 

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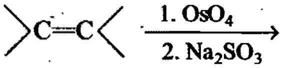
(b) 

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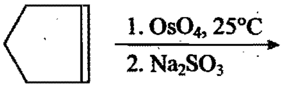
(c) 

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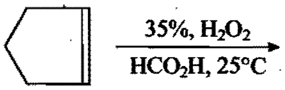
(d) 

☐

49. Ionic addition of bromine to *cis*-2-butene yields:
(a) meso-2,3-dibromobutane ☐
(b) racemic-2,3-dibromobutane ☐
(c) *d*-2,3-dibromobutane ☐
(d) *l*-2,3-dibromobutane ☐

50. The exacts representation(s) of molecular formula C_6H_8 containing *sp*, sp^2 and sp^3-hybrid-states of carbon atoms is/are:
(a) $H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$ ☐
(b) $H_2C{=}CH{-}C{\equiv}C{-}CH_2{-}CH_3$ ☐
(c) $CH_3{-}CH{=}C{=}CH{-}CH{=}CH_2$ ☐
(d) $HC{\equiv}C{-}CH_2{-}CH_2{-}CH{=}CH_2$ ☐

ANSWERS : BRAIN STORMING PROBLEMS

17.	(d)	**18.**	(c)	**19.**	(c)	**20.**	(c)	**21.**	(a)	**22.**	(b)	**23.**	(d)	**24.**	(c)	**25.**	(c)	**26.**	(a)
27.	(a)	**28.**	(b)	**29.**	(c)	**30.**	(b)	**31.**	(b)	**32.**	(d)	**33.**	(b)	**34.**	(b)	**35.**	(a)	**36.**	(a)
37.	(d)	**38.**	(a)	**39.**	(b)	**40.**	(a)	**41.**	(b,c)	**42.**	(a,b,c)	**43.**	(c,d)	**44.**	(a,b,c)	**45.**	(c,d)	**46.**	(a,b)
47.	(a,b)	**48.**	(a,b,c)	**49.**	(b)	**50.**	(b,c,d)												

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

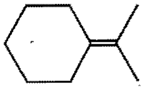
Hydrogenation of alkenes and alkynes takes place in presence of certain catalysts. In Sabatier Senderen's reaction, the addition of hydrogen takes place in presence of Raney nickel catalyst. Platinum and palladium can also be used as catalyst in these reactions. These are heterogeneous catalyst and used in finely divided state. Experimentally, it is observed that less crowded alkenes adsorb H_2 with faster rate. Controlled hydrogenation of alkyne in presence of Lindlar's catalyst yields *cis* product *i.e.*, '*cis*' alkene. Thus, in presence of Lindlar's catalyst 'syn' addition takes place. The relative rate of hydrogenation follows the order:

$$-C\equiv C- \; > \; >C=C< \; > \; >C=O \; > \; C_6H_6$$

Non-terminal alkynes an reduced in presence of Na or Li metal dissolved in liquid ammonia. In this reaction, anti-addition of hydrogen results into the *trans*-product.

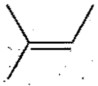
Answer the following questions:

1. The relative rate of catalytic hydrogenation of following alkenes is:


I

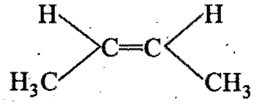
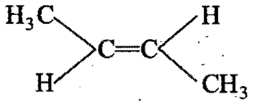

II


III

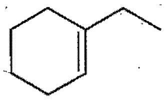
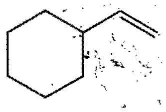
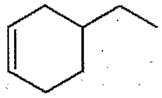
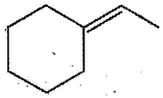

IV

(a) II > III > IV > I (b) I > IV > III > II
(c) III > IV > I > II (d) II > IV > I > III

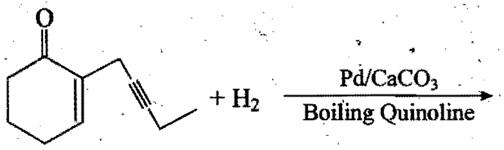
2. $H_3C-C\equiv C-CH_3 + H_2 \xrightarrow[\text{Boiling Quinoline}]{Pd/CaCO_3} (A)$

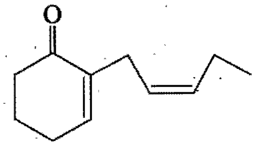
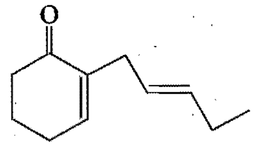
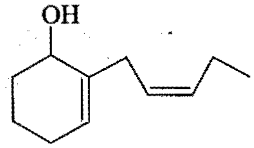
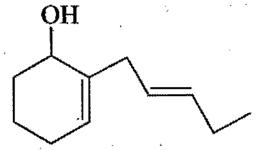
The product (A) will be:
(a) $CH_3CH_2CH_2CH_3$
(b) 
$$\begin{matrix} H & & H \\ & C=C & \\ H_3C & & CH_3 \end{matrix}$$
(c) 
$$\begin{matrix} H_3C & & H \\ & C=C & \\ H & & CH_3 \end{matrix}$$
(d) $CH_3-CH_2-CH=CH_2$

3. In which of the following cases, the reaction is most exothermic?

(a) 
(b) 
(c) 
(d) 

4. The product of the following reaction is:

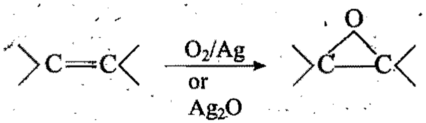


(a) 
(b) 
(c) 
(d) 

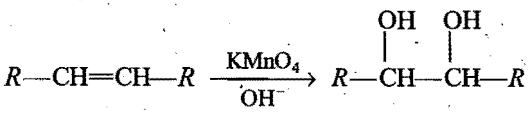
5. Powdered nickel is more effective than grannular nickel because:
(a) Surface area of powdered nickel is maximum
(b) Free valencies are large in number
(c) powdered nickel increases the activation energy of the reaction
(d) powdered nickel increases the intermolecular collision of reactant molecules

Passage 2

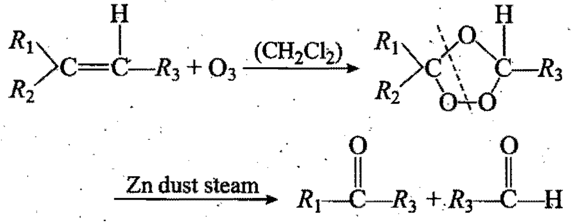
Oxidation without cleavage of sigma bond takes place in alkenes.



Presence of unsaturation in alkenes is detected by using Baeyer's reagent. Alkenes decolourise pink colour of Baeyer's reagent. In presence of Baeyer's reagent, 'syn' addition of —OH groups takes place on both carbons of double bond. The net reaction can be given as,


$$R-CH=CH-R \xrightarrow[OH^-]{KMnO_4} R-\underset{OH}{\underset{|}{C}H}-\underset{OH}{\underset{|}{C}H}-R$$

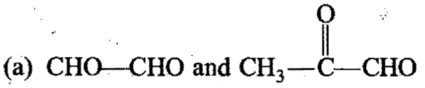
Ozonolysis of alkenes gives ozonide, which on further hydrolysis gives aldehyde and/or ketone.

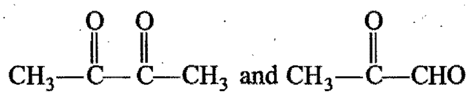


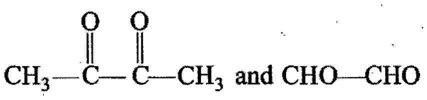
Answer the following questions:

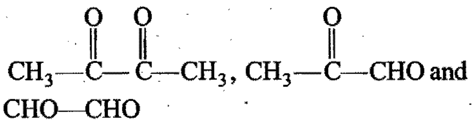
1. Linear polyenes on ozonolysis gives two moles of acetaldehyde and one mole of propanedial. Linear polyene will be:
(a) alkadiene (b) alkatriene
(c) alkatetraene (d) alkapentaene

2. *Ortho* xylene on reductive ozonolysis will give:

(a) 
$$CHO-CHO \text{ and } CH_3-\overset{O}{\overset{\|}{C}}-CHO$$

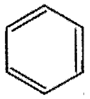
(b) 
$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$ and $CH_3-\overset{O}{\overset{\|}{C}}-CHO$

(c) 
$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$ and $CHO-CHO$

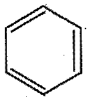
(d) 
$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$, $CH_3-\overset{O}{\overset{\|}{C}}-CHO$ and $CHO-CHO$

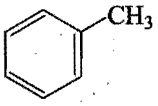
3. Which of the following will give only formaldehyde on ozonolysis?

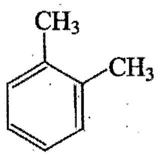
(a) $H_2C{=}CH_2$ (b) $CH_3-CH{=}CH_2$

(c) $CH_3-CH{=}CH-CH_3$ (d) 

4. Which of these compounds give glyoxal only on ozonolysis?

(a) 

(b) 

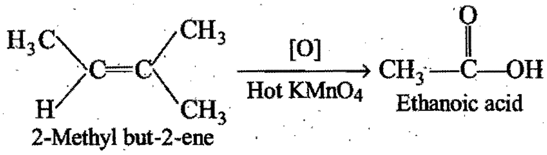
(c) 

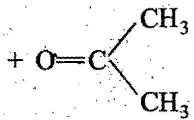
(d) All of these

5. Product of ozonolysis gives information about:
(a) configuration (b) conformation
(c) both of these (d) none of these

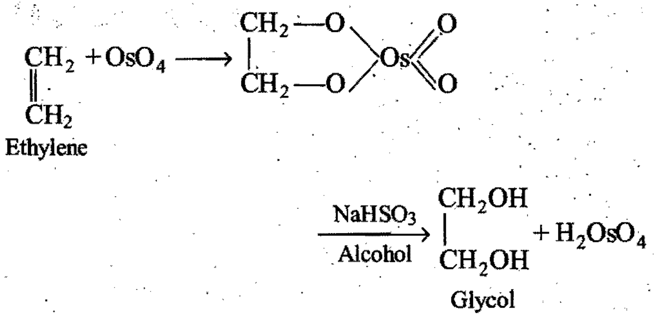
Passage 3

Oxidation of alkenes by cleavage with acidic or alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$ at higher temperature yields products depending upon the nature of alkene. A hot solution of $KMnO_4$ is a strong oxidising agent which gives only ketones and carboxylic acids and not aldehydes (as they cannot be isolated).





Oxidation of alkenes with OsO_4 followed by alcoholic $NaHSO_3$ or Na_2SO_3 yields glycols.



Answer the following questions:

1. Which of these compounds on oxidation with hot $KMnO_4$ gives only butanoic acid?
(a) Oct-3-ene (b) Oct-4-ene
(c) Oct-2-ene (d) 3-Methyl-hept-3-ene
2. Which of these compounds on treatment with OsO_4, followed by Na_2SO_3 will give *cis*-2-methyl butan-2,3-diol?
(a) 2-Methyl-2-pentene (b) 4-Methyl-2-pentene
(c) 2,3-Dimethyl-2-butene (d) 2,2-Dimethyl-2-butene
3. An alkene 1-methyl cyclohexene on oxidation with hot basic $KMnO_4$ gives:
(a) heptanoic acid
(b) 2-methyl hexanoic acid
(c) 6-keto heptanoic acid
(d) butanoic acid and acetone
4. Which of the following alkenes on oxidation with hot $KMnO_4$ gives cyclopentanone?
(a) 2-Methyl cyclopentene (b) Cyclopentene
(c) Methylene cyclobutane (d) Methylene cyclopentane
5. An alkene 1,2-dimethyl cyclobutene on oxidation with hot $KMnO_4$ gives:
(a) 4-ketopentanoic acid
(b) 2,3-diketo cyclohexane
(c) hexane-2,5-dione
(d) ethanoic acid and butanoic acid

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1.	**1.** (a)	**2.** (b)	**3.** (b)	**4.** (a)	**5.** (a,b)
Passage 2.	**1.** (a)	**2.** (d)	**3.** (a)	**4.** (a)	**5.** (d)
Passage 3.	**1.** (b)	**2.** (a)	**3.** (c)	**4.** (d)	**5.** (c)

8

HALOGENATED ALIPHATIC HYDROCARBONS

Compounds derived from hydrocarbons by the replacement of one or more hydrogen atoms by the corresponding number of halogen atoms are termed as halogen derivatives. The halogen derivatives of aliphatic hydrocarbons are broadly classified into two classes:

(i) Halogen derivatives of alkanes or halo-alkanes.

(ii) Halogen derivatives of unsaturated hydrocarbons, *i.e.*, derivatives of alkenes and alkynes.

8.1 HALOGEN DERIVATIVES OF ALKANES OR HALO-ALKANES

Compounds derived from alkanes by the replacement of one or more hydrogen atoms by the corresponding number of halogen atoms (fluorine, chlorine, bromine or iodine) are termed halogen derivatives of alkanes or halo-alkanes. Depending on the number of halogen atoms present in the halogen derivative, these are termed as mono-, di-, tri-, tetra- and polyhalogen derivatives.

$$\underset{\text{Methane}}{CH_4} \xrightarrow[+X]{-H} \underset{\text{Mono}}{CH_3—X} \xrightarrow[+X]{-H} \underset{\text{Di}}{CH_2—X_2} \xrightarrow[+X]{-H} \underset{\text{Tri}}{CH—X_3} \xrightarrow[+X]{-H} \underset{\text{Tetra}}{C—X_4}$$

1. Monohalogen derivatives : One halogen atom is attached to carbon atom. They are commonly represented by the formula $R—X$ where R is an alkyl radical and X is a halogen atom.

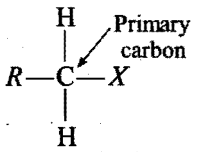
$$\underset{\text{Alkane}}{R—H} \xrightarrow[+X]{-H} \underset{\text{Alkyl halide}}{R—X}$$

These are termed **alkyl halides** and the homologous series has the general formula $C_nH_{2n+1}X$.

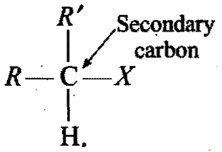
Examples :

CH_3Cl	C_2H_5Br	C_3H_7I
Methyl chloride	Ethyl bromide	Propyl iodide

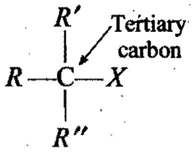
Monohalogen derivatives or alkyl halides are classified as primary (1°), secondary (2°) or tertiary (3°) depending upon whether the halogen atom is attached to primary, secondary or tertiary carbon atoms.



Primary alkyl halide



Secondary alkyl halide



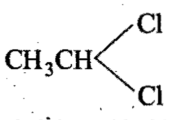
Tertiary alkyl halide

2. Di-halogen derivatives : The dihalogen derivatives of alkanes are derived by the replacement of two hydrogen atoms by two halogen atoms.

$$\underset{\text{Alkane}}{C_nH_{2n+2}} \xrightarrow[+2X]{-2H} \underset{\text{Dihalogen derivative}}{C_nH_{2n}X_2}$$

The dihalogen derivatives are mainly of three types:

(i) Gem-dihalides : In these derivatives both the halogen atoms are attached to the same carbon atom. These are also called **alkylidene (di) halides.**



Ethylidene chloride (1,1-Dichloroethane) ;

$CH_3—CBr_2—CH_3$

Isopropylidene bromide (2,2-Dibromopropane)

(ii) Vic-dihalides : In these derivatives, the halogen atoms are attached to adjacent (vicinal) carbon atoms. These are also termed **alkylene (di) halides.**

CH_2ClCH_2Cl ;	$CH_3CHClCH_2Cl$
Ethylene chloride (1,2-Dichloroethane)	Propylene chloride (1,2-Dichloropropane)

(iii) α-ω halides (terminal dihalides) : In these derivatives, the halogen atoms are attached to terminal carbon atoms. These are also called **polymethylene halides.**

$CH_2BrCH_2CH_2Br$;	$ClCH_2CH_2CH_2CH_2Cl$
Trimethylene bromide (1,3-Dibromopropane)	Tetramethylene chloride (1,4-Dichlorobutane)

3. Tri-halogen derivatives : Tri-halogen derivatives are derived by the replacement of three hydrogen atoms from alkanes by three halogen atoms. They have the general formula $C_nH_{2n-1}X_3$. The tri-halogen derivatives of first alkane (methane) are:

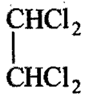
$CHCl_3$;	$CHBr_3$;	CHI_3
Chloroform	Bromoform	Iodoform

These compounds are termed as haloforms.

4. Tetra-halogen derivatives : The tetra-halogen derivatives are derived by the replacement of four hydrogen atoms from alkanes by four halogen atoms. All the four halogen atoms are attached to the same carbon atom in derivatives of methane.

CCl_4	CBr_4
Carbon tetrachloride	Carbon tetrabromide

In other derivatives, the four halogen atoms are attached to different carbon atoms, *e.g.*,



$$\begin{array}{l} CHCl_2 \\ | \\ CHCl_2 \end{array}$$

Acetylene tetrachloride or 1,1,2,2 - tetrachloroethane

Similarly, **Polyhalogen derivative is:**

C_2Cl_6 Hexachloroethane

Classification

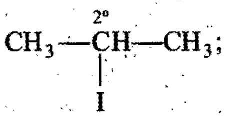
Monohalogen compounds may further be classified according to the **nature of C—*X* bond** in haloalkanes and haloalkenes particularly to the hybridization of the carbon atom linked to the halogen.

(A) Compounds containing C—*X* bond, where carbon is *sp*³-hybridized.

(i) Alkyl halides or Haloalkanes: In alkyl halides, the halogen atom is bonded to an alkyl group. The homologous series is represented by $C_nH_{2n+1}X$. They are further classified as primary (1°), secondary (2°) and tertiary (3°) halides depending upon whether the halogen atom is attached to a primary, secondary or tertiary carbon atom. Examples are:

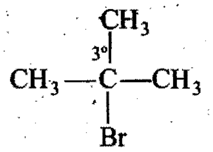
$CH_3—CH_2—\overset{1°}{CH_2}—Cl$;

1-Chloropropane
(primary or 1°)



$$CH_3—\overset{2°}{\underset{\underset{I}{|}}{CH}}—CH_3;$$

2-Iodopropane
(secondary or 2°)



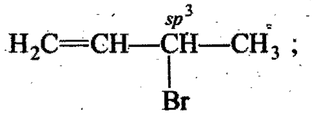
$$CH_3—\overset{\overset{CH_3}{|}\,3°}{\underset{\underset{Br}{|}}{C}}—CH_3$$

2-Bromo-2-methylpropane
(tertiary or 3°)

(ii) Allylic halides: In these halides, the halogen atom is attached to allylic carbon (C=C—C—*X*), *i.e.*, carbon atom next to C=C. Examples are:

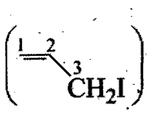
$H_2C=CH—\overset{sp^3}{CH_2}—I$;

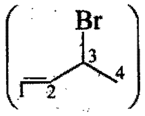
3-Iodoprop-1-ene
(Allyl iodide)

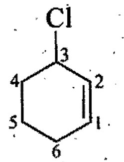


$$H_2C=CH—\overset{sp^3}{\underset{\underset{Br}{|}}{CH}}—CH_3 ;$$

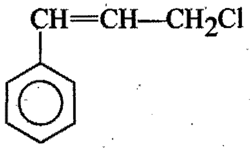
3-Bromobut-1-ene







3-Chlorocyclohex-1-ene



3-Chloro-1-phenylprop-1-ene
(Cinnamyl chloride)

$CH_3—CH=CH—CH_2Br$
1-Bromobut-2-ene
(Crotyl bromide)

Allylic halides may be primary, secondary or tertiary.

(iii) Benzylic halides: In these halides, the halogen atom is attached to a benzylic carbon ($C_6H_5\overset{*}{C}H_2$—, $C_6H_5\overset{*}{C}H\lt$ or $C_6H_5\overset{*}{C}\lessdot$), *i.e.*, the carbon atoms of the side chain carrying the aryl group. Examples are:

Benzyl chloride ; Benzal chloride;
Benzo trichloride ; β-Phenyl ethyl bromide ...... etc.

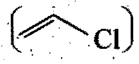
(B) Compounds containing C—*X* bond, where carbon is *sp*²-hybridized.

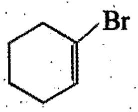
(i) Arylhalides: In these halides, the halogen atom is directly attached to the carbon atom of an aromatic ring. These halides are also called haloarenes. Examples are:

Chlorobenzene ; Bromobenzene;
Iodobenzene ; 2-Chlorotoluene;
3-Bromotoluene ; 4-Bromotoluene

(ii) Vinylic halides: In these halides, the halogen atom is attached to vinylic carbon (C=$\overset{*}{C}$—*X*), *i.e.*, one of the carbon atoms of C=C. Examples are:

$H_2C=CH—Cl$;
Chloroethene
(Vinyl chloride)





1-Bromocyclohex-1-ene

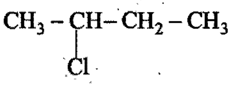
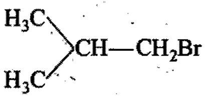
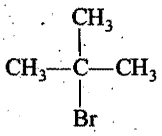
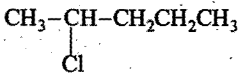
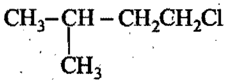
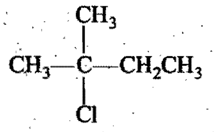
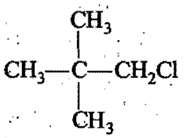
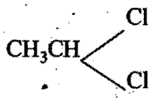
(C) Compounds containing C—X bond, where carbon is *sp*-hybridized.

Alkynyl halides or Haloalkynes: In these halides, the halogen atom is attached to one of the carbon atoms of a C≡C. Examples are:

$HC{\equiv}C{-}Br$; $H_3C{-}C{\equiv}C{-}Cl$

Bromoethyne (Bromoacetylene) ; 1-Chloroprop-1-yne

Nomenclature

Formula of halogen derivative	Common name	IUPAC name
CH_3Cl	Methyl chloride	Chloromethane
CH_3CH_2Br	Ethyl bromide	Bromoethane
$CH_3CH_2CH_2I$	*n*-Propyl iodide	1-Iodopropane
$CH_3CHBrCH_3$	Isopropyl bromide	2-Bromopropane
$CH_3CH_2CH_2CH_2Cl$	*n*-Butyl chloride	1-Chlorobutane
 $CH_3-\underset{Cl}{CH}-CH_2-CH_3$	*Sec*.-butyl chloride	2-Chlorobutane
 $(H_3C)_2CH-CH_2Br$	Isobutyl bromide	1-Bromo-2-methyl-propane
 $CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_3$	Tertiary butyl bromide	2-Bromo-2-methyl-propane
$CH_3CH_2CH_2CH_2CH_2Cl$	*n*-Pentyl chloride or *n*-Amyl chloride	1-Chloropentane
 $CH_3-\underset{Cl}{CH}-CH_2CH_2CH_3$	*Sec*.-pentyl chloride or *Sec*.-amyl chloride	2-Chloropentane
 $CH_3-\underset{CH_3}{CH}-CH_2CH_2Cl$	Isopentyl chloride or Isoamyl chloride	1-Chloro-3-methyl-butane
 $CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2CH_3$	*Tert*. pentyl chloride or *Tert*. amyl chloride	2-Chloro-2-methyl-butane
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Cl$	Neo-pentyl chloride or Neo-amyl chloride	1-Chloro-2,2-dimethylpropane
CH_2Cl_2	Methylene chloride	Dichloromethane
 CH_3CHCl_2	Ethylidene chloride	1,1-Dichloroethane
CH_2Cl-CH_2Cl	Ethylene chloride	1,2-Dichloroethane
$CHCl_3$	Chloroform	Trichloromethane
CHI_3	Iodoform	Triiodomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CHCl_2-CHCl_2$	Acetylene tetrachloride	1,1,2,2-Tetrachloro-ethane

Usually, the simple and lower members are called by common names and higher members are given IUPAC names. Halogen derivatives of alkanes are highly reactive as the halogen atoms are easily replaced. These do not occur in nature and are entirely of synthetic origin. These derivatives especially the alkyl halides are widely used in the synthesis of many organic compounds.

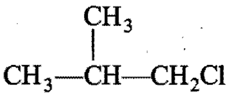
8.2 ISOMERISM IN MONOHALOGEN DERIVATIVES

Higher members of alkyl halides show the following types of isomerism:

(i) Chain isomerism : This is due to different arrangements of carbon atoms in the alkyl group. For example, C_4H_9Cl.

$CH_3CH_2CH_2CH_2Cl$

1-Chlorobutane



$CH_3-\overset{CH_3}{CH}-CH_2Cl$

1-Chloro-2-methyl propane

(ii) Position isomerism : This is due to different positions of the halogen atom in the molecule.

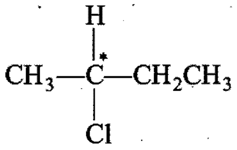
$CH_3CH_2CH_2CH_2Cl$

1-Chlorobutane

$CH_3CH_2\overset{Cl}{CH}-CH_3$

2-Chlorobutane

(iii) Optical isomerism : This is due to the presence of asymmetric carbon atom in secondary butyl halide.



$CH_3-\overset{H}{\underset{Cl}{\overset{*}{C}}}-CH_2CH_3$

2-Chlorobutane

The total number of isomers in alkyl halides are:

Propyl (C_3H_7—X) has two isomers,

Butyl (C_4H_9—X) has four isomers and

Pentyl (C_5H_{11}—X) has eight isomers.

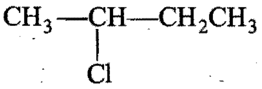
(iv) Conformations : Alkyl halides can also form conformers due to the free rotation of C—C bond.

SOME SOLVED EXAMPLES

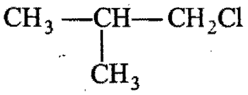
Example 1. *Write structural formula and give their IUPAC names:*

(*a*) *Sec-butyl chloride*	(*b*) *Iso-butyl chloride*
(*c*) *Tert.-butyl chloride*	(*d*) *Iso-propyl bromide*
(*e*) *Tert-amyl iodide*	(*f*) *Iso-pentyl bromide*
(*g*) *Neo-pentyl chloride*	(*h*) *Neo-hexyl bromide*
(*i*) *Iso-propylidene bromide*	(*j*) *Allyl iodide*
(*k*) *Crotyl bromide*	(*l*) *Propargyl bromide*
(*m*) 4-*Chloro-2-pentene*	

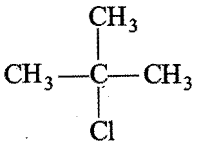
Solution:

(a) 

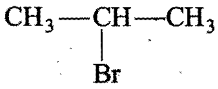
$CH_3—\underset{\substack{|\\Cl}}{CH}—CH_2CH_3$ 2-Chlorobutane

(b) 

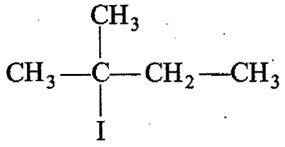
$CH_3—\underset{\substack{|\\CH_3}}{CH}—CH_2Cl$ 1-Chloro-2-methylpropane

(c) 

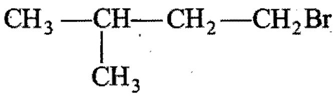
$CH_3—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\Cl}}{C}}—CH_3$ 2-Chloro-2-methylpropane

(d) 

$CH_3—\underset{\substack{|\\Br}}{CH}—CH_3$ 2-Bromopropane

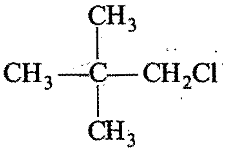
(e) 

$CH_3—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\I}}{C}}—CH_2—CH_3$ 2-Iodo-2-methylbutane

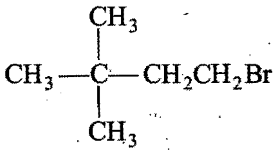
(f) 

$CH_3—\underset{\substack{|\\CH_3}}{CH}—CH_2—CH_2Br$

1-Bromo-3-methylbutane

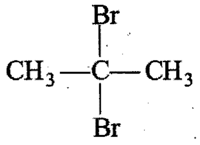
(g) 

$CH_3—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}—CH_2Cl$ 1-Chloro-2,2-dimethylpropane

(h) 

$CH_3—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}—CH_2CH_2Br$

1-Bromo-3,3-dimethylbutane

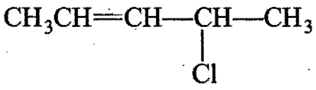
(i) 

$CH_3—\overset{\substack{Br\\|}}{\underset{\substack{|\\Br}}{C}}—CH_3$ 2,2-Dibromopropane

(j) $H_2C{=}CH—CH_2I$ 3-Iodoprop-1-ene

(k) $CH_3CH{=}CHCH_2Br$ 1-Bromo-but-2-ene

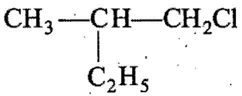
(l) $HC{\equiv}C—CH_2Br$ 3-Bromoprop-1-yne

(m) 

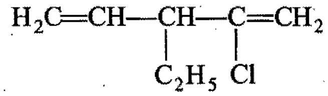
$CH_3CH{=}CH—\underset{\substack{|\\Cl}}{CH}—CH_3$ 4-Chloropent-2-ene

Example 2. *Give the* IUPAC *names of the following compounds:*

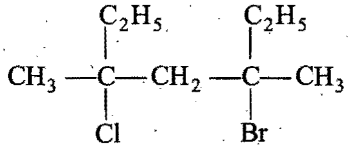
(*a*) $(CH_3)_3C—Cl$

(*b*) 

$CH_3—\underset{\substack{|\\C_2H_5}}{CH}—CH_2Cl$

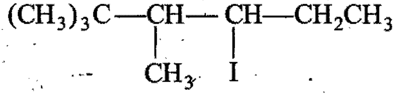
(*c*) 

$H_2C{=}CH—\underset{\substack{|\\C_2H_5}}{CH}—\underset{\substack{|\\Cl}}{C}{=}CH_2$

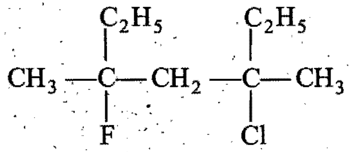
(*d*) 

$CH_3—\overset{\substack{C_2H_5\\|}}{\underset{\substack{|\\Cl}}{C}}—CH_2—\overset{\substack{C_2H_5\\|}}{\underset{\substack{|\\Br}}{C}}—CH_3$

(*e*) $(CH_3)_3C—CH_2—CH_2Cl$

(*f*) 

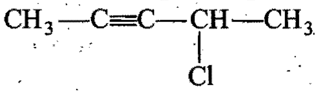
$(CH_3)_3C—\underset{\substack{|\\CH_3}}{CH}—\underset{\substack{|\\I}}{CH}—CH_2CH_3$

(*g*) 

$CH_3—\overset{\substack{C_2H_5\\|}}{\underset{\substack{|\\F}}{C}}—CH_2—\overset{\substack{C_2H_5\\|}}{\underset{\substack{|\\Cl}}{C}}—CH_3$

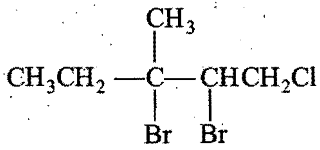
(*h*) $HC{\equiv}C—CH_2—CH{=}CHCl$

(*i*) $BrCH_2—CH_2—CH_2—CH_2Cl$

(*j*) 

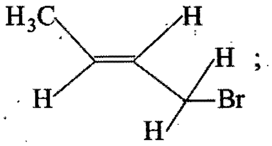
$CH_3—C{\equiv}C—\underset{\substack{|\\Cl}}{CH}—CH_3$

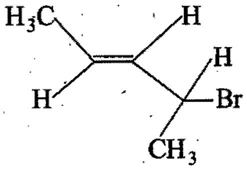
(*k*) $(C_2H_5)_3C—Cl$

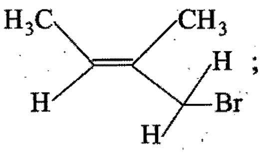
(*l*) 

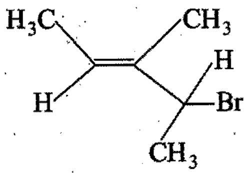
$CH_3CH_2—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\Br}}{C}}—\underset{\substack{|\\Br}}{CH}CH_2Cl$

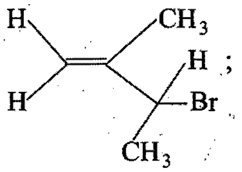
(*m*) $HC{\equiv}C—CH_2Br$

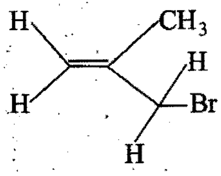
(*n*) 

(*o*) 

(*p*) 

(*q*) 

(*r*) 

(*s*) 

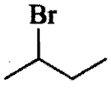
Solution: (a) 2-Chloro-2-methylpropane
(b) 1-Chloro-2-methylbutane
(c) 2-Chloro-3-ethylpenta-1,4-diene
(d) 3-Bromo-5-chloro-3,5-dimethylheptane
(e) 1-Chloro-3,3-dimethylbutane
(f) 4-Iodo-2,2,3-trimethylhexane
(g) 3-Chloro-5-fluoro-3,5-dimethylheptane
(h) 1-Chloropent-1-en-4-yne
(i) 1-Bromo-4-chlorobutane
(j) 4-Chloro-pent-2-yne
(k) 3-Chloro-3-ethylpentane
(l) 2,3-Dibromo-1-chloro-3-methylpentane
(m) 3-Bromoprop-1-yne
(n) 1-Bromobut-2-ene

(o) 4-Bromopent-2-ene
(p) 1-Bromo-2-methylbut-2-ene
(q) 4-Bromo-3-methylpent-2-ene
(r) 3-Bromo-2-methylbut-1-ene
(s) 3-Bromo-2-methylpropene

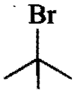
Example 3. *Draw the bond line structures of the following compounds whose IUPAC names are given as under:*

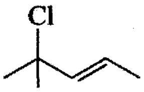
(*a*) 2-*Bromobutane*
(*b*) 1-*Chloro*-3-*Methylbutane*
(*c*) 2-*Bromo*-2-*methylpropane*
(*d*) 4-*Chloro*-4-*methylpent*-2-*ene*
(*e*) 2-*Iodo*-3-*methylpentane*
(*f*) 2,3-*Dibromobutane*
(*g*) 3-*Iodopropene*
(*h*) *Bromoethene*
(*i*) 1,4-*Dibromobut*-2-*ene*
(*j*) 4-*Tert. butyl*-3-*iodoheptane*
(*k*) 2-*Chloro*-3-*methylpentane*

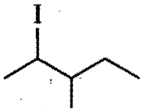
Solution:

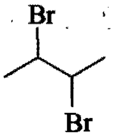
(a)


(b)


(c)


(d)


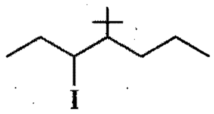
(e)


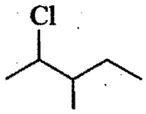
(f)


(g)


(h)


(i)

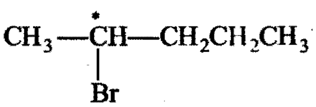

(j)


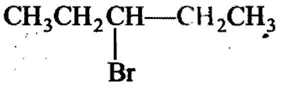
(k)


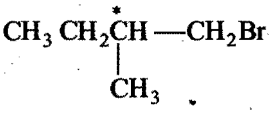
Example 4. *Write all the possible structures for the molecular formula* $C_5H_{11}Br$. *Give their* IUPAC *names. Which of these are optically active?*

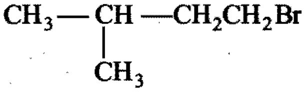
Solution:

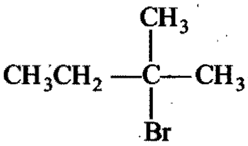
(i) $CH_3CH_2CH_2CH_2CH_2Br$ 1-Bromopentane (primary)

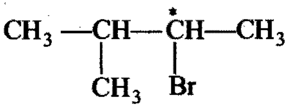
(ii)

$CH_3-\overset{*}{C}H(Br)-CH_2CH_2CH_3$ 2-Bromopentane (secondary)

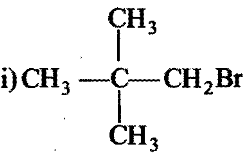
(iii)

$CH_3CH_2CH(Br)-CH_2CH_3$ 3-Bromopentane (secondary)

(iv)

$CH_3\,CH_2\overset{*}{C}H(CH_3)-CH_2Br$ 1-Bromo-2-methylbutane (primary)

(v)

$CH_3-CH(CH_3)-CH_2CH_2Br$ 1-Bromo-3-methylbutane (primary)

(vi)

$CH_3CH_2-C(CH_3)(Br)-CH_3$ 2-Bromo-2-methylbutane (tertiary).

(vii)

$CH_3-CH(CH_3)-\overset{*}{C}H(Br)-CH_3$ 2-Bromo-3-methylbutane (secondary)

(viii)

$CH_3-C(CH_3)_2-CH_2Br$ 1-Bromo-2,2-dimethylpropane (primary)

The optically active isomers; (ii), (iv) and (vii).

8.3 GENERAL METHODS OF PREPARATION OF MONOHALOGEN DERIVATIVES OR ALKYL HALIDES

The following general methods are used for the preparation of alkyl halides.

1. From alkanes : Direct halogenation of alkanes in presence of sunlight, heat or suitable catalyst yields alkyl halides. Chlorination is fast, bromination is slow while direct iodination is not possible as the reaction is reversible and highly endothermic. (However, iodination can be done in presence of oxidising agents such as HNO_3 or iodic acid, HIO_3).

The reactivity of the alkanes follows the following order:

Tertiary alkane > Secondary alkane > Primary alkane

$$\underset{\text{Alkane}}{R\text{—H}} + X_2 \xrightarrow{h\nu} \underset{\text{Alkyl halide}}{R\text{—}X} + HX$$

Direct halogenation proceeds through free radical mechanism : Direct halogenation does not form pure monohalogen derivatives but a mixture of polyhalogen derivatives is always obtained. For example, methane reacts with chlorine in presence of diffused sunlight or at 250–400°C to form a mixture of methyl chloride, methylene chloride, chloroform and carbon tetrachloride.

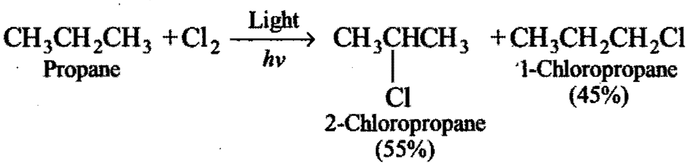
$$CH_4 + Cl_2 \xrightarrow[-HCl]{h\nu} CH_3Cl \xrightarrow[-HCl]{Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{Cl_2} CHCl_3$$

$$\xrightarrow[-HCl]{Cl_2} CCl_4$$

This method is, thus not used in laboratory because it is not easy to separate the individual members from the mixture. However, it is the most important **commercial method** for obtaining alkyl halides because alkanes are available in large amounts from petroleum and natural gas. If the conditions are well maintained especially the ratio of halogen and alkane, the halogenation may be suppressed beyond monosubstituted product. The displacement of H from hydrocarbon is in the order:

Allylic > 3° > 2° > 1° > CH_4

$$\underset{\text{Ethane}}{C_2H_6\ (\text{Excess})} + Cl_2 \xrightarrow[h\nu]{\text{Light}} \underset{\substack{\text{Ethyl chloride}\\ \text{(Major product)}}}{C_2H_5Cl} + HCl$$



$$\underset{\text{Propane}}{CH_3CH_2CH_3} + Cl_2 \xrightarrow[h\nu]{\text{Light}} \underset{\substack{\text{2-Chloropropane}\\ (55\%)}}{CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3} + \underset{\substack{\text{1-Chloropropane}\\ (45\%)}}{CH_3CH_2CH_2Cl}$$

Similarly, bromination takes place, but not so vigorous as chlorination. However, iodination can be done by heating with iodine in the presence of oxidising agents such as conc. HNO_3 or HIO_3 (to oxidise HI formed during the reaction to iodine). and hence, shift the equilibrium in the forward reaction.

$$RH + I_2 \overset{\text{Heat}}{\rightleftharpoons} RI + HI$$

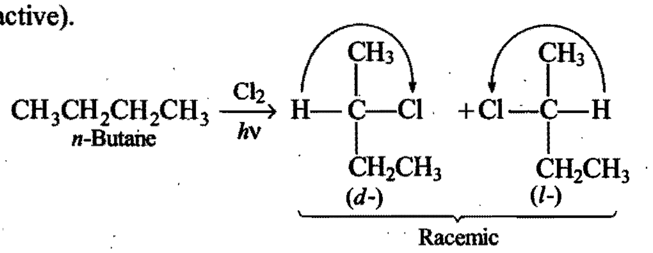
$$(5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O)$$

The reactivity of halogens decreases in the order:

$$F_2 > Cl_2 > Br_2 > I_2.$$

Bromination of alkanes is less exothermic than chlorination and so with fluorination. Iodine is unique as its reaction with alkanes is endothermic.

Chlorination of n-alkanes (C_4 and above) gives a mixture of d- and l- optical isomers, *i.e.*, racemic mixture (optically inactive).



$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[h\nu]{Cl_2} \underbrace{\underset{(d\text{-})}{H-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2CH_3}{C}}-Cl} + \underset{(l\text{-})}{Cl-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2CH_3}{C}}-H}}_{\text{Racemic}}$$

Alkane can react with sulphuryl chloride only in presence of light and traces of organic peroxide.

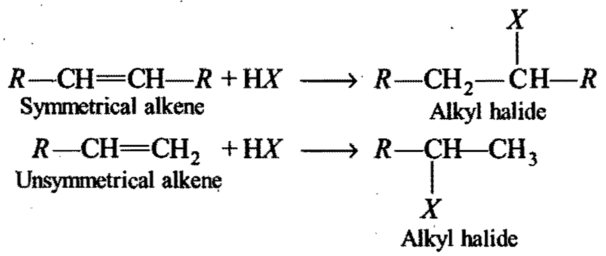
$$\underset{\text{Alkane}}{RH} + \underset{\substack{\text{Sulphuryl}\\ \text{chloride}}}{SO_2Cl_2} \xrightarrow[\text{or Peroxide}]{h\nu} \underset{\text{Chloroalkane}}{R-Cl} + HCl + SO_2$$

2. From alkenes : Halogen acids (HCl, HBr, HI) react readily with alkenes to form alkyl halides. The order of reactivity of halogen acids is:

$$HI > HBr > HCl > HF$$

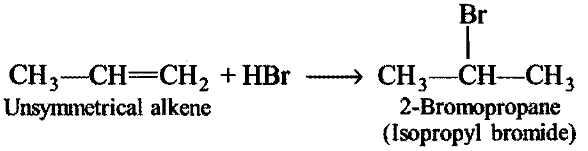
$$H_2C{=}CH_2 + HBr \longrightarrow CH_3CH_2Br$$

The unsymmetrical alkenes follow **Markownikoff's rule** during addition forming secondary or tertiary alkyl halides predominantly through the formation of most stable carbocation. Addition occurs through electrophilic attack. However, in presence of peroxide (R—O—O—R), such as benzoyl peroxide ($C_6H_5CO—O—O—COC_6H_5$), the HBr addition follows anti-Markownikoff's rule **(peroxide effect** or **Kharasch effect)** and form primary or normal alkyl bromides. Such an addition follows free radical mechanism. This method is well suited for the industrial preparation of alkyl halides as the lower alkenes are obtained during cracking of petroleum products.

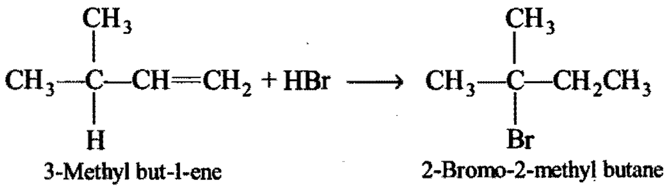


$$\underset{\text{Symmetrical alkene}}{R-CH{=}CH-R} + HX \longrightarrow \underset{\text{Alkyl halide}}{R-CH_2-\overset{\displaystyle X}{\overset{|}{C}}H-R}$$

$$\underset{\text{Unsymmetrical alkene}}{R-CH{=}CH_2} + HX \longrightarrow \underset{\text{Alkyl halide}}{R-\underset{\displaystyle X}{\underset{|}{C}}H-CH_3}$$

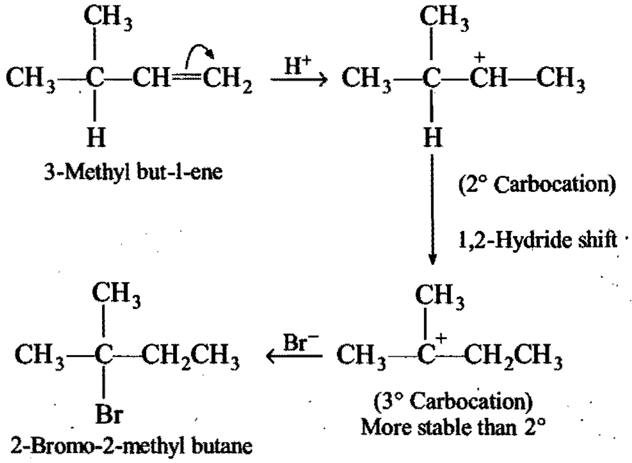


$$\underset{\text{Unsymmetrical alkene}}{CH_3-CH{=}CH_2} + HBr \longrightarrow \underset{\substack{\text{2-Bromopropane}\\ \text{(Isopropyl bromide)}}}{CH_3-\overset{\displaystyle Br}{\overset{|}{C}}H-CH_3}$$



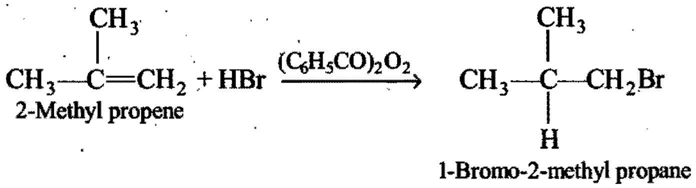
$$\underset{\text{3-Methyl but-1-ene}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-CH{=}CH_2} + HBr \longrightarrow \underset{\text{2-Bromo-2-methyl butane}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-CH_2CH_3}$$

This can be explained by **1,2-Hydride shift** to attain greater stability of carbocation.



$$\underset{\text{3-Methyl but-1-ene}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-CH{=}CH_2} \xrightarrow{H^+} \underset{(2^\circ\text{ Carbocation})}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-\overset{+}{C}H-CH_3} \xrightarrow{\text{1,2-Hydride shift}} \underset{\substack{(3^\circ\text{ Carbocation})\\ \text{More stable than } 2^\circ}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\overset{+}{C}}}-CH_2CH_3} \xrightarrow{Br^-} \underset{\text{2-Bromo-2-methyl butane}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-CH_2CH_3}$$

$$\underset{\text{Propene}}{CH_3-CH{=}CH_2} + HBr \xrightarrow[\substack{\text{(Anti-MR}\\ \text{addition)}}]{\text{Peroxide}} \underset{\substack{\text{1-Bromopropane}\\ (n\text{-Propyl bromide})}}{CH_3-CH_2-CH_2Br}$$



$$\underset{\text{2-Methyl propene}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2} + HBr \xrightarrow{(C_6H_5CO)_2O_2} \underset{\text{1-Bromo-2-methyl propane}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-CH_2Br}$$

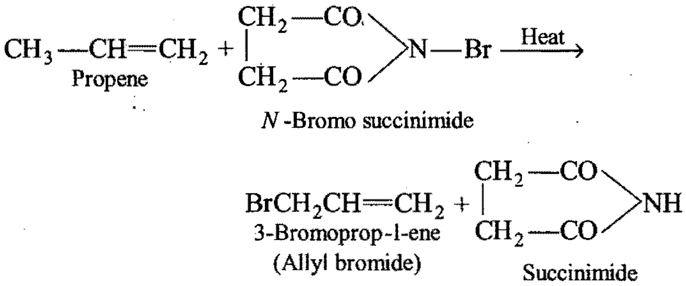
It may be noted that the peroxide effect applies to the **addition of HBr only** and not to the addition of HCl or HI.

Allylic substitution

When alkenes are heated with Cl_2 or Br_2 at a high temperature of about 500°C, the hydrogen atom of the allylic carbon (*i.e.*, carbon atom next to the double bonds) is substituted with the halogen atom without breaking the double bond (allylic substitution) and forms allyl halide. For example,

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + Cl_2 \xrightarrow{500°C} \underset{\substack{\text{Allyl chloride}\\ \text{(3-Chloroprop-1-ene)}}}{ClCH_2CH{=}CH_2} + HCl$$

The allylic substitution can also be carried out by heating the alkene with N-bromo succinimide **(NBS)** or sulphuryl chloride (SO_2Cl_2) at 200°C in presence of light and traces of organic peroxides such as benzoyl peroxide.



$$\underset{\text{Propene}}{CH_3—CH{=}CH_2} + SO_2Cl_2 \xrightarrow[\text{UV light}]{200°C} \underset{\substack{\text{3-Chloroprop-1-ene}\\ \text{(Allyl chloride)}}}{ClCH_2CH{=}CH_2} + SO_2 + HCl$$

3. From alcohols : Generally alkyl halides are prepared from alcohols by replacement of —OH by an halogen atom **(S_N reaction).**

$$R—OH + H—X \longrightarrow R—X + H_2O$$

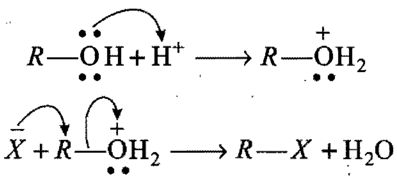
The replacement of —OH group can be done with halogen acids, phosphorus halides or thionyl chloride.

(i) By the action of halogen acids : Almost quantitative yield of alkyl halides is obtained when alcohols react with halogen acids in presence of a dehydrating agent such as anhydrous zinc chloride or concentrated sulphuric acid. The reactivity of the halogen acids and that of alcohols follow the following orders:

$$HI > HBr > HCl > HF$$

$$\text{Allyl} > 3° \text{ alcohol} > 2° \text{ alcohol} > 1° \text{ alcohol}$$

In this S_N reaction, the nucleophile ($\bar{X}$) attacks the protonated alcohol molecule with the elimination of water (a good leaving group).



$$R—\ddot{O}H + H^+ \longrightarrow R—\overset{+}{O}H_2$$

$$\bar{X} + R—\overset{+}{O}H_2 \longrightarrow R—X + H_2O$$

Since, the nucleophilicity (*i.e.*, tendency to donate electron pair to the carbon) of halide ions decreases in the order, $I^- > Br^- > Cl^-$, the order of reactivity of the halogen acids decreases in the same order, *i.e.*,

$$HI > HBr > HCl$$

(a) Alkyl chlorides are obtained by passing hydrogen chloride (gas) through alcohol in presence of anhydrous zinc chloride (Lewis acid).

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{(Conc.)}}{HCl(g)} \xrightarrow[ZnCl_2]{\text{Anhydrous}} CH_3CH_2Cl + H_2O$$

This mixture (1 : 1) of conc. HCl and anhyd. $ZnCl_2$ is called **Lucas reagent.**

The yield can be improved when the vapours of alcohol and HCl are passed over alumina at 350°C.

It must be noted that 1° and 2° alkyl chlorides are prepared from their respective alcohols by using HCl gas and anhydrous $ZnCl_2$ **(Groove's process).**

Tertiary alcohols are very reactive and therefore, they react readily with conc. HCl even in the absence of $ZnCl_2$.

$$\underset{\substack{\text{2-Methyl-2-propanol}\\ \text{(\textit{Tert.} butyl alcohol)}}}{(CH_3)_3C—OH} + \underset{\text{(conc.)}}{HCl} \xrightarrow[\text{Temp.}]{\text{Room}} \underset{\substack{\text{2-Chloro-2-}\\ \text{methyl propane}\\ \text{(\textit{Tert.} butyl chloride)}}}{(CH_3)_3C—Cl} + H_2O$$

1° alcohols follow S_N2 path while 2° and 3° alcohols S_N1 path (proceeds through most stable carbocation intermediate).

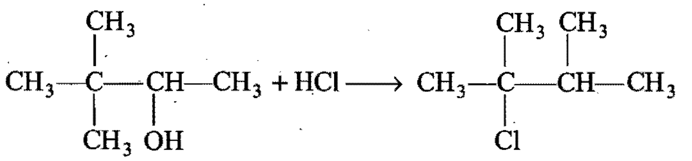
(b) Alkyl bromides are obtained in a similar manner by refluxing the alcohol with constant boiling HBr (48%) in presence of a little concentrated sulphuric acid. These are also obtained when the alcohol is heated with potassium bromide in presence of conc. H_2SO_4 in excess **(Lab method).**

$$\underset{\text{Ethanol}}{C_2H_5OH} + HBr \xrightarrow[\text{Reflux}]{H_2SO_4\text{ (conc.)}} \underset{\text{Bromoethane}}{C_2H_5Br} + H_2O$$

$$C_2H_5OH + KBr + H_2SO_4 \xrightarrow{\text{Heat}} C_2H_5Br + KHSO_4 + H_2O$$

Note : The mixture of KBr and H_2SO_4 is not used in case of secondary and tertiary alcohols as their dehydration may occur.

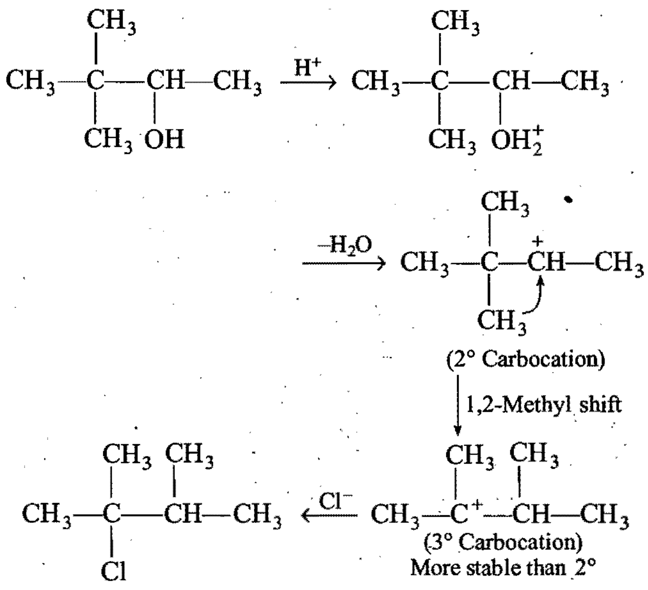
In case of higher alcohols, there can be 1,2-methyl (CH_3^-) or 1,2-hydride (H^-) shift to form more stable carbocation.



$$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—\underset{OH}{CH}—CH_3 + HCl \longrightarrow CH_3—\overset{CH_3}{\underset{Cl}{C}}—\overset{CH_3}{CH}—CH_3$$

3,3-Dimethyl-2-butanol 2-Chloro-2,3-dimethyl butane

This is due to **1,2-Methyl shift.**



(c) Alkyl iodides are prepared by refluxing alcohol with excess of HI (57%). These are also obtained when the alcohol is heated with potassium iodide in presence of phosphoric acid.

$$\underset{\text{Ethanol}}{C_2H_5OH} + KI + H_3PO_4 \xrightarrow{\text{Heat}} \underset{\text{Iodoethane}}{C_2H_5I} + KH_2PO_4 + H_2O$$

$$[C_2H_5OH + HI \xrightarrow{\text{Heat}} C_2H_5I + H_2O]$$

(ii) Action of phosphorus halides : Action of phosphorus halides on alcohols converts them readily into alkyl halides.

$$3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$$

The alkyl chlorides are formed by the action of PCl_3 or PCl_5 on alcohols.

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

$$\underset{\text{1-Propanol}}{CH_3CH_2CH_2OH} + PCl_5 \longrightarrow \underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} + POCl_3 + HCl$$

In the case of preparation of alkyl bromides and iodides, PBr_3 or PI_3 required for the reaction is generally produced *in situ* by the action of red phosphorus on bromine or iodine. Thus, the overall reaction may be depicted as:

$$(2P + 3I_2 \longrightarrow 2PI_3) \quad \text{or} \quad (2P + 3Br_2 \longrightarrow 2PBr_3)$$

$$R\text{—}OH \xrightarrow{P + I_2} R\text{—}I\,; \qquad R\text{—}OH \xrightarrow{P + Br_2} R\text{—}Br$$

$$3C_2H_5OH + PI_3 \longrightarrow 3C_2H_5I + H_3PO_3$$

The method gives good yield of primary alkyl halides but poor yields of secondary and tertiary alkyl halides because secondary and tertiary alcohols on heating forms alkenes. The method is useful for preparing lower alkyl bromides and iodides in the **laboratory.**

(iii) Action of thionyl chloride (Darzen's method) : Alkyl chlorides are prepared when thionyl chloride and alcohols are refluxed in presence of pyridine.

$$ROH + SOCl_2 \xrightarrow[\text{Reflux}]{\text{Pyridine}} RCl + SO_2\uparrow + HCl\uparrow$$

$$\underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Chloroethane}}{C_2H_5Cl} + SO_2\uparrow + HCl\uparrow$$

This method is widely used for the preparation of alkyl chlorides only as it has advantage over phosphorus chloride because the byproducts sulphur dioxide and hydrogen chloride are gases which can be easily removed from the reaction mixture. Bromides and iodides are not prepared by this method, because thionyl bromide is unstable and thionyl iodide does not exist.

4. From silver salts of fatty acids: Alkyl chlorides or alkyl bromides are prepared by the action of chlorine or bromine in CCl_4 on silver salt of the fatty acids. This reaction is called **Borodine-Hunsdiecker reaction** or **Hunsdiecker reaction.**

$$RCOOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} R\text{—}Br + CO_2 + AgBr$$

$$\underset{\text{Silver propionate}}{CH_3CH_2COOAg} + Br_2 \xrightarrow{CCl_4} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} + CO_2 + AgBr$$

This reaction gives the product with one carbon atom less than the fatty acid and the yield of halide is $1° > 2° > 3°$.

But iodine forms ester instead of alkyl halide and is called **Birnbaum-Simonini reaction.**

$$2RCOOAg + I_2 \longrightarrow \underset{\text{Ester}}{RCOOR} + 2CO_2 + 2AgI$$

One useful modification of this reaction is the use of HgO or $Pb(OAc)_4$ in place of silver salt to form alkyl halides.

$$2RCOOH \xrightarrow[\Delta]{X_2/HgO} 2R\text{—}X + 2CO_2 + HgX_2 + H_2O$$

$$RCOOH \xrightarrow[I_2,\, h\nu]{Pb(OAc)_4} R\text{—}I$$

5. By halide exchange method: This is a convenient method for the preparation of alkyl iodides. The corresponding alkyl bromides or chlorides are heated with a solution of sodium iodide in acetone or methanol.

$$RCl + NaI \xrightarrow[\Delta]{\text{Acetone}} RI + NaCl$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + NaI \xrightarrow[\text{Heat}]{\text{Acetone}} \underset{\text{Ethyl iodide}}{C_2H_5I} + NaBr$$

This reaction is called **Finkelstein reaction.**

Even alkyl fluorides which cannot be prepared by the above methods may be obtained from corresponding chlorides by the action of mercurous fluoride or antimony trifluoride or AsF_3 or AgF, etc., **(Swarts reaction).**

$$2CH_3Cl + Hg_2F_2 \longrightarrow \underset{\text{Methyl fluoride}}{2CH_3F} + Hg_2Cl_2$$

$$C_2H_5Br + AgF \longrightarrow \underset{\text{Fluoro ethane}}{C_2H_5F} + AgBr$$

$$3CH_3CCl_2CH_3 + 2SbF_3 \longrightarrow 3CH_3CF_2CH_3 + 2SbCl_3$$

6. By Rydons method: An alcohol on heating with halogen in presence of triphenyl phosphate $(PhO)_3PO$ produces alkyl halides.

$$R\text{—}CH_2OH + Br_2 + (C_6H_5O)_3PO \xrightarrow{\text{Heat}} R\text{—}CH_2Br + C_6H_5OH + (C_6H_5O)_2POBr$$

8.4 PROPERTIES OF ALKYL HALIDES

Physical properties : (i) CH_3F, CH_3Cl, CH_3Br and C_2H_5Cl are gases at room temperature, while CH_3I is a liquid at room temperature. The alkyl halides upto C_{18} are colourless liquids while higher members are colourless solids.

(ii) Alkyl halides are insoluble in water but soluble in organic solvents.

(iii) They burn on copper wire with green edged flame (Beilstein test for halogens).

(iv) Alkyl bromides and iodides are heavier than water. Alkyl chlorides and fluorides are lighter than water.

(v) Alkyl iodides become violet or brown in colour on exposure as they decompose in light.

$$2RI \xrightarrow{\text{Light}} R—R + I_2$$

(vi) For a given alkyl group, the boiling points of alkyl halides are in the order $RI > R\text{Br} > R\text{Cl} > R\text{F}$ and for a given halogen, the boiling points of alkyl halides increase with the increase of the size of the alkyl group. In a group of isomeric alkyl halides, the order of boiling point is:

Primary > Secondary > Tertiary

(vii) Alkyl halides are in general toxic compounds and bring unconsciousness when inhaled in large amounts.

Chemical properties : The alkyl halides are highly reactive, the order of reactivity is:

Iodide > Bromide > Chloride (nature of the halogen atom)

Tertiary > Secondary > Primary (type of halogen atom)

Amongst the primary alkyl halides the order of reactivity is:

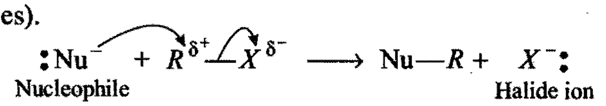
$$CH_3X > C_2H_5X > C_3H_7X, \text{ etc.}$$

The high reactivity of alkyl halides can be explained in terms of the nature of C—X bond which is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atoms. The halogen is far more electronegative than carbon and tends to pull the electrons away from carbon, *i.e.*, halogen acquires a small negative charge and carbon a small positive charge.

$$—\overset{\delta^+}{C}——\overset{\delta^-}{X}$$

This polarity gives rise to two types of reactions.

(i) Nucleophilic substitution : The C^{δ^+} site is susceptible to attack by nucleophiles (an electron rich species).



$$\underset{\text{Nucleophile}}{:\text{Nu}^-} + R^{\delta^+}—X^{\delta^-} \longrightarrow \text{Nu}—R + \underset{\text{Halide ion}}{X^-:}$$

$$R—X \xrightarrow[\text{Slow}]{-X^-} R^+ \xrightarrow[\text{Fast}]{\text{Nu}^-} R—\text{Nu} \quad (S_N1 \text{ reaction})$$

$$\text{Nu}^- + R—X \xrightarrow{\text{Slow}} \underset{\text{Transition state}}{\text{Nu}...R...X} \xrightarrow{\text{Fast}} \text{Nu}—R + X^-$$

(S_N2 reaction)

In S_N1 reaction, there can be racemization and inversion and order of reactivity is:

S_N1 order : Benzyl > allyl > 3° > 2° > 1° > $CH_3—X$

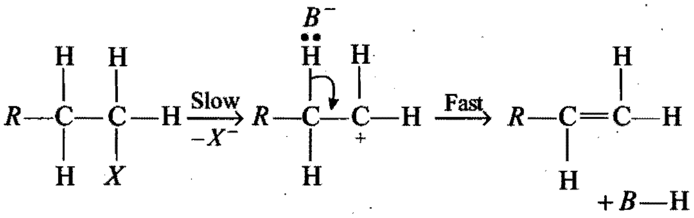
S_N2 reactions are concerted reactions and configuration of carbon is changed (Walden Inversion).

S_N2 order : Methyl > 1° > 2° > 3° > allyl > benzyl halides.

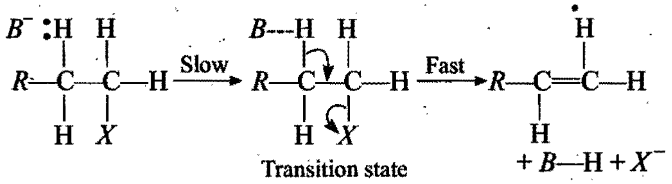
So, tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of steric hindrance.

(ii) Elimination reactions : The positive charge on carbon is propagated to the neighbouring carbon atoms by inductive effect. When approached by a strongest base (B), it tends to lose a proton usually from the β-carbon atom. Such reactions are termed elimination reactions. They are also E_1 and E_2 reactions.

E_1 reaction :



E_2 reaction :



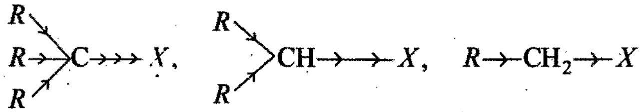
As the above reactions involve leaving of X^-, the reactivity of alkyl halides (same alkyl group, different halogens) should be limited with C—X bond strength.

Type of bond	C—I	C—Br	C—Cl
Bond strength (kcal/mol)	45.5	54	66.5

Bond strength increases →

The breaking of the bond becomes more and more difficult and thus, the reactivity decreases.

The order of reactivity (tertiary > secondary > primary) is due to $+I$ effect of the alkyl groups which increases the polarity of C—X bond.



The primary alkyl halides undergo reactions either by S_N2 or E_2 mechanisms which involve the formation of transition state. The bulky groups cause steric hindrance in the formation of transition state. Therefore, higher homologues are less reactive than lower homologues.

$$CH_3X > C_2H_5X > C_3H_7X, \text{ etc.}$$

Alkyl halides are extremely important reagents in organic synthesis as they undergo a large variety of reactions which are listed below.

1. Nucleophilic Substitution Reactions

(i) Hydrolysis (Formation of alcohols) : Alkyl halides are hydrolysed to corresponding alcohols by moist silver oxide (AgOH) or by boiling with aqueous alkali solution (NaOH or KOH). The attacking nucleophile is OH^-.

$$\underset{\text{Alkyl halide}}{RX} + \underset{\substack{\text{Moist}\\\text{silver oxide}}}{\text{AgOH}} \xrightarrow{\text{Heat}} \underset{\text{Alcohol}}{ROH} + \text{Ag}X$$

$$RX + \overset{+}{\text{K}}\overset{-}{\text{O}}\text{H}(aq.) \xrightarrow{\text{Heat}} ROH + KX$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + AgOH \xrightarrow{\text{Heat}} \underset{\text{Ethyl alcohol}}{C_2H_5OH} + AgBr$$

[With the help of this reaction an alkene can be converted into alcohol. Alkene is first reacted with HBr to form alkyl bromide and then hydrolysis is done.

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} \xrightarrow{HBr} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow{AgOH} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}]$$

(ii) Reaction with alkoxides or dry silver oxide (Formation of ethers) : Ethers are formed by heating alkyl halides with sodium or potassium alkoxides or dry silver oxide. The attacking nucleophile is OR^- **(Williamson's synthesis).**

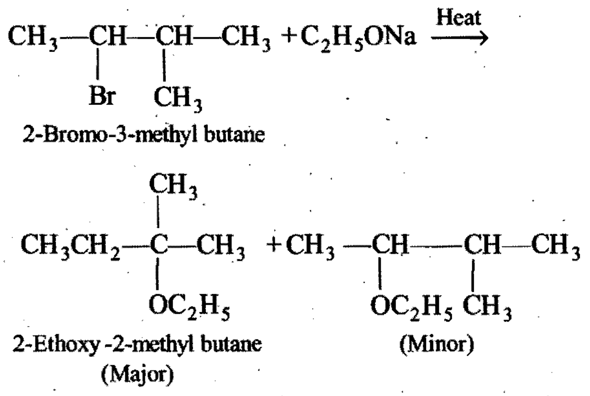
$$RX + \underset{\text{Sod. alkoxide}}{NaOR'} \xrightarrow{\text{Heat}} \underset{\text{Unsym. ether}}{ROR'} + NaX$$

$$\underset{\text{Alkyl halide}}{2RX} + \underset{\text{(Dry)}}{Ag_2O} \xrightarrow{\text{Heat}} \underset{\text{Sym. ether}}{R{-}O{-}R} + 2AgX$$

$$\underset{\text{Bromoethane}}{2C_2H_5Br} + \underset{\text{(Dry)}}{Ag_2O} \xrightarrow{\text{Heat}} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + 2AgBr$$

$$C_2H_5Br + \underset{\text{Sodium methoxide}}{NaOCH_3} \xrightarrow{\text{Heat}} \underset{\text{Ethyl methyl ether}}{C_2H_5OCH_3} + NaBr$$

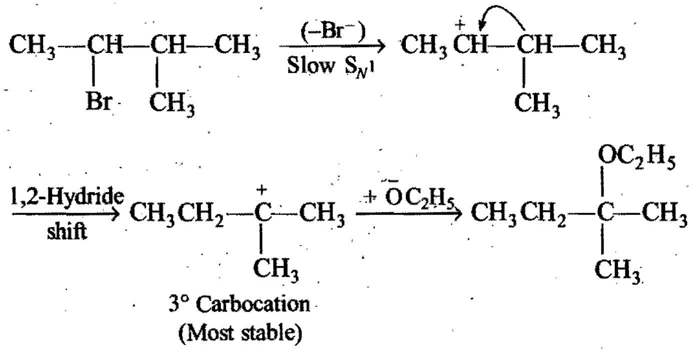
$$C_2H_5Br + \underset{\text{Sodium ethoxide}}{NaOC_2H_5} \xrightarrow{\text{Heat}} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + NaBr$$



$$\underset{\text{2-Bromo-3-methyl butane}}{CH_3-\underset{Br}{CH}-\underset{CH_3}{CH}-CH_3} + C_2H_5ONa \xrightarrow{\text{Heat}}$$

$$\underset{\substack{\text{2-Ethoxy-2-methyl butane}\\ \text{(Major)}}}{CH_3CH_2-\overset{CH_3}{\underset{OC_2H_5}{C}}-CH_3} + \underset{\text{(Minor)}}{CH_3-\underset{OC_2H_5}{CH}-\underset{CH_3}{CH}-CH_3}$$

Mechanism :



$$CH_3-\underset{Br}{CH}-\underset{CH_3}{CH}-CH_3 \xrightarrow[\text{Slow } S_N1]{(-Br^-)} CH_3\overset{+}{C}H-\underset{CH_3}{CH}-CH_3$$

$$\xrightarrow[\text{shift}]{\text{1,2-Hydride}} \underset{\substack{3^\circ\text{ Carbocation}\\ \text{(Most stable)}}}{CH_3CH_2-\overset{+}{\underset{CH_3}{C}}-CH_3} \xrightarrow{+\bar{O}C_2H_5} CH_3CH_2-\overset{OC_2H_5}{\underset{CH_3}{C}}-CH_3$$

There can also be elimination from 2° and 3° carbocation to give an alkene.

(iii) Reaction with sodium or potassium hydrogen sulphide (Formation of thioalcohols) : Alkyl halides form thioalcohols with aqueous alcoholic sodium hydrogen sulphide or potassium hydrogen sulphide. The nucleophile is SH^-.

$$RX + \underset{\substack{\text{Sodium hydrogen}\\ \text{sulphide}}}{\overset{+}{Na}\overset{-}{SH}} \xrightarrow[\Delta]{C_2H_5OH/H_2O} \underset{\substack{\text{Thioalcohol}\\ \text{or Alkanethiol}}}{RSH} + NaX$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + NaSH \xrightarrow[\Delta]{C_2H_5OH/H_2O} \underset{\substack{\text{Ethyl thioalcohol}\\ \text{or Ethyl mercaptan}}}{C_2H_5SH} + NaBr$$

(iv) Reaction with alcoholic potassium cyanide and silver cyanide (Formation of alkane nitriles and isocyanides) : Alkyl cyanides are formed as the major product when alkyl halides are heated with alcoholic potassium cyanide (attack occurs through C). The nucleophile is CN^-.

$$\underset{\text{Alkyl halide}}{RX} + \overset{+}{K}\overset{-}{CN} \xrightarrow[\Delta]{\text{Alcohol}} \underset{\substack{\text{Alkane nitrile}\\ \text{(Alkyl cyanide)}}}{RCN} + KX$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + KCN \xrightarrow[\Delta]{\text{Alcohol}} \underset{\substack{\text{Propane nitrile}\\ \text{(Ethyl cyanide)}}}{C_2H_5CN} + KBr$$

Alkyl cyanides are used to prepare many other types of compounds.

(a) Carboxylic acids are obtained by hydrolysis of cyanides with mineral acids dil. HCl or alkalies.

$$\underset{\text{Alkyl cyanide}}{RC{\equiv}N} \xrightarrow[\text{Conc. HCl}]{H_2O} \underset{\text{Amide}}{RCONH_2} \xrightarrow[\text{Dil. HCl}]{H_2O} \underset{\text{Acid}}{RCOOH} + NH_3$$

$$\underset{\substack{\text{Ethane nitrile}\\ \text{(Methyl cyanide)}}}{CH_3C{\equiv}N} + 2H_2O \xrightarrow{\text{Dil. HCl}} \underset{\substack{\text{Ethanoic acid}\\ \text{(Acetic acid)}}}{CH_3COOH} + NH_3$$

(b) Amides are obtained by partial hydrolysis of cyanides with alk. H_2O_2 or conc. HCl.

$$\underset{\text{Alkyl cyanide}}{RC{\equiv}N} + H_2O \xrightarrow[\text{or Conc. HCl}]{\text{Alk. } H_2O_2} \underset{\text{Acidamide}}{RCONH_2}$$

$$\underset{\substack{\text{Ethane nitrile}\\ \text{(Acetonitrile)}}}{CH_3{-}C{\equiv}N} + H_2O \xrightarrow[\text{or } (H_2O_2{-}NaOH)]{\text{Conc. HCl}} \underset{\substack{\text{Ethanamide}\\ \text{(Acetamide)}}}{CH_3CONH_2}$$

(c) Primary amines are obtained by the reduction of cyanides with nascent hydrogen obtained by action of sodium and ethanol or with $LiAlH_4$ or with nickel **(Mendius reaction).**

$$\underset{\text{Alkyl cyanide}}{RC{\equiv}N} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Primary amine}}{RCH_2NH_2}$$

$$\underset{\substack{\text{Propane nitrile}\\ \text{(Ethyl cyanide)}}}{CH_3CH_2C{\equiv}N} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\substack{\text{Propan-1-amine}\\ (n\text{-Propylamine})}}{CH_3CH_2CH_2NH_2}$$

(d) Aldehydes are obtained by partial reduction of cyanides with $SnCl_2$ and HCl and then steam distilled **(Stephen's reaction).**

$$\underset{\text{Alkyl cyanide}}{R\text{—C}\equiv\text{N}} + 2\text{H} \xrightarrow[\text{HCl}]{\text{SnCl}_2} \underset{\text{Imine hydrochloride}}{R\text{—CH}=\text{NH}\cdot\text{HCl}} \xrightarrow[\text{H}^+]{\text{H}_2\text{O}} \underset{\text{Aldehyde}}{R\text{—CHO}} + \text{NH}_4\text{Cl}$$

When alkyl halides are heated with aqueous ethanolic silver cyanide, **alkyl isocyanides (carbylamines)** are formed as the major product (attack occurs through N). Isomeric alkyl cyanides are also formed in small amounts.

$$\underset{}{RX} + \underset{\text{(Alc.)}}{\text{AgCN}} \xrightarrow{\Delta} \underset{\text{Alkyl isocyanide}}{R\text{—N}\overset{\rightarrow}{=}\text{C}} + \text{Ag}X$$

$$\underset{\text{Bromoethane}}{\text{C}_2\text{H}_5\text{Br}} + \underset{\text{(Alc.)}}{\text{AgCN}} \xrightarrow{\Delta} \underset{\substack{\text{Ethyl isocyanide}\\ \text{(Ethylcarbylamine)}}}{\text{C}_2\text{H}_5\overset{+}{\text{N}}\equiv\overset{-}{\text{C}}} + \text{AgBr}$$

Alkyl isocyanides on reduction with sodium and alcohol gives secondary amines.

$$\underset{\text{Methyl isocyanide}}{\text{CH}_3\text{—N}\overset{\rightarrow}{=}\text{C}} + 4\text{H} \xrightarrow{\text{Na/C}_2\text{H}_5\text{OH}} \underset{\text{Dimethylamine}}{\text{CH}_3\text{—NH—CH}_3}$$

Explanation : The formation of cyanides or isocyanides from alkyl halides involves **nucleophilic substitution reaction.** The cyanide ion ($:\overset{-}{\text{C}}\text{N}$) is a resonance hybrid of the following structures:

$$\underset{\text{Resonating structure}}{[:\overset{-}{\text{C}}\equiv\text{N}: \longleftrightarrow :\text{C}=\overset{\bullet\bullet}{\text{N}}:^{-}]} \qquad \underset{\text{Hybrid structure}}{\overset{\delta^-}{\text{C}}\equiv\overset{\delta^-}{\text{N}}}$$

As is evident from the hybrid structure in the cyanide ion, both the carbon and the nitrogen atoms have a pair of electrons. Therefore, either the carbon or the nitrogen atom can act as the electron donor to the alkyl halide. Such a nucleophilic species which is capable of attacking the molecule through two sites is called **ambident nucleophiles.** Thus, CN^- ion is an ambident nucleophile.

Now alkali metal cyanides (KCN or NaCN) are predominantly **ionic.** Therefore, both carbon and nitrogen atoms are free to donate electron pair. Since C—C bond is relatively stronger than C—N bond, therefore, in this case attack mostly occurs through the carbon atom of the cyanide group and **alkyl cyanides** are the major product.

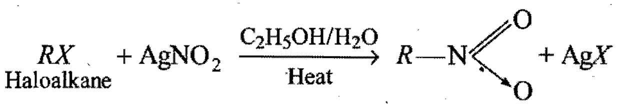
On the other hand, silver cyanide is predominantly **covalent.** Consequently only nitrogen electron pair is available for bond formation, and the attack mostly occurs through the nitrogen atom of cyanide group giving **alkyl isocyanides** as the major product.

(v) Reaction with potassium nitrite or silver nitrite (Formation of alkyl nitrite and nitro alkanes) : On heating an alkyl halide with potassium nitrite in an aqueous ethanolic solution, alkyl nitrite is obtained as the main product though some nitroalkane is also formed. It is because the bond between K—O is **ionic** in nature, therefore, negative charge on oxygen serves as attacking site. The nucleophile is —ONO^-.

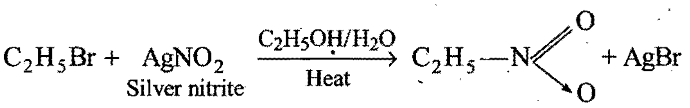
$$\underset{\text{Haloalkane}}{RX} + \text{K}^+\text{—O—N}=\text{O}^- \xrightarrow{\text{Heat}} \underset{\text{Alkyl nitrite}}{R\text{—O—N}=\text{O}} + \text{K}X$$

$$\underset{\text{Ethyl bromide}}{\text{C}_2\text{H}_5\text{Br}} + \text{K—O—N}=\text{O} \xrightarrow{\text{Heat}} \underset{\text{Ethyl nitrite}}{\text{C}_2\text{H}_5\text{—O—N}=\text{O}} + \text{KBr}$$

However, when alkyl halide is heated with silver nitrite in an aqueous ethanolic solution, nitroalkane is the main product. Some alkyl nitrite is also obtained. It is because the bond between Ag—O being **covalent.** The lone pair on nitrogen acts as attacking site for nucleophilic substitution.



Nitroalkane



Nitroethane

(vi) Reaction with ammonia (Formation of amines) : On heating with aqueous or alcoholic solution of ammonia in a sealed tube at 100°C, alkyl halides yield a mixture of amines and quaternary ammonium salt. The nucleophile is NH_2^- in the first reaction.

$$\text{C}_2\text{H}_5\text{Br} + \underset{\text{(Alc.)}}{\text{H—NH}_2} \xrightarrow{\text{Heat}} \underset{\text{Ethylamine (1°)}}{\text{C}_2\text{H}_5\text{NH}_2} + \text{HBr}$$

$$\underset{\text{Ethanamine (1°)}}{\text{C}_2\text{H}_5\text{NH}_2} + \text{Br C}_2\text{H}_5 \xrightarrow[\text{Heat}]{\text{C}_2\text{H}_5\text{OH}} \underset{\text{Diethylamine (2°)}}{\text{C}_2\text{H}_5\text{NHC}_2\text{H}_5} + \text{HBr}$$

$$\underset{\substack{\text{N-Ethyl}\\ \text{ethanamine (2°)}}}{(\text{C}_2\text{H}_5)_2\text{NH}} + \text{Br C}_2\text{H}_5 \xrightarrow[\text{Heat}]{\text{C}_2\text{H}_5\text{OH}} \underset{\text{Triethylamine (3°)}}{(\text{C}_2\text{H}_5)_3\text{N}} + \text{HBr}$$

$$\underset{\substack{\text{N,N-Diethyl}\\ \text{ethanamine (3°)}}}{(\text{C}_2\text{H}_5)_3\text{N}} + \text{Br C}_2\text{H}_5 \xrightarrow[\text{Heat}]{\text{C}_2\text{H}_5\text{OH}} \underset{\substack{\text{Tetraethylammonium}\\ \text{bromide (Quaternary salt)}}}{[(\text{C}_2\text{H}_5)_4\text{N}^+]\text{Br}^-}$$

This reaction is called **Hofmann ammonolysis** of alkyl halides.

(vii) Reaction with silver salts of carboxylic acids (Formation of esters) : On heating with silver salts of carboxylic acids in alcoholic solution, alkyl halides yield esters. The nucleophile is $R'\text{COO}^-$.

$$R'\text{COOAg} + XR \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}} \underset{\text{Ester}}{R'\text{COO}R} + \text{Ag}X$$

$$\underset{\text{Silver acetate}}{\text{CH}_3\text{COOAg}} + \text{Br C}_2\text{H}_5 \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}} \underset{\text{Ethyl acetate}}{\text{CH}_3\text{COOC}_2\text{H}_5} + \text{AgBr}$$

(viii) Reaction with sodium acetylide (Formation of higher alkynes) : Alkyl halides react with sodium alkynide (R—C≡C—Na) to form higher alkynes. The nucleophile is $\text{CH}\equiv\text{C}^-$.

$$RX + \underset{\text{Sod. acetylide}}{\overset{+}{\text{Na}}\text{—}\overset{-}{\text{C}}\equiv\text{CH}} \longrightarrow \underset{\text{Higher alkyne}}{R\text{—C}\equiv\text{CH}} + \text{Na}X$$

$$\underset{\text{Bromoethane}}{\text{CH}_3\text{CH}_2\text{Br}} + \text{NaC}\equiv\text{CH} \longrightarrow \underset{\text{But-1-yne}}{\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}} + \text{NaBr}$$

Note: Sodium alkynides are prepared when terminal alkynes react with sodamide (or sodium in liquid NH_3) at 197 K.

$$\underset{\text{Terminal alkyne}}{R—C{\equiv}CH} + NaNH_2 \xrightarrow[197\,K]{\text{Liq. }NH_3} \underset{\text{Sod. alkynide}}{R—C{\equiv}C—Na} + NH_3$$

(ix) Reaction with sodium or potassium sulphide (Formation of thioethers) : Alkyl halides react with sodium or potassium sulphide in alcoholic solution to form thioethers. The nucleophile is $—\bar{S}R$.

$$2RX + \underset{\text{Sod. sulphide}}{Na_2S} \xrightarrow[\text{Heat}]{C_2H_5OH/H_2O} \underset{\text{Thioether}}{R—S—R} + 2NaX$$

$$\underset{\text{Bromoethane}}{2C_2H_5Br} + Na_2S \xrightarrow[\text{Heat}]{C_2H_5OH/H_2O} \underset{\substack{\text{Ethyl thioethane}\\ \text{(Diethyl thioether)}}}{C_2H_5—S—C_2H_5} + 2NaBr$$

Thioethers can also be obtained by heating alkyl halides with alcoholic solution of sodium mercaptide ($NaSR'$), *i.e.*, metallic derivative of a thioalcohol.

$$RX + \underset{\substack{\text{Sodium}\\ \text{mercaptide}}}{\overset{+}{Na}—\bar{S}R'} \xrightarrow[\text{Heat}]{C_2H_5OH/H_2O} \underset{\text{Thioether}}{R—S—R'} + NaX$$

$$C_2H_5Br + \underset{\substack{\text{Sodium methyl}\\ \text{mercaptide}}}{NaSCH_3} \xrightarrow[\text{Heat}]{C_2H_5OH/H_2O} \underset{\substack{\text{Ethyl methyl thioether}\\ \text{(Methyl thioethane)}}}{C_2H_5—S—CH_3} + NaBr$$

(x) Reaction with halides (Formation of alkyl iodides): Alkyl chlorides react with sodium bromide or sodium iodide (in acetone or methanol) to form alkyl bromide or alkyl iodide. Similarly, alkyl bromides react with sodium iodide (in acetone or methanol) to form alkyl iodides.

$$\underset{\substack{\text{Alkyl}\\ \text{chloride}}}{RCl} + NaBr \xrightarrow{\text{Acetone}} \underset{\substack{\text{Alkyl}\\ \text{bromide}}}{RBr} \xrightarrow{NaI} \underset{\substack{\text{Alkyl}\\ \text{iodide}}}{RI}$$

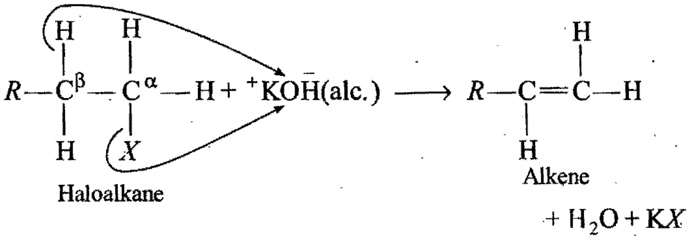
$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + NaI \xrightarrow{\text{Acetone}} \underset{\text{Ethyl iodide}}{C_2H_5I} + NaBr$$

This is called **Finkelstein reaction.**

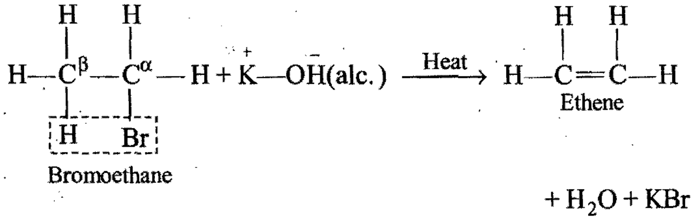
2. Elimination Reactions

(xi) Dehydrohalogenation (Formation of alkenes): When alkyl halides are boiled with a concentrated alcoholic potassium hydroxide, they undergo dehydrohalogenation ($—HX$) and alkenes are formed.

These reactions are called **β-elimination reactions** because the hydrogen atom of haloalkane which is eliminated comes from a β-carbon (*i.e.*, the carbon atom next to that which carries the halogen).



$$\underset{\text{Haloalkane}}{R—\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C^{\beta}}}—\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C^{\alpha}}}—H} + {}^{+}K\bar{O}H(\text{alc.}) \longrightarrow \underset{\text{Alkene}}{R—\underset{\underset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}—H} + H_2O + KX$$



$$\underset{\text{Bromoethane}}{H—\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C^{\beta}}}—\overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{C^{\alpha}}}—H} + \overset{+}{K}—\bar{O}H(\text{alc.}) \xrightarrow{\text{Heat}} \underset{\text{Ethene}}{H—\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}—H} + H_2O + KBr$$

In this reaction, ether is a by-product as potassium ethoxide is always present in small quantity.

$$C_2H_5Br + KOC_2H_5 \longrightarrow C_2H_5—O—C_2H_5 + KBr$$

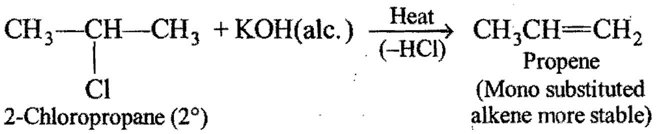
The reactivity of haloalkanes towards elimination reactions is:

Tertiary (3°) > Secondary (2°) > Primary (1°)

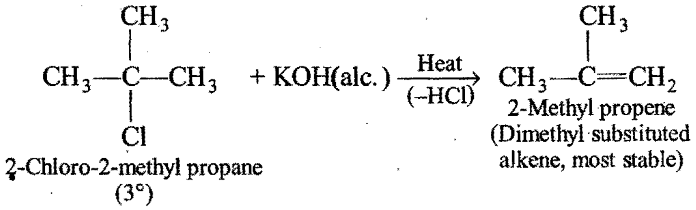
This is due to $+I$ effect of the alkyl groups which increases the polarity of $C—X$ bond.

This can also be explained on the basis of the stability of the alkene formed after dehydrohalogenation of haloalkanes. Tertiary alkyl halides on dehydrohalogenation form more substituted alkenes, which being more stable are formed at faster rate, while primary alkyl halides yield least substituted alkenes, which being less stable are formed at slower rate.

$$\underset{\text{Chloroethane (1°)}}{CH_3—CH_2Cl} + KOH(\text{alc.}) \xrightarrow[(-HCl)]{\text{Heat}} \underset{\substack{\text{Ethene}\\ \text{(Unsubstituted alkene,}\\ \text{least stable)}}}{H_2C{=}CH_2}$$

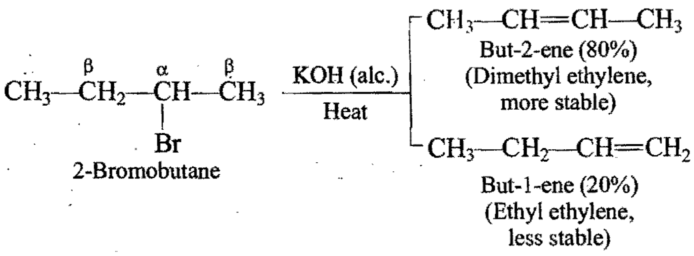


$$\underset{\text{2-Chloropropane (2°)}}{CH_3—\underset{\underset{Cl}{|}}{CH}—CH_3} + KOH(\text{alc.}) \xrightarrow[(-HCl)]{\text{Heat}} \underset{\substack{\text{Propene}\\ \text{(Mono substituted}\\ \text{alkene more stable)}}}{CH_3CH{=}CH_2}$$



$$\underset{\substack{\text{2-Chloro-2-methyl propane}\\ (3°)}}{CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}—CH_3} + KOH(\text{alc.}) \xrightarrow[(-HCl)]{\text{Heat}} \underset{\substack{\text{2-Methyl propene}\\ \text{(Dimethyl substituted}\\ \text{alkene, most stable)}}}{CH_3—\overset{\overset{CH_3}{|}}{C}{=}CH_2}$$

In the dehydrohalogenation of secondary and tertiary haloalkanes, when there is a possibility of formation of two isomers, the hydrogen atom is preferentially eliminated from the adjacent carbon atom with lesser number of hydrogen atoms. This generalization is known as **Saytzeff's rule,** *i.e.*, the more substituted alkene is more stable. For example,



$$\underset{\text{2-Bromobutane}}{CH_3—\overset{\beta}{CH_2}—\overset{\alpha}{\underset{\underset{Br}{|}}{CH}}—\overset{\beta}{CH_3}} \xrightarrow[\text{Heat}]{KOH(\text{alc.})} \begin{cases} \underset{\substack{\text{But-2-ene (80\%)}\\ \text{(Dimethyl ethylene,}\\ \text{more stable)}}}{CH_3—CH{=}CH—CH_3} \\ \underset{\substack{\text{But-1-ene (20\%)}\\ \text{(Ethyl ethylene,}\\ \text{less stable)}}}{CH_3—CH_2—CH{=}CH_2} \end{cases}$$

The **ease of dehydrohalogenation** is in the order:

Tertiary alkyl halide > Secondary alkyl halide > Primary alkyl halide

and the **ease of formation of alkenes** is:

$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > RCH{=}CHR > RCH{=}CH_2 > H_2C{=}CH_2$$

For different halogens it is in the order:

Iodide > Bromide > Chloride

(xii) Action of heat : Alkyl halides when heated above 300°C, tend to lose a molecule of hydrogen halide forming alkenes.

$$RCH_2CH_2X \xrightarrow{300°C} \underset{\text{Alkene}}{RCH{=}CH_2} + HX$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} \xrightarrow{300°C} \underset{\text{Ethene}}{H_2C{=}CH_2} + HBr$$

The decomposition follows the following order:

Iodide > Bromide > Chloride

(When same alkyl group is present)

and Tertiary > Secondary > Primary

(When same halogen is present).

3. Miscellaneous Reactions

(xiii) Reduction (Formation of alkanes): Alkanes are formed when alkyl halides are reduced with nascent hydrogen obtained by Zn/HCl or sodium and alcohol or Zn/Cu couple on alcohol or $LiAlH_4$ or palladium carbon or Mg-Hg/water or tributyl tin hydride (Bu_3SnH) etc.

$$RX + 2H \xrightarrow[200°C]{\text{Ni or Pd}} R{-}H + HX$$

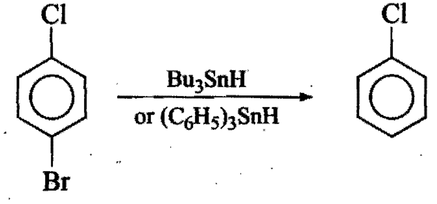
$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + 2H \xrightarrow[\text{Heat}]{\text{Ni or Pd}} \underset{\text{Ethane}}{C_2H_6} + HBr$$

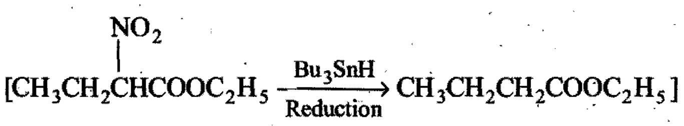
The reaction is used for the preparation of pure alkanes.

Metal catalyst such as Ni, Pd or Pt at 200 – 250°C, or HI in presence of red phosphorus at 150°C can also be used for the reduction of alkyl halides into corresponding alkanes.

Bu_3SnH is a selective reducing agent because it reduces only halides (and nitroalkanes) and has no effect on any other functional groups.

Among halides, $RI > RBr > RCl$. Due to this reason, the reagent tributyl tin hydride (Bu_3SnH) shows substantial selectivity towards polyhalogenated compounds.





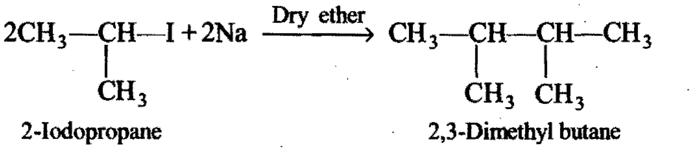
$$[CH_3CH_2\overset{\overset{\large NO_2}{|}}{C}HCOOC_2H_5 \xrightarrow[\text{Reduction}]{Bu_3SnH} CH_3CH_2CH_2COOC_2H_5]$$

(xiv) Wurtz reaction : An ether solution of an alkyl halide (preferably bromide or iodide) forms symmetrical alkanes when heated with metallic sodium.

$$\underset{\text{Alkyl halide}}{2RX} + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R{-}R} + 2NaX$$

$$\underset{\text{Methyl iodide}}{CH_3\boxed{-I \;+2Na+I}-CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaI$$

$$\underset{\text{Bromoethane}}{2C_2H_5Br} + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{C_2H_5{-}C_2H_5} + 2NaBr$$



$$\underset{\text{2-Iodopropane}}{2CH_3{-}\underset{\underset{\large CH_3}{|}}{C}H{-}I} + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{2,3-Dimethyl butane}}{CH_3{-}\underset{\underset{\large CH_3}{|}}{C}H{-}\underset{\underset{\large CH_3}{|}}{C}H{-}CH_3} + 2NaI$$

Tertiary halides do not undergo this reaction.

Unsymmetrical alkanes can be conveniently prepared by **Corey-House reaction.**

(xv) Reaction with magnesium : Alkyl halides form **Grignard reagents** when treated with dry magnesium powder in dry ether.

$$RX + \underset{\text{(Powder)}}{\text{Dry Mg}} \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R{-}Mg{-}X}$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{(Dry)}}{Mg} \xrightarrow{\text{Dry ether}} \underset{\text{Ethyl magnesium bromide}}{C_2H_5MgBr}$$

Grignard reagents are used for making a very large number of organic compounds. Reactivity order is $RI > RBr > RCl$.

(xvi) Reaction with other metals : Organometallic compounds are formed.

(a) When heated with zinc powder in ether, alkyl halides form dialkyl zinc compounds. These are called **Frankland reagents.**

$$2C_2H_5Br + 2Zn \xrightarrow[\text{Heat}]{\text{Ether}} (C_2H_5)_2Zn + ZnBr_2$$

(b) When heated with lead-sodium alloy, ethyl bromide gives tetra ethyl lead **(TEL)** which is used as antiknock compound in petrol.

$$4C_2H_5Br + 4Pb(Na) \xrightarrow{\text{Dry ether}} \underset{\text{TEL}}{(C_2H_5)_4Pb} + 4NaBr + 3Pb$$

(c) Alkyl halides form dialkyl mercury compounds when treated with sodium amalgam.

$$\underset{\text{Bromoethane}}{2C_2H_5Br} + Na{-}Hg \longrightarrow \underset{\text{Diethyl mercury}}{(C_2H_5)_2Hg} + NaBr$$

(d) Reaction with Lithium : Alkyl halides react with lithium in dry ether to form alkyl lithiums.

$$RX + 2Li \xrightarrow{\text{Ether}} R{-}Li + LiX$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + 2Li \longrightarrow \underset{\text{Ethyl lithium}}{C_2H_5{-}Li} + LiBr$$

$$\underset{\text{Alkyl lithium}}{2R{-}Li} + CuI \longrightarrow \underset{\text{Lithium dialkyl copper}}{LiR_2Cu}$$

Alkyl lithiums are similar in properties with Grignard reagents. These are reactive reagents also and serve as strong bases.

Alkyl halide reacts with lithium dialkyl cuprate (R_2CuLi) to form unsymmetrical alkanes **(Corey-House synthesis).**

$$R_2CuLi + R'X \longrightarrow \underset{\text{Alkane}}{R{-}R'} + R{-}Cu + LiX$$

$$\underset{\text{Lithium dimethyl cuprate}}{(CH_3)_2CuLi} + \underset{\text{Ethyl bromide}}{Br\,CH_2CH_3} \longrightarrow \underset{\text{Propane}}{CH_3CH_2CH_3} + CH_3Cu + LiBr$$

(xvii) Friedel-Crafts reaction : Alkyl halides react with benzene in presence of anhydrous aluminium halides to form a homologue of benzene.

$$\underset{\text{Benzene}}{C_6H_6} + RCl \xrightarrow{AlCl_3(\text{anhyd.})} \underset{\text{Alkyl benzene}}{C_6H_5R} + HCl$$

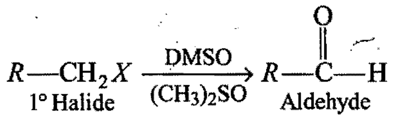
$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Bromoethane}}{C_2H_5Br} \xrightarrow{AlBr_3(\text{anhyd.})} \underset{\text{Ethyl benzene}}{C_6H_5C_2H_5} + HBr$$

(xviii) Substitution (Halogenation) : Alkyl halides undergo further halogenation in presence of sunlight, heat energy or peroxide.

$$C_2H_5Br \xrightarrow[h\nu]{Br_2} C_2H_4Br_2 \xrightarrow[h\nu]{Br_2} C_2H_3Br_3 \ldots$$

(xix) Oxidation reaction : Only primary and secondary alkyl halides undergo oxidation while tertiary alkyl halide does not.

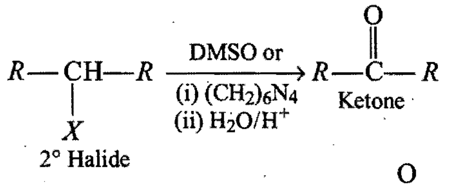
Primary (1°) alkyl halides on oxidation with dimethyl sulphoxide, $(CH_3)_2SO(DMSO)$ give aldehydes **(Swern oxidation).**



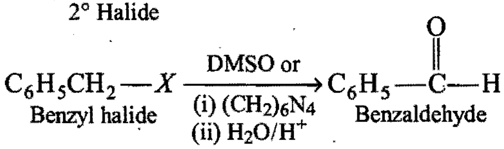
$$\underset{1°\text{ Halide}}{R{-}CH_2X} \xrightarrow[(CH_3)_2SO]{DMSO} \underset{\text{Aldehyde}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}$$

Oxidation can also be done with hexamethylene tetramine, $(CH_2)_6N_4$ followed by hydrolysis.

Secondary (2°) alkyl halides give ketone in this reaction.



$$\underset{2°\text{ Halide}}{R{-}\underset{\underset{\displaystyle X}{|}}{CH}{-}R} \xrightarrow[\substack{(i)\ (CH_2)_6N_4\\ (ii)\ H_2O/H^+}]{DMSO\text{ or}} \underset{\text{Ketone}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R}$$



$$\underset{\text{Benzyl halide}}{C_6H_5CH_2{-}X} \xrightarrow[\substack{(i)\ (CH_2)_6N_4\\ (ii)\ H_2O/H^+}]{DMSO\text{ or}} \underset{\text{Benzaldehyde}}{C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}$$

Oxidation of benzyl halides with $(CH_2)_6N_4$ is known as **Sommelet aldehyde synthesis.**

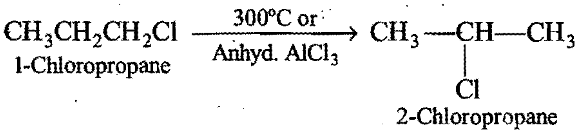
(a) Reactivity for oxidation reaction depends on the number of hydrogen atoms on alpha (α-) carbon of alkyl halides:

Reactivity ∝ number of α-hydrogen

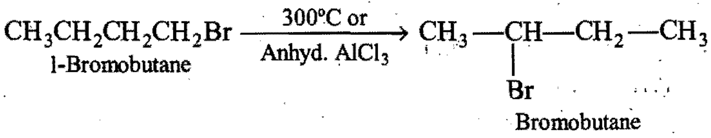
(b) Reactivity of different halides in decreasing order is as follows:

Benzyl halides > Allyl halides > Alkyl halides

(xx) Isomerisation: Haloalkanes on heating at 300°C or in presence of anhydrous $AlCl_3$ at low temperature undergo molecular rearrangement to form an isomeric haloalkane. For example,



$$\underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} \xrightarrow[\text{Anhyd. }AlCl_3]{300°C\text{ or}} \underset{\text{2-Chloropropane}}{CH_3{-}\underset{\underset{\displaystyle Cl}{|}}{CH}{-}CH_3}$$



$$\underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow[\text{Anhyd. }AlCl_3]{300°C\text{ or}} \underset{\text{Bromobutane}}{CH_3{-}\underset{\underset{\displaystyle Br}{|}}{CH}{-}CH_2{-}CH_3}$$

Uses : (i) Lower members are used as anaesthetic agent, refrigerant and solvents.

(ii) Alkyl halides are used as alkylating agents, *i.e.*, to introduce the alkyl group in a molecule.

(iii) Alkyl halides are starting materials for the preparation of many organic compounds. Ethyl chloride is employed for the manufacture of tetraethyl lead, $Pb(C_2H_5)_4$, used as antiknock in gasoline for running automobiles.

8.5 DI-HALOGEN DERIVATIVES

General Methods of Preparation

(i) Alkylidene halides or gem-dihalides or 1,1-dihaloalkanes : The given general methods are used for the preparation of gem-dihalides:

(a) By the action of phosphorus pentahalides on aldehydes and ketones : Two halogen atoms can be added to same carbon atom when aldehydes or ketones are treated with phosphorus pentahalide.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + PCl_5 \longrightarrow \underset{\substack{\text{1,1-Dichloroethane}\\ \text{(Ethylidene chloride)}}}{CH_3CHCl_2} + POCl_3$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + PCl_5 \longrightarrow \underset{\substack{\text{2,2-Dichloropropane}\\ \text{(Isopropylidene chloride)}}}{CH_3CCl_2CH_3} + POCl_3$$

(b) From alkynes : Addition of halogen acids to alkynes form gem-dihalides. For each molecule of an alkyne, two molecules of halogen acid are required, *i.e.*, triple bond is first converted into double bond and then double bond into single bond.

$$\underset{\text{Acetylene}}{HC{\equiv}CH} + HCl \rightarrow \underset{\text{Vinyl chloride}}{H_2C{=}CH{-}Cl} \xrightarrow{+HCl} \underset{\text{1,1-Dichloroethane}}{H_3C{-}CHCl_2}$$

$$\underset{\text{Acetylene}}{HC{\equiv}CH} + 2HBr \longrightarrow \underset{\substack{\text{1,1-Dibromoethane}\\ \text{(Ethylidene bromide)}}}{CH_3CHBr_2}$$

$$\underset{\text{Propyne}}{CH_3C{\equiv}CH} + 2HCl \longrightarrow \underset{\substack{\text{2,2-Dichloropropane}\\ \text{(Isopropylidene chloride)}}}{CH_3CCl_2CH_3}$$

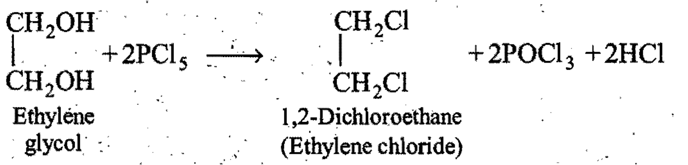
ne halides or vic-dihalides or 1,2-dihalo- These may be obtained by following methods:

y the addition of halogens to alkenes :, Addition occurs on the two carbon atoms linked by a double bond.

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + Cl_2 \longrightarrow \underset{\substack{\text{1,2-Dichloroethane}\\ \text{(Ethylene chloride)}}}{CH_2ClCH_2Cl}$$

$$CH_3CH{=}CH_2 + Br_2 \longrightarrow \underset{\substack{\text{1,2-Dibromopropane}\\ \text{(Propylene bromide)}}}{CH_3CHBrCH_2Br}$$

(b) By the action of phosphorus halides on glycols : Glycols or dihydric alcohols react with phosphorus halides or halogen acids or $SOCl_2$ to form vic-dihalides.



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + 2PCl_5 \longrightarrow \begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} + 2POCl_3 + 2HCl$$

Ethylene glycol → 1,2-Dichloroethane (Ethylene chloride)

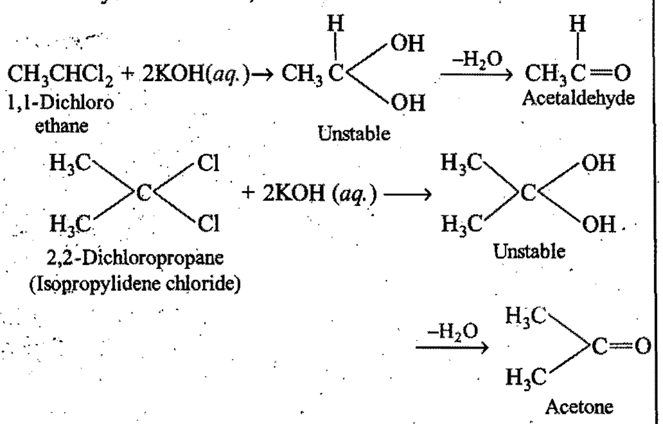
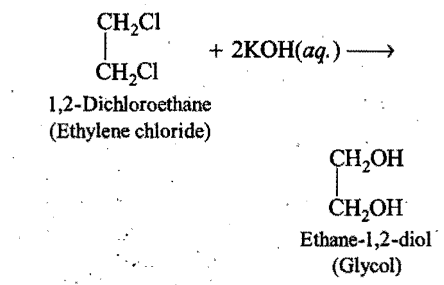
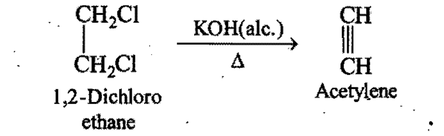
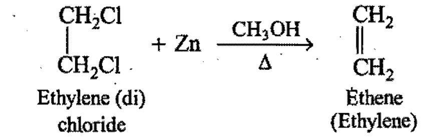
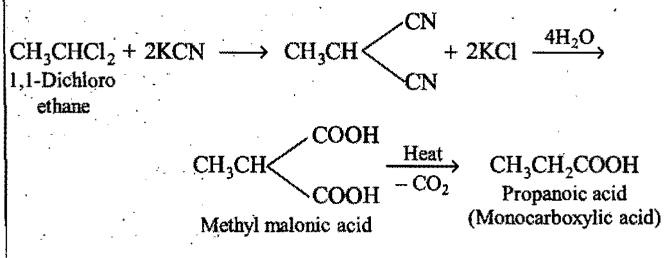
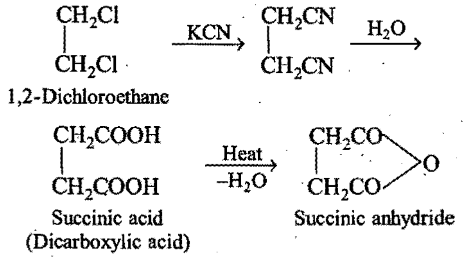
Note : Alkylidene or alkylene iodides are prepared by halide exchange reaction.

Physical properties : (i) Dihalogen derivatives of lower alkanes are colourless, sweet smelling liquids. Higher homologues are solids.

(ii) They are insoluble in water but soluble in organic solvents.

(iii) They are heavier than water. The relative density of methylene iodide (CH_2I_2) is 3.325 which is the heaviest liquid known (except mercury).

(iv) They have high boiling points. Their boiling and melting points show regular gradation.

	Property	Alkylidene halides (Gem-dihalides)	Alkylene halides (Vic-dihalides)
1.	Hydrolysis (With *aq*. KOH)	Form aldehydes or ketones,  $CH_3CHCl_2 + 2KOH(aq.) \rightarrow CH_3CH(OH)_2 \xrightarrow{-H_2O} CH_3CH{=}O$ 1,1-Dichloro ethane; Unstable; Acetaldehyde 2,2-Dichloropropane (Isopropylidene chloride) + 2KOH (*aq.*) ⟶ Unstable $\xrightarrow{-H_2O}$ Acetone	Form glycols,  $\begin{matrix} CH_2Cl \\ \vert \\ CH_2Cl \end{matrix} + 2KOH(aq.) \longrightarrow \begin{matrix} CH_2OH \\ \vert \\ CH_2OH \end{matrix}$ 1,2-Dichloroethane (Ethylene chloride); Ethane-1,2-diol (Glycol)
2.	Reaction with alcoholic KOH (Dehydrohalogenation)	Form alkynes, $CH_3CHCl_2 \xrightarrow[\Delta]{KOH\ (alc.)} HC\equiv CH$ 1,1-Dichloroethane; Acetylene	Form alkynes,  $\begin{matrix} CH_2Cl \\ \vert \\ CH_2Cl \end{matrix} \xrightarrow[\Delta]{KOH(alc.)} \begin{matrix} CH \\ \vert\vert\vert \\ CH \end{matrix}$ 1,2-Dichloro ethane; Acetylene
3.	Reaction with Zn dust in methanol	Form alkenes, $CH_3CHCl_2 + Zn \xrightarrow[\Delta]{CH_3OH} H_2C{=}CH_2$ Ethylidene (di) chloride; Ethene (Ethylene)	Form alkenes,  $\begin{matrix} CH_2Cl \\ \vert \\ CH_2Cl \end{matrix} + Zn \xrightarrow[\Delta]{CH_3OH} \begin{matrix} CH_2 \\ \vert\vert \\ CH_2 \end{matrix}$ Ethylene (di) chloride; Ethene (Ethylene)
4.	Reaction with alc. KCN followed by hydrolysis and heating the product	 $CH_3CHCl_2 + 2KCN \longrightarrow CH_3CH(CN)_2 + 2KCl \xrightarrow{4H_2O} CH_3CH(COOH)_2 \xrightarrow[-CO_2]{Heat} CH_3CH_2COOH$ 1,1-Dichloro ethane; Methyl malonic acid; Propanoic acid (Monocarboxylic acid)	 $\begin{matrix} CH_2Cl \\ \vert \\ CH_2Cl \end{matrix} \xrightarrow{KCN} \begin{matrix} CH_2CN \\ \vert \\ CH_2CN \end{matrix} \xrightarrow{H_2O} \begin{matrix} CH_2COOH \\ \vert \\ CH_2COOH \end{matrix} \xrightarrow[-H_2O]{Heat}$ Succinic anhydride 1,2-Dichloroethane; Succinic acid (Dicarboxylic acid); Succinic anhydride

Chemical properties : Chemically, alkylidene halides are less reactive while alkylene halides have nearly the same reactivity as alkyl halides. The important chemical properties are given ahead in comparative form.

8.6 TRI-HALOGEN DERIVATIVES

Chloroform or Trichloromethane ($CHCl_3$)

It is an important trihalogen derivative of methane. It was discovered by Liebig in 1831 and its name chloroform was proposed by Dumas as it gave formic acid on hydrolysis. In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage.

Preparation : 1. Chloroform is prepared both in the laboratory and on large scale by distilling ethyl alcohol or acetone with bleaching powder and water. The yield is about 40%. The available chlorine of bleaching powder serves both as oxidising as well as chlorinating agent.

$$\underset{\text{Bleaching powder}}{CaOCl_2} + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

From alcohol : (i) Alcohol is first oxidised to acetaldehyde by chlorine.

$$[Cl_2 + H_2O \longrightarrow 2HCl + O]$$

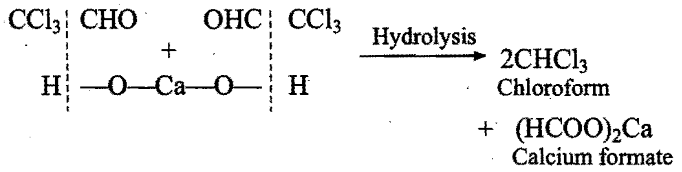
$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + Cl_2 \xrightarrow{\text{Oxidation}} \underset{\text{Acetaldehyde}}{CH_3CHO} + 2HCl$$

(ii) Acetaldehyde then reacts with chlorine to form chloral (trichloro acetaldehyde).

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3Cl_2 \xrightarrow{\text{Chlorination}} \underset{\substack{\text{Trichloroacetaldehyde}\\ \text{(Chloral)}}}{CCl_3CHO} + 3HCl$$

[So, Cl_2 acts both as an oxidising (i) and chlorinating agent (ii)]

(iii) Chloral thus formed, is hydrolysed by calcium hydroxide.



$$CCl_3CHO + H\text{—O—Ca—O—}H + OHC\,CCl_3 \xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium formate}}{(HCOO)_2Ca}$$

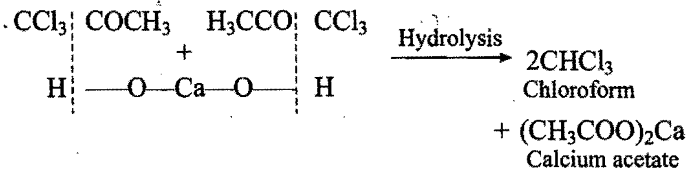
or

$$[2CCl_3CHO + Ca(OH)_2 \xrightarrow{\text{Hydrolysis}} 2CHCl_3 + (HCOO)_2Ca]$$

From acetone : (i) Acetone first reacts with chlorine to form trichloroacetone.

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3Cl_2 \xrightarrow{\text{Chlorination}} \underset{\text{Trichloroacetone}}{CCl_3COCH_3} + 3HCl$$

(ii) Trichloroacetone is then hydrolysed by calcium hydroxide.



$$CCl_3COCH_3 + H\text{—O—Ca—O—}H + H_3CCO\,CCl_3 \xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca}$$

2. From carbon tetrachloride : Now-a-days, chloroform is obtained on a large scale by the reduction of carbon tetrachloride with iron fillings and water. This method is used in countries like USA.

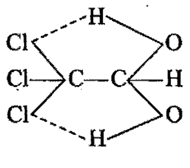
$$CCl_4 + 2H \xrightarrow[\text{Heat}]{Fe/H_2O} CHCl_3 + HCl$$

This chloroform is not pure and used mainly as a solvent.

3. Pure chloroform : It is obtained by distilling chloral hydrate with concentrated sodium hydroxide solution.

$$\underset{\text{Chloral hydrate}}{CCl_3CH(OH)_2} + NaOH \longrightarrow CHCl_3 + HCOONa + H_2O$$

Note : Chloral hydrate is a stable compound inspite of the fact that two —OH groups are linked to the same carbon atom. This is due to the fact that intramolecular hydrogen bonding exists in the molecule between chlorine and hydrogen atom of —OH group.



Physical properties : (i) It is a sweet smelling colourless liquid.

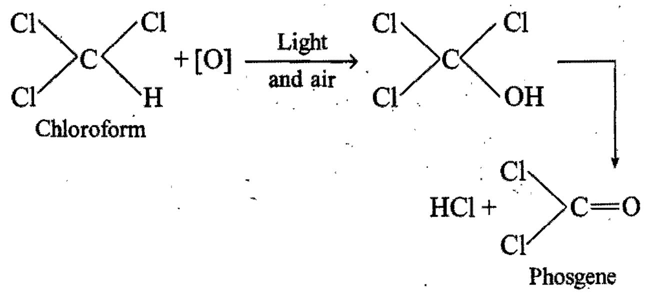
(ii) It is heavy liquid. Its density is 1.485. It boils at 61°C.

(iii) It is practically insoluble in water but dissolves in organic solvents such as alcohol, ether, etc.

(iv) It is non-inflammable but its vapours may burn with green flame.

(v) It brings temporary unconsciousness when vapours are inhaled for sufficient time.

Chemical properties : (i) Oxidation : When exposed to sunlight and air, it slowly decomposes into phosgene and hydrogen chloride.



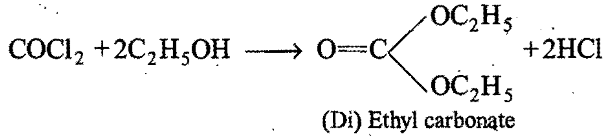
or $\left[CHCl_3 + \frac{1}{2}O_2 \xrightarrow[\text{and air}]{\text{Light}} COCl_2 + HCl\right]$

or $4CHCl_3 + 3[O]_2 \xrightarrow{\text{Sunlight}} 4COCl_2 + 2Cl_2 + 2H_2O$

Phosgene is extremely poisonous gas. To use chloroform as an anaesthetic agent, it is necessary to prevent the above reaction. The following two precautions are taken when chloroform is stored.

(a) It is stored in dark blue or brown coloured bottles which are filled upto the brim.

(b) 1% ethyl alcohol is added. This retards the oxidation and converts the phosgene formed into harmless ethyl carbonate.



$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{(Di) Ethyl carbonate}}{O{=}C(OC_2H_5)_2} + 2HCl$$

(ii) Reduction : When reduced with zinc and hydrochloric acid in presence of ethyl alcohol, it forms methylene chloride.

$$\underset{\text{Chloroform}}{CHCl_3} + 2H \xrightarrow[\text{(Alc.)}]{Zn/HCl} \underset{\substack{\text{Methylene}\\ \text{chloride}}}{CH_2Cl_2} + HCl$$

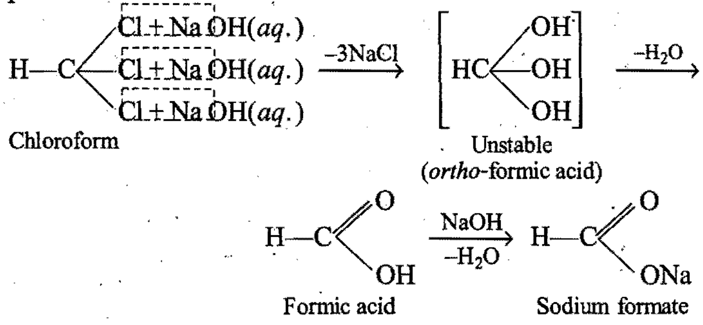
When reduced with zinc dust and water, methane is the main product.

$$CHCl_3 + 6H \xrightarrow{Zn/H_2O} \underset{\text{Methane}}{CH_4} + 3HCl$$

(iii) Chlorination : Chloroform reacts with chlorine in presence of diffused sunlight or UV light to form carbon tetrachloride.

$$\underset{\text{Chloroform}}{CHCl_3} + Cl_2 \xrightarrow{\text{UV light}} \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$$

(iv) Hydrolysis : Chloroform is hydrolysed when treated with hot aqueous solution of sodium hydroxide or potassium hydroxide. The final product is sodium or potassium salt of formic acid.



$$[\text{So, } CHCl_3 + 4KOH(aq.) \xrightarrow{\text{Hydrolysis}} HCOOK + 3KCl + 2H_2O]$$

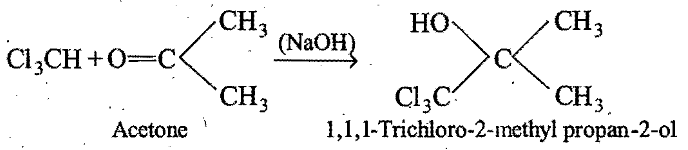
(v) Nitration : The hydrogen of the chloroform is replaced by nitro group when it is treated with concentrated nitric acid. The product formed is chloropicrin or trichloro nitro methane or nitro chloroform. It is a liquid, poisonous and used as an insecticide and a war gas (tear gas).

$$CHCl_3 + \underset{\text{Nitric acid}}{HONO_2} \longrightarrow \underset{\text{Chloropicrin}}{CNO_2Cl_3} + H_2O$$

(vi) Heating with silver powder : Acetylene is formed when chloroform is heated at high temperature with silver powder.

$$\underset{\text{Chloroform}}{H-C-\boxed{Cl_3 + 6Ag + Cl_3}-C-H} \xrightarrow{\Delta} \underset{\text{Acetylene}}{HC\equiv CH} + 6AgCl$$

(vii) Condensation with acetone : Chloroform condenses with acetone on heating in presence of caustic alkalies. The product formed is a colourless crystalline solid called chloretone and is used as a **hypnotic** (drug) in medicine.

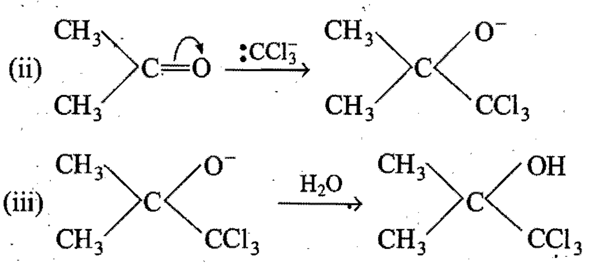


1,1,1-Trichloro-2-methyl propan-2-ol
(Chloretone)

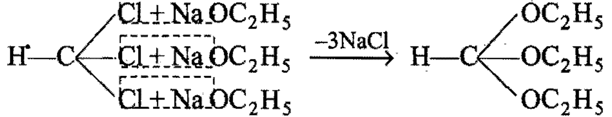
Mechanism :

(i) $CHCl_3 + OH^- \longrightarrow :CCl_3^- + H_2O$

$(:CCl_3^- \longrightarrow :CCl_2 + Cl^-)$

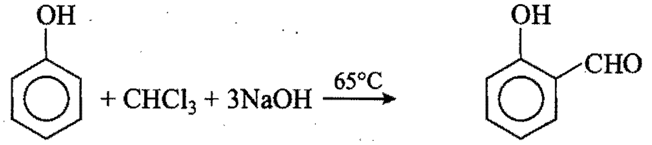


(viii) Reaction with sodium ethoxide : When heated with sodium ethoxide, ethyl *ortho*-formate is formed.



Ethyl *ortho*-formate

(ix) Reimer-Tiemann reaction : Chloroform reacts with phenol when heated in presence of sodium hydroxide or potassium hydroxide. The product formed is salicylaldehyde.



Phenol

o-Hydroxy benzaldehyde
(Salicylaldehyde)

$+ 3NaCl + 2H_2O$

(x) Carbylamine reaction (isocyanide test) : This reaction is actually a **test of primary amines.** Chloroform, when heated with primary amine in presence of alcoholic potassium hydroxide forms a derivative called isocyanide (carbylamine) which has a very offensive smell.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH \xrightarrow{\text{(Warm)}} \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

$$\underset{\text{1° Amine}}{RNH_2} + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} \underset{\substack{\text{Carbylaminoalkane}\\ \text{(Alkyl isonitrile)}}}{RNC} + 3KCl + 3H_2O$$

This reaction is also used for the test of chloroform.

(xi) α-Elimination reaction: Chloroform undergoes α-elimination reaction to give dichlorocarbene (singlet) which is a reaction intermediate.

$$CHCl_3 \xrightarrow[\Delta]{\text{Alc. KOH}} \underset{\text{Dichloro-carbene}}{:CCl_2} + \bar{Cl} + HOH$$

Uses : (i) It is used as a solvent for fats, waxes, rubber, resins, iodine, etc.

(ii) It is used for the preparation of chloretone (a drug) and chloropicrin (insecticide).

(iii) It is used in laboratory for the test of primary amines, iodides and bromides.

(iv) It can be used as anaesthetic but due to harmful effects it is not used these days for this purpose. It causes liver damage when inhaled in excess (SO is CCl_4).

(v) It may be used to prevent putrefaction of organic materials, *i.e.*, in the preservation of anatomical species.

Tests of chloroform : (i) It gives isocyanide test (carbylamine test).

(ii) It forms silver mirror with Tollens' reagent.

(iii) Pure chloroform does not give white precipitate with silver nitrate.

8.7 IODOFORM OR TRI-IODOMETHANE (CHI_3)

Iodoform resembles chloroform in the methods of preparation and properties.

Laboratory preparation : Iodoform is prepared in the laboratory by heating ethanol or acetone with iodine and alkali.

(a) With ethanol: The reactions taking place are:

$$2NaOH + I_2 \longrightarrow \underset{\text{Sodium hypoiodite}}{NaOI} + NaI + H_2O$$

(i) Oxidation

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + NaOI \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + NaI + H_2O$$

(ii) Iodination

$$CH_3CHO + 3NaOI \longrightarrow \underset{\text{Iodal}}{CI_3CHO} + 3NaOH$$

(iii) Hydrolysis

$$\underset{\text{Tri-iodoacetaldehyde}}{CI_3CHO} + NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium formate}}{HCOONa}$$

(b) With acetone : (i) Iodination

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3NaOI \longrightarrow \underset{\text{Tri-iodoacetone}}{CI_3COCH_3} + NaOH$$

(ii) Hydrolysis

$$CI_3COCH_3 + NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium acetate}}{CH_3COONa}$$

The complete reaction may be written as:

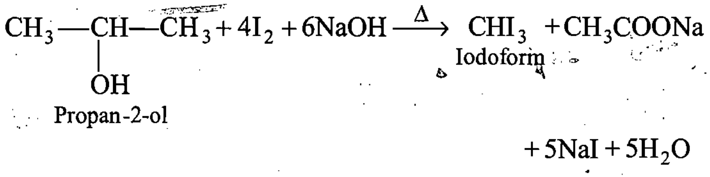
$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3\downarrow} + HCOONa + 5NaI + 5H_2O$$

Sodium carbonate can be used in place of KOH or NaOH.

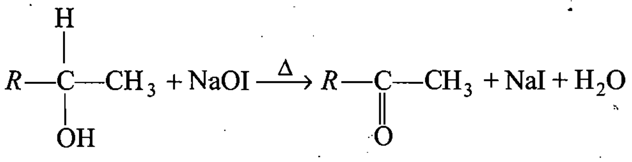
$$\underset{\text{Acetone}}{CH_3COCH_3} + 3I_2 + 2Na_2CO_3 \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3\downarrow} + 3NaI + CH_3COONa + 2CO_2$$

These reactions are called **iodoform reactions.**

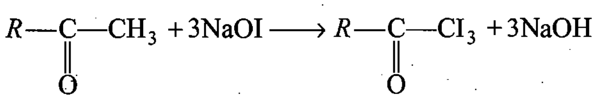
The **iodoform test** is exhibited by ethyl alcohol, acetaldehyde, acetone, those alcohols which possess —CHOH—CH_3 group (2-ols) and methyl ketones etc.



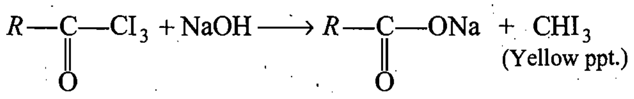
$$\underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 5NaI + 5H_2O$$



$$R-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 + NaOI \xrightarrow{\Delta} R-\underset{\underset{O}{\|}}{C}-CH_3 + NaI + H_2O$$

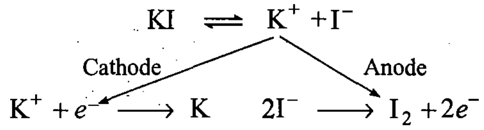


$$R-\underset{\underset{O}{\|}}{C}-CH_3 + 3NaOI \longrightarrow R-\underset{\underset{O}{\|}}{C}-CI_3 + 3NaOH$$



$$R-\underset{\underset{O}{\|}}{C}-CI_3 + NaOH \longrightarrow R-\underset{\underset{O}{\|}}{C}-ONa + \underset{\text{(Yellow ppt.)}}{CHI_3}$$

Industrial preparation : Iodoform is prepared on large scale by electrolysis of a solution containing ethanol, sodium carbonate and potassium iodide. The iodine set free, combine with ethanol in presence of alkali to form iodoform. The electrolysis carried out in presence of CO_2 and the temperature is maintained at 60–70°C.



$$KI \rightleftharpoons K^+ + I^-$$

$$K^+ + e^- \longrightarrow K \qquad 2I^- \longrightarrow I_2 + 2e^-$$

$$K + H_2O \longrightarrow KOH + \frac{1}{2}H_2$$

KOH is neutralised by CO_2

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + 4I_2 + 3Na_2CO_3 \longrightarrow CHI_3 + HCOONa + 5NaI + 3CO_2 + 2H_2O$$

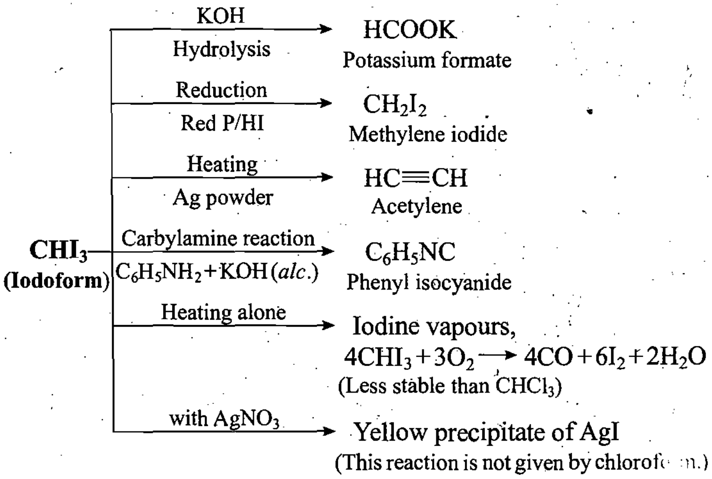
Properties : (i) It is a yellow crystalline solid.

(ii) It has a pungent characteristic odour.

(iii) It is insoluble in water but soluble in organic solvents such as alcohol, ether, etc.

(iv) It has melting point 119°C. It is steam volatile.

Reactions of Iodoform



Uses : Iodoform is extensively used as an antiseptic for dressing of wounds; but the antiseptic action is due to the liberation of free iodine and not due to iodoform itself. When it comes in contact with organic matter, iodine is liberated which is responsible for antiseptic properties.

Tests of Iodoform

1. **With $AgNO_3$:** CHI_3 gives a yellow precipitate of AgI.

2. **Carbylamine reaction :** CHI_3 on heating with primary amine and alcoholic KOH solution, gives an offensive smell of isocyanide (carbylamine).

3. Iodoform reaction : With I_2 and NaOH or I_2 and Na_2CO_3, the iodoform test is mainly given by ethyl alcohol **(CH_3CH_2OH)**, acetaldehyde **($CH_3-\overset{\overset{O}{\|}}{C}-H$)**, α-methyl ketone or 2-one ($-\overset{\overset{O}{\|}}{C}-CH_3$), secondary alcohols or 2-ol ($-\overset{\overset{OH}{|}}{CH}-CH_3$) and secondary alkyl halide at C_2 ($-\overset{\overset{Cl}{|}}{CH}-CH_3$). Also lactic acid **($CH_3-CHOH-COOH$)**, pyruvic acid **($CH_3-\overset{\overset{O}{\|}}{C}-COOH$)**, methyl phenyl ketone ($C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$) and 2-amino alkanes ($R-\underset{\underset{NH_2}{|}}{CH}-R$) give this test.

8.8 CARBON TETRACHLORIDE OR TETRACHLOROMETHANE, (CCl_4)

It is the most important tetrahalogen derivative of methane.

Manufacture : (i) From methane : Chlorination of methane with excess of chlorine at 400°C yields impure carbon tetrachloride.

$$\underset{}{CH_4} + \underset{(Excess)}{4Cl_2} \xrightarrow{400°C} CCl_4 + 4HCl$$

Methane used in this process is obtained from natural gas.

(ii) From carbon disulphide : Chlorine reacts with carbon disulphide in presence of catalysts like iron, iodine, aluminium chloride or antimony pentachloride.

$$CS_2 + 3Cl_2 \xrightarrow[\text{(Catalyst)}]{AlCl_3 \text{ or } SbCl_5} CCl_4 + \underset{\substack{\text{Sulphur}\\ \text{monochloride}}}{S_2Cl_2}$$

S_2Cl_2 further reacts with CS_2 to form more of carbon tetrachloride.

$$CS_2 + 2S_2Cl_2 \xrightarrow{AlCl_3} CCl_4 + 6S$$

Carbon tetrachloride is obtained by fractional distillation. It is washed with sodium hydroxide and then distilled to get a pure sample.

(iii) From propane : Propane is reacted with chlorine at about 400°C and at a pressure of 70 –100 atmosphere.

$$\underset{\text{Propane}}{C_3H_8} + 9Cl_2 \xrightarrow[\text{Pressure}]{\text{Heat}} \underset{\substack{\text{Carbon}\\ \text{tetrachloride}\\ \text{(Liquid)}}}{CCl_4} + \underset{\substack{\text{Hexachloro-}\\ \text{ethane}\\ \text{(Solid)}}}{C_2Cl_6} + 8HCl$$

Physical properties : (i) It is a colourless liquid having characteristic smell.

(ii) It is non-inflammable and poisonous. It has boiling point 77°C.

(iii) It is insoluble in water but soluble in organic solvents.

(iv) It is an excellent solvent for oils, fats, waxes and greases.

Chemical properties : Carbon tetrachloride is less reactive and inert to most organic reagents. However, the following reactions are observed.

(i) Reaction with steam (oxidation) : Carbon tetrachloride vapours react with steam above 500°C to form phosgene, a poisonous gas.

$$CCl_4 + H_2O \xrightarrow[\text{Steam, 500°C}]{\text{Superheated}} \underset{\text{Phosgene}}{COCl_2} + 2HCl$$

(ii) Reduction : It is reduced by moist iron filling into chloroform.

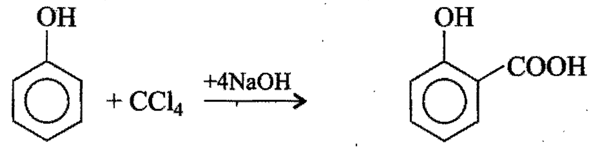
$$CCl_4 + 2H \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

(iii) Hydrolysis : On heating with aqueous potassium hydroxide it forms carbon dioxide which combines with potassium hydroxide to give KCl and potassium carbonate (inorganic salts).

$$CCl_4 + 4KOH \xrightarrow{-4KCl} \underset{\text{Unstable}}{[C(OH)_4]} \xrightarrow{-2H_2O} CO_2$$

$$\xrightarrow{2KOH} K_2CO_3 + H_2O$$

(iv) Reaction with phenol (Reimer-Tiemann reaction) : It combines with phenol in presence of sodium hydroxide to form salicylic acid.



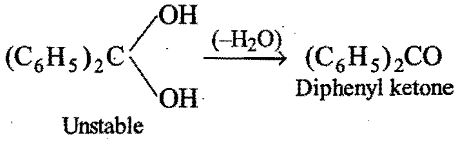
Phenol

o-Hydroxy benzoic acid (Salicylic acid)

$$+ 4NaCl + 2H_2O$$

(v) Friedel-Crafts reaction: Benzene on treatment with CCl_4 in presence of anhydrous $AlCl_3$ gives **dichloro-diphenyl methane** which on hydrolysis forms **diphenyl ketone** (benzophenone).

$$\underset{\text{Benzene}}{2C_6H_6} + CCl_4 \xrightarrow[\Delta, (-2HCl)]{\text{Anhyd. } AlCl_3} \underset{\substack{\text{Dichloro-}\\ \text{diphenyl methane}}}{(C_6H_5)_2CCl_2} \xrightarrow[(-2HCl)]{2HOH}$$



$$\underset{\text{Unstable}}{(C_6H_5)_2C(OH)_2} \xrightarrow{(-H_2O)} \underset{\text{Diphenyl ketone}}{(C_6H_5)_2CO}$$

Uses : (i) It is used as a fire extinguisher under the name **pyrene.** The dense vapours form a protective layer on the burning objects and prevent the oxygen or air to come in contact with the burning objects, hence the room or windows should be well ventilated.

(ii) It is used as a solvent for fats, oils, waxes and greases, resins, iodine, etc. and also in drycleaning.

(iii) It finds use in medicine as **helminthicide** for elimination of hook worms.

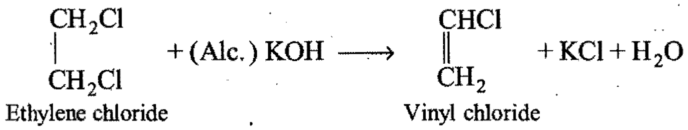
8.9 UNSATURATED HALIDES

The most common and important members of alkenyl halides are vinyl chloride and allyl iodide.

1. Vinyl chloride or chloroethene ($H_2C{=}CHCl$)

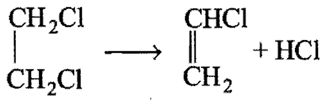
Vinyl chloride can be synthesised by a number of methods described below:

(i) From ethylene chloride : It is easily prepared in the laboratory by the action of dilute alcoholic solution of potassium hydroxide on ethylene chloride.



$$\underset{\text{Ethylene chloride}}{\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}} + (\text{Alc.})\,KOH \longrightarrow \underset{\text{Vinyl chloride}}{\begin{matrix}CHCl\\\|\\CH_2\end{matrix}} + KCl + H_2O$$

Vinyl chloride can also be obtained from ethylene chloride by thermal decomposition at 600–650°C.



$$\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix} \longrightarrow \begin{matrix}CHCl\\\|\\CH_2\end{matrix} + HCl$$

(ii) From ethylene : Free radical chlorination of ethylene at 500°C yields vinyl chloride.

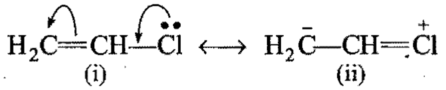
$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + Cl_2 \xrightarrow{500^\circ C} \underset{\text{Vinyl chloride}}{H_2C{=}CHCl}$$

(iii) From acetylene : Vinyl chloride is obtained by controlled addition of HCl on acetylene. Acetylene is passed through dilute hydrochloric acid at about 70°C in presence of $HgCl_2$ as a catalyst to form vinyl chloride. This method is also used for its manufacture.

$$\underset{\text{Acetylene}}{HC{\equiv}CH} + HCl \xrightarrow[70^\circ C]{HgCl_2} \underset{\text{Vinyl chloride}}{H_2C{=}CHCl}$$

It is a colourless gas at room temperature. Its boiling point is $-13^\circ C$. The halogen atom in vinyl chloride is not reactive as in other alkyl halides. However, C=C bond of vinyl chloride gives the usual addition reactions.

The non-reactivity of chlorine atom is due to resonance stabilization. The lone pair on chlorine can participate in delocalization (resonance) to give two structures.



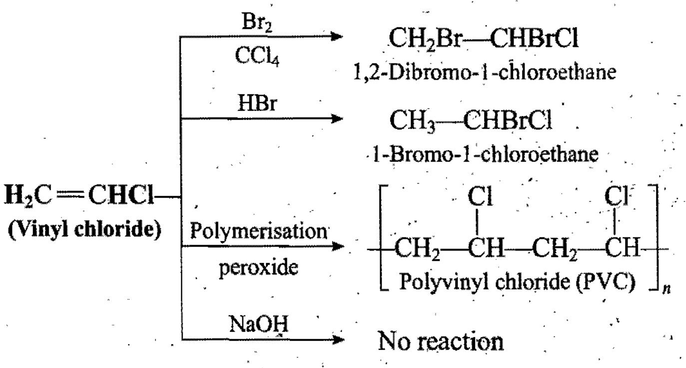
$$\underset{\text{(i)}}{H_2C{=}CH{-}\ddot{Cl}} \longleftrightarrow \underset{\text{(ii)}}{H_2\bar{C}{-}CH{=}\overset{+}{Cl}}$$

The following two effects are observed due to resonance stabilization.

(i) Carbon-chlorine bond in vinyl chloride has some double bond character and is, therefore, stronger than a pure single bond.

(ii) Carbon atom is sp^2-hybridized and C—Cl bond length is shorter (1.69 Å) and stronger than in alkyl halides (1.80 Å) due to sp^3-hybridization of the carbon atom.

Addition Reactions

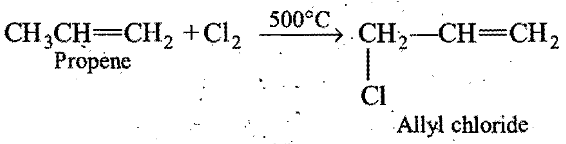


The main use of vinyl chloride is in the manufacture of polyvinyl chloride plastic which is employed these days for making synthetic leather goods, rain coats, pipes, floor tiles, gramophone records, packaging materials, etc.

2. Allyl Iodide or 3-Iodoprop-1-ene ($ICH_2CH{=}CH_2$)

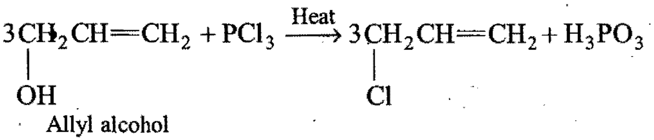
It is obtained:

(i) by heating allyl chloride with sodium iodide in acetone. Allyl chloride required in the reaction is prepared either by chlorination of propene at 500°C or by action of PCl_3 on allyl alcohol.

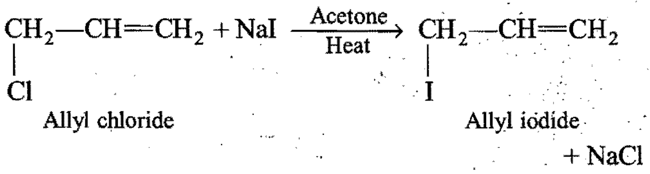


$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + Cl_2 \xrightarrow{500^\circ C} \underset{\text{Allyl chloride}}{\underset{\displaystyle Cl}{\underset{|}{CH_2}}{-}CH{=}CH_2}$$

or



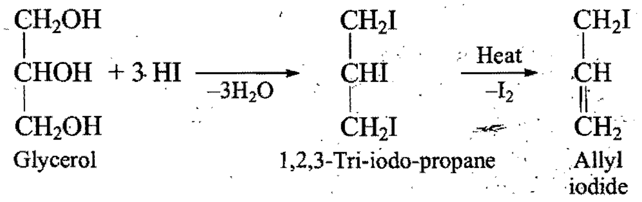
$$3\underset{\text{Allyl alcohol}}{\underset{\displaystyle OH}{\underset{|}{CH_2}}CH{=}CH_2} + PCl_3 \xrightarrow{\text{Heat}} 3\underset{\displaystyle Cl}{\underset{|}{CH_2}}CH{=}CH_2 + H_3PO_3$$



$$\underset{\text{Allyl chloride}}{\underset{\displaystyle Cl}{\underset{|}{CH_2}}{-}CH{=}CH_2} + NaI \xrightarrow[\text{Heat}]{\text{Acetone}} \underset{\text{Allyl iodide}}{\underset{\displaystyle I}{\underset{|}{CH_2}}{-}CH{=}CH_2} + NaCl$$

This is halogen-exchange reaction and is called **Finkelstein reaction.**

(ii) by heating glycerol with HI.



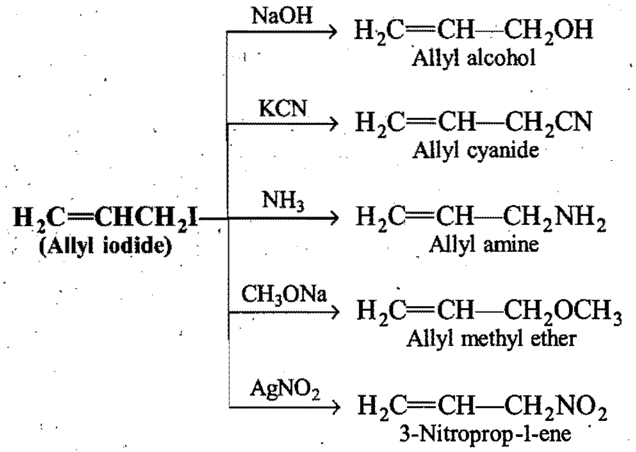
It is a colourless liquid. It boils at 103.1°C. The halogen atom in allyl iodide is quite reactive. The p-orbital of the halogen atom does not interact with π-molecular orbital of the double bond because these are separated by a saturated sp^3-hybridized carbon atom. Thus, the halogen atom in allyl halides can be easily replaced and the reactions of allyl halides are similar to the reaction of alkyl halides.

In terms of valence bond approach, the reactivity of halogen atom is due to ionisation to yield a carbonium ion which can stabilize by resonance as shown below.

$$H_2C{=}CH{-}CH_2I \longrightarrow$$

$$[H_2C{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow H_2\overset{+}{C}{-}CH{=}CH_2]+I^-$$

Substitution Reactions : Nucleophilic substitution reactions occur.



$$H_2C{=}CHCH_2I \xrightarrow{NaOH} \underset{\text{Allyl alcohol}}{H_2C{=}CH{-}CH_2OH}$$

$$H_2C{=}CHCH_2I \xrightarrow{KCN} \underset{\text{Allyl cyanide}}{H_2C{=}CH{-}CH_2CN}$$

$$\underset{\textbf{(Allyl iodide)}}{H_2C{=}CHCH_2I} \xrightarrow{NH_3} \underset{\text{Allyl amine}}{H_2C{=}CH{-}CH_2NH_2}$$

$$H_2C{=}CHCH_2I \xrightarrow{CH_3ONa} \underset{\text{Allyl methyl ether}}{H_2C{=}CH{-}CH_2OCH_3}$$

$$H_2C{=}CHCH_2I \xrightarrow{AgNO_2} \underset{\text{3-Nitroprop-1-ene}}{H_2C{=}CH{-}CH_2NO_2}$$

Addition Reactions : Electrophilic addition reactions take place in accordance to Markownikoff's rule.

$$H_2C{=}CH{-}CH_2I + Br_2 \longrightarrow \underset{\text{1,2-Dibromo-3-iodopropane}}{CH_2BrCHBrCH_2I}$$

$$H_2C{=}CH{-}CH_2I + HBr \longrightarrow \underset{\text{2-Bromo-1-iodopropane}}{CH_3CHBrCH_2I}$$

Allyl iodide is widely used in organic synthesis.

8.10 SOME MORE IMPORTANT HALOGEN DERIVATIVES

1. Freons : The chloro fluoro derivatives of methane and ethane are called *freons*. Some of the derivatives are: CHF_2Cl (monochlorodifluoromethane), CF_2Cl_2 (dichlorodifluoromethane), HCF_2CHCl_2 (1,1-dichloro-2,2-difluoroethane) and CF_3Cl (chlorotrifluoromethane or **freon-11**). These derivatives are non-inflammable, colourless, non-toxic, low boiling liquids. These are stable upto 550°C. The most important and useful derivative is CF_2Cl_2 which is commonly known as **freon** and **freon-12.**

Freon or freon-12 (CF_2Cl_2) is prepared by treating carbon tetrachloride with antimony trifluoride in the presence of antimony pentachloride as a catalyst.

$$3CCl_4 + 2SbF_3 \xrightarrow[\text{Catalyst}]{SbCl_5,\ \Delta} 3CCl_2F_2 + 2SbCl_3$$

Or it can be obtained by reacting carbon tetrachloride with hydrofluoric acid in presence of antimony pentafluoride.

$$CCl_4 + 2HF \xrightarrow{SbF_5} CCl_2F_2 + 2HCl$$

Under ordinary conditions freon is a gas. Its boiling point is $-29.8°$C. It can easily be liquefied. It is chemically inert. It is used in air-conditioning and in domestic refrigerators for cooling purposes (as refrigerant). **Halothane** ($CF_3CHBrCl$) and methoxy flurane ($CH_3OCF_2CHCl_2$) are used as inhalation anaesthetic.

2. Teflon : It is a plastic like substance produced by the polymerisation of tetrafluoroethylene ($F_2C{=}CF_2$).

Tetrafluoroethylene is formed when chloroform is treated with antimony trifluoride and hydrofluoric acid.

$$CHCl_3 \xrightarrow[HF]{SbF_3} CHF_2Cl \xrightarrow[-HCl]{800°C} \underset{\text{(b.pt. }-76°\text{C)}}{F_2C{=}CF_2}$$

On polymerisation tetrafluoroethylene forms a plastic-like material which is called **teflon.**

$$\underset{\text{Tetrafluoroethylene}}{nCF_2{=}CF_2} \longrightarrow \underset{\text{Teflon}}{+\!\!\!(CF_2{-}CF_2)\!\!\!+_n}$$

Teflon is chemically inert substance. It is not affected by strong acids and even by boiling aqua-regia. It is stable at high temperatures. It is, thus, used for electrical insulation and preparation of gasket materials.

3. Acetylene tetrachloride (westron)($CHCl_2{-}CHCl_2$): Acetylene tetrachloride is also known as sym. tetrachloroethane. It is prepared by the action of chlorine on acetylene in presence of a catalyst such as ferric chloride, aluminium chloride, iron, quartz or kieselguhr.

$$HC{\equiv}CH + 2Cl_2 \xrightarrow[\text{Catalyst}]{FeCl_3 \text{ or } AlCl_3} \underset{\text{(1,1,2,2-Tetrachloroethane)}}{CHCl_2{-}CHCl_2}$$

In absence of catalyst, the reaction between chlorine and acetylene is highly explosive producing carbon and HCl. The reaction is less violent in presence of a catalyst.

It is a heavy, non-inflammable liquid. It boils at 146°C. It is highly toxic in nature. Its smell is similar to chloroform. It is insoluble in water but soluble in organic solvents.

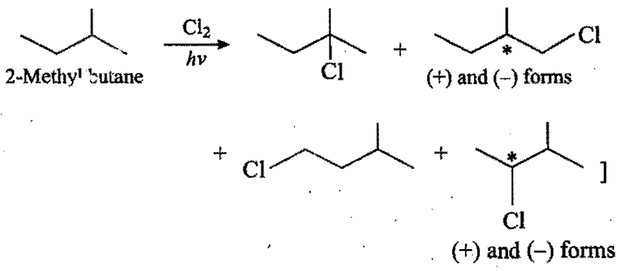
On further chlorination, it forms penta and hexa-chloroethane. On heating with lime (calcium hydroxide), it is converted to a useful product **westrosol** ($CCl_2{=}CHCl$).

$$\underset{\text{Westron}}{CHCl_2{-}CHCl_2} + Ca(OH)_2 \longrightarrow \underset{\substack{\text{Westrosol}\\\text{(Trichloroethene)}}}{2CHCl{=}CCl_2} + CaCl_2 + 2H_2O$$

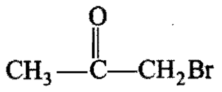
Both westron and westrosol are used as solvents for oils, fats, waxes, resins, varnishes and paints, etc.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. On monochlorination of 2-methyl butane, the total number of chiral compounds is: **[IIT 2004]**
   (a) 2 (b) 4
   (c) 6 (d) 8
   [Ans. (b)]
   [Hint: The number of monohalogenation products obtained from any alkane depends upon the number of different types of hydrogen it contains. The possible monochlorinated products of 2-methyl butane are:

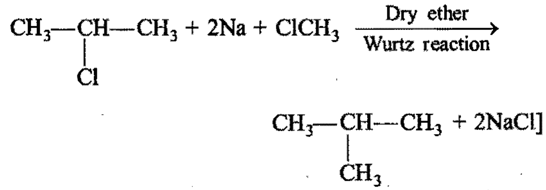


2. Which of the following will not give iodoform test? **[UPSEAT 2004]**
   (a) Ethanol (b) Isopropyl alcohol
   (c) Ethanal (d) Benzyl alcohol
   [Ans. (d)]
3. Which one of the following is excellent substrate for S_N1 reaction?
   (a) $(CH_3)_3C—Cl$ (b) $(CH_3)_2CH—Cl$
   (c) $(CH_3)_2N—CH_2Cl$ (d) $(CH_3)_3C—Br$
   [Ans. (c)]
   [Hint: Carbocation of the substrate (c) is stabilized by delocalisation.]
4. Which of the following will have a meso-isomer also? **[AIEEE 2004]**
   (a) 2-Chlorobutane
   (b) 2,3-Dichlorobutane
   (c) 2,3-Dichloropentane
   (d) 2-Hydroxy propanoic acid
   [Ans. (b)]
   [Hint: 2,3-Dichlorobutane have meso-isomer due to the presence of the plane of symmetry.]
5. The compound added to prevent chloroform to form phosgene gas (poisonous gas) is: **[PMT (MP) 2004]**
   (a) CH_3COOH (b) CH_3OH
   (c) CH_3COCH_3 (d) C_2H_5OH
   [Ans. (d)]
6. Among the halogens, the one which is oxidised by nitric acid is:
   (a) iodine (b) chlorine
   (c) bromine (d) fluorine
   [Ans. (a)]
   [Hint: $I_2 + 10HNO_3 \longrightarrow \underset{\text{Iodic acid}}{2HIO_3} + 10NO_2 + 4H_2O$]
7. Which one of the following is excellent substrate for S_N2 reaction?
   (a) $CH_3—Br$ (b) CH_3CH_2I
   (c) $CH_3—O—CH_2Br$ (d)



$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_2Br$

   [Ans. (d)]
   [Hint: Strong –*I* group present on the α-carbon stabilises transition state of the S_N2 reaction.]
8. On treating a mixture of two alkyl halides with sodium metal in dry ether, 2-methyl propane was obtained. The alkyl halides are:
   (a) 1-chloropropane and chloroethane
   (b) 2-chloropropane and chloroethane
   (c) 2-chloropropane and chloromethane
   (d) 1-chloropropane and chloromethane
   [Ans. (c)]
   [Hint:



$$CH_3—\underset{\underset{\displaystyle Cl}{|}}{CH}—CH_3 + 2Na + ClCH_3 \xrightarrow[\text{Wurtz reaction}]{\text{Dry ether}} CH_3—\underset{\underset{\displaystyle CH_3}{|}}{CH}—CH_3 + 2NaCl]$$

SOME SOLVED PROBLEMS

Problem 1. *How do alkyl, allyl and vinyl halides differ in structure?*

Solution : The *X* in an alkyl halide is bonded to sp^3-hybridized carbon of an alkyl group.

$$\underset{sp^3\text{-hybridized}}{\underset{\downarrow}{CH_3X}}; \qquad \underset{sp^3\text{-hybridized}}{CH_3\underset{\downarrow}{CH_2}X}$$

In an allyl halide, there is a C=C bonded to the carbon bearing the *X*.

$$H_2C{=}CHCH_2X \quad \text{Allyl halide}$$

In vinyl halides, *X* is bonded to an sp^2-hybridized carbon of an alkene.

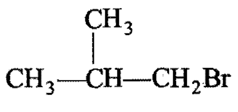
$$\underset{sp^2\text{-hybridized}}{H_2C{=}\underset{\downarrow}{C}HX} \quad \text{or} \quad \underset{sp^2\text{-hybridized}}{CH_3CH{=}\underset{\downarrow}{C}XCH_3}$$

Problem 2. *Give the common and IUPAC names for* C_4H_9Br *isomers and classify them as to whether they are* 1°, 2° *or* 3°.

Solution : The isomers of C_4H_9Br are the following with common and IUPAC names:

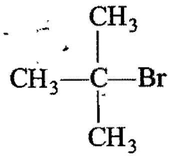
$CH_3CH_2CH_2CH_2Br$;
(1-Bromobutane)
n-Butyl bromide
(1° Bromide)

$CH_3CH_2CHBrCH_3$
(2-Bromobutane)
Sec. butyl bromide
(2° Bromide)



$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2Br$;

(1-Bromo-2-methyl propane)
Isobutyl bromide
(1° Bromide)



$CH_3—\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}—Br$

(2-Bromo-2-methyl propane)
Tert. butyl bromide
(3° Bromide)

Problem 3. (*a*) *Give simple test to distinguish among hexane and* $CH_3—CH{=}CHCl$.

(*b*) *Give simple test to distinguish among* $CH_3—CH{=}CHCl$, $CH_3CH_2CH_2Cl$ *and* $CH_2{=}CH—CH_2Cl$.

Solution : (a) Hexane and methyl vinyl chloride are distinguished by adding bromine in CCl_4 to each. The red brown bromine colour persists in alkane but disappears in methyl vinyl chloride.

(b) $H_2C{=}CH—CH_2Cl$ is an allylic chloride (The Cl is very reactive). This reacts rapidly with $AgNO_3$ in the cold to give a white ppt. of AgCl. $CH_3CH_2CH_2Cl$ gives white ppt. when warmed with $AgNO_3$ as it is comparatively less reactive. $CH_3—CH{=}CHCl$ is inert and does not form white ppt. with $AgNO_3$.

Problem 4. *Give reasons for the following:*

(*a*) *Potassium cyanide reacts with R—X to give alkyl cyanide, while silver cyanide forms an isocyanide as a major product.*

(*b*) *Silver nitrite reacts with R—X to give a mixture of nitroalkane and alkyl nitrite.*

(*c*) *ROH does not react with NaBr but on adding* H_2SO_4, *it forms RBr.*

(*d*) *Alcohols do not undergo substitution in neutral or alkaline solution.*

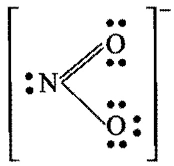
Solution : (a) Potassium cyanide is an ionic compound, $K^+[:C{\equiv}N:]^-$ and provide cyanide ions in solution, in which each of carbon and nitrogen carry a lone pair of electrons [CN is an ambident nucleophile (ligand)].

As lone pair on carbon is more reactive, the carbocation, R^+, preferentially attacks the carbon atom and thereby forms an alkyl cyanide predominantly.

$$R^+ + [:C{\equiv}N:]^- \longrightarrow \underset{\text{Alkyl cyanide}}{R—CN:}$$

On the other hand, AgCN (being insoluble) is a covalent compound and only nitrogen has the lone pair of electrons. Thus, carbocation attacks through nitrogen and thereby forms an alkyl isocyanide as a major product.

$$Ag—C{\equiv}N: + RX \longrightarrow RNC: + AgX$$

(b) The nitrite ion  has two nucleophilic sites, *i.e.*, N and either of the oxygen atoms. The carbocation can attack either N or O, thereby forming a mixture of nitroalkane, $R—NO_2$ and alkyl nitrite, $R—ONO$.

(c) Br^- ion is a very weak Bronsted base and thus, it can not displace the strong base $—OH^-$. When H_2SO_4 acid is added, H^+ are available which form $R\overset{+}{O}H_2$. Under this condition, Br^- displaces H_2O which is a very weak base.

$$R\overset{+}{O}H_2 + Br^- \longrightarrow R^+ + H_2O + Br^- \longrightarrow RBr + H_2O$$

(d) A leaving group must be a weak base. The leaving —OH group of alcohols in neutral or alkaline solution would be stronger base, hence cannot be removed by weaker bases like Cl^-, Br^-, I^-.

Problem 5. *A halide,* $C_5H_{11}X$, *on treating with alc.* KOH *gives only pent-2-ene. What is halide?*

Solution : Two possible halides which on elimination of HX can form pent-2-ene are:

$$\underset{\text{(I)}}{CH_3CH_2CH_2CHXCH_3}; \quad \underset{\text{(II)}}{CH_3CH_2CHXCH_2CH_3}$$

The (II) structure being symmetrical gives only pent-2-ene on elimination of HX

$$CH_3CH_2CHXCH_2CH_3 \xrightarrow{\text{Alc. KOH}} \underset{\text{Pent-2-ene}}{CH_3CH{=}CHCH_2CH_3}$$

Thus, the halide is 3-halopentane.

Note : The structure (I) forms a mixture,

$$\underset{\text{(Major product)}}{CH_3CH_2CH{=}CHCH_3} \text{ and } \underset{\text{(Minor product)}}{CH_3CH_2CH_2CH{=}CH_2}.$$

Problem 6. *A white precipitate was formed slowly when* $AgNO_3$ *is added to a compound (A) with molecular formula* $C_6H_{13}Cl$. *Compound (A) on treatment with hot alcoholic* KOH *gave a mixture of two isomeric alkenes (B) and (C) having formula,* C_6H_{12}. *The mixture of (B) and (C) on ozonolysis furnished four compounds.*

(*i*) CH_3CHO, (*ii*) C_2H_5CHO,

(*iii*) CH_3COCH_3, (*iv*) $(CH_3)_2CHCHO$.

What are (A), (B) and (C)?

Solution : Given $C_6H_{13}Cl \xrightarrow[-HCl]{\text{Alc. KOH}} (B) + (C)$

The molecular formula of (*B*) and (*C*) is C_6H_{12}. Thus, on ozonolysis of each alkene, the two products must have six carbon atoms.

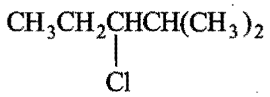
One alkene gives CH_3CHO and $(CH_3)_2CHCHO$. Thus, the hydrocarbon should have the structure,

$$CH_3CH{=}CHCH(CH_3)_2 \quad \ldots (B)$$

Other alkene gives C_2H_5CHO and CH_3COCH_3. Thus, the hydrocarbon should have the structure,

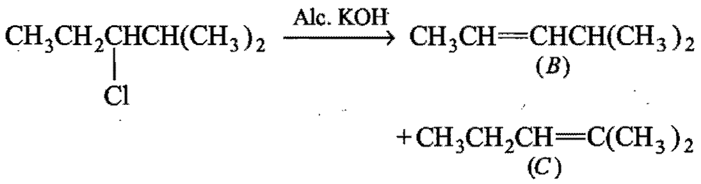
$$C_2H_5CH{=}C(CH_3)_2 \quad \ldots (C)$$

Since (*B*) and (*C*) are formed from (*A*) by dehydrohalogenation, the structure of (*A*) is:



$$CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH(CH_3)_2$$

3-Chloro-2-methyl pentane



$$CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH(CH_3)_2 \xrightarrow{\text{Alc. KOH}} \underset{(B)}{CH_3CH{=}CHCH(CH_3)_2} + \underset{(C)}{CH_3CH_2CH{=}C(CH_3)_2}$$

As it is 2° halide, it slowly reacts with the $AgNO_3$ to form white ppt.

Problem 7. *How many isomers are possible for* $C_4H_8F_2$ *and give their* IUPAC *names?*

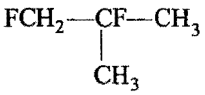
Solution : *n*-Butane can have two possible gem-difluoro isomers:

$F_2CHCH_2CH_2CH_3$ 1,1-Difluorobutane	$CH_3CF_2CH_2CH_3$ 2,2-Difluorobutane

There are four isomers with two fluorine on different carbon atoms:

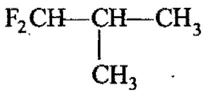
$FCH_2CHFCH_2CH_3$ 1,2-Difluorobutane (vic)	$CH_3CHFCHFCH_3$ 2,3-Difluorobutane (vic)
$FCH_2CH_2CHFCH_3$ 1,3-Difluorobutane	$FCH_2CH_2CH_2CH_2F$ 1,4-Difluorobutane

The isobutane can have three possible difluoro isomers:



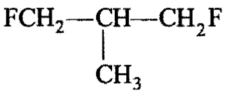
$FCH_2—\underset{CH_3}{\underset{|}{C}}F—CH_3$

1,2-Difluoro-2-methyl propane (vic)



$F_2CH—\underset{CH_3}{\underset{|}{C}}H—CH_3$

1,1-Difluoro-2-methyl propane (gem)



$FCH_2—\underset{CH_3}{\underset{|}{C}}H—CH_2F$

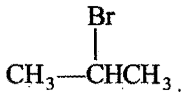
1,3-Difluoro-2-methyl propane

Problem 8. *Give the structures of two different alkyl bromides both of which yield the indicated alkene as the exclusive product of* E_2 *elimination :*

(*a*) $CH_3CH{=}CH_2$ (*b*) $(CH_3)_2C{=}CH_2$

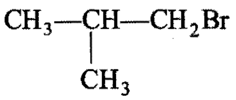
(*c*) $BrCH{=}CBr_2$

Solution : (a) $CH_3CH_2CH_2Br$ and



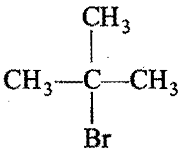
$CH_3—\overset{Br}{\overset{|}{C}}HCH_3$

(b)



$CH_3—\underset{CH_3}{\underset{|}{C}}H—CH_2Br$

and



$CH_3—\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—CH_3$

(c) $Br_2HC—CHBr_2$ and $BrH_2C—CBr_3$

SUPPLEMENTARY READING

8.11 ORGANOMETALLIC COMPOUNDS

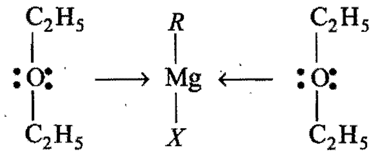
Organic compounds in which a metal atom is directly linked to carbon or organic compounds which contain at least one carbon-metal bond are called organometallic compounds. Some common examples are:

CH_3Li Methyl lithium	$(CH_3)_2Zn$ Dimethyl zinc	$(C_2H_5)_4Pb$ Tetraethyl lead
$(C_2H_5)_4Sn$ Tetraethyl tin	$(C_2H_5)_2Hg$ Diethyl mercury	CH_3Na Methyl sodium
$R—Mg—X$ Alkyl magnesium halide	CH_3MgBr Methyl magnesium bromide	$R—C{\equiv}C—Ag$ Silver alkynide
	C_6H_5HgCl Phenyl mercuric chloride	R_2CuLi Lithium dialkyl cuprate

Most widely studied and synthetically most useful organometallic compounds are those of magnesium and lithium. Alkyl magnesium halides are termed as Grignard reagents as these were discovered by Grignard in 1900. The Grignard reagents are very reactive and used as synthetic reagents for the synthesis of alkanes, alcohols, aldehydes, ketones, acids, etc.

Organometallic compounds are prepared from the respective alkyl or aryl halides in solvents like ether. These compounds are mostly colourless, mobile liquids having low boiling points and are generally very unstable. A number of these compounds burn violently in air and are readily decomposed by water and alcohol.

Grignard reagents are prepared by the action of alkyl halides on dry magnesium turnings in presence of dry alcohol-free diethyl ether. The ether solution of the Grignard reagent is used immediately in the apparatus in which it has been prepared. Dry ether dissolves the Grignard reagent through solvolysis.



$$\underset{C_2H_5}{\underset{|}{\overset{C_2H_5}{\overset{|}{:\ddot{O}:}}}} \longrightarrow \underset{X}{\underset{|}{\overset{R}{\overset{|}{Mg}}}} \longleftarrow \underset{C_2H_5}{\underset{|}{\overset{C_2H_5}{\overset{|}{:\ddot{O}:}}}}$$

Grignard reagents are never isolated in free state on account of their explosive nature.

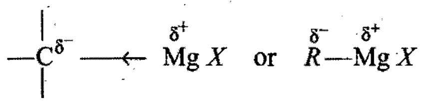
Note :
- (i) For a given alkyl radical, the ease of formation of a Grignard reagent is,

  Iodide > Bromide > Chloride

  Usually alkyl bromides are used.
- (ii) For a given halogen, the ease of formation of a Grignard reagent is,

  $CH_3X > C_2H_5X > C_3H_7X$ .....
- (iii) Since, tertiary alkyl iodides eliminate HI to form an alkene, tertiary alkyl chlorides are used in their place.
- (iv) Grignard reagent cannot be prepared from a compound which consists in addition to halogen, some reactive group such as —OH because it will react rapidly with the GR.

The C—Mg bond in Grignard reagent is somewhat covalent but highly polar. Carbon being more electronegative than magnesium acquires partial negative charge and the magnesium has a partial positive charge.



$$—\underset{|}{\overset{|}{C}}{}^{\delta^-} \longleftarrow \overset{\delta^+}{Mg}X \quad \text{or} \quad \overset{\delta^-}{R}—\overset{\delta^+}{Mg}X$$

The alkyl group thus acts as a carbanion or nucleophile. The majority of reactions of Grignard reagent fall into two groups:

(i) Double decomposition with compounds containing active hydrogen atom or reactive halogen atom.

$$RMgX + HOH \longrightarrow RH + Mg(OH)X$$

$$RMgX + D_2O \longrightarrow RD + Mg(OD)X$$

$$RMgX + R'OH \longrightarrow RH + Mg(OR')X$$

$$RMgX + R'NH_2 \longrightarrow RH + Mg(R'NH)X$$

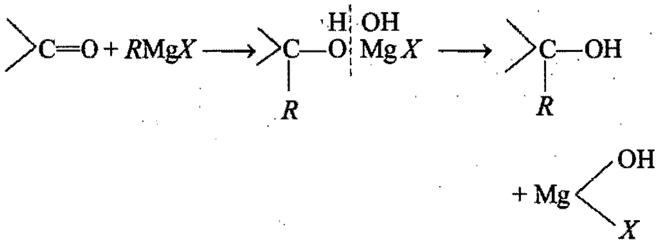
$$RMgX + R'I \longrightarrow R—R' + MgIX$$

$$RMgX + ClCH_2OR' \longrightarrow RCH_2OR' + MgClX$$

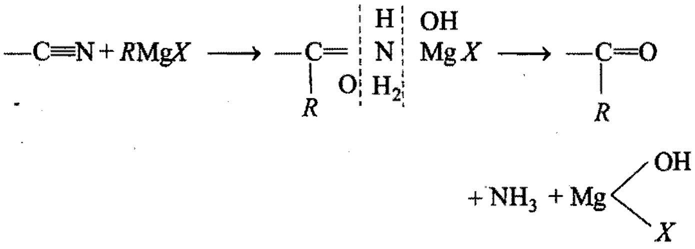
(ii) Addition reactions with compounds containing the following groups.

$$>C{=}O, \quad -C{\equiv}N, \quad >C{=}S$$

In each case, alkyl group attaches to carbon atom and MgX part to the oxygen, nitrogen or sulphur atom.



$$>C{=}O + RMgX \longrightarrow >\underset{R}{C}-O\overset{H}{}MgX \xrightarrow{HOH} >\underset{R}{C}-OH + Mg\begin{matrix}OH\\X\end{matrix}$$



$$-C{\equiv}N + RMgX \longrightarrow -\underset{R}{C}{=}NMgX \xrightarrow{H_2O} -\underset{R}{C}{=}O + NH_3 + Mg\begin{matrix}OH\\X\end{matrix}$$

The addition products decompose with water or dilute acid. These type of reactions are given by molecules such as O_2, CO_2, etc.

Alkyl lithiums : Organo-lithium compounds are prepared by the action of alkyl halides with lithium metal in dry ether at low temperature in the presence of an inert atmosphere of nitrogen.

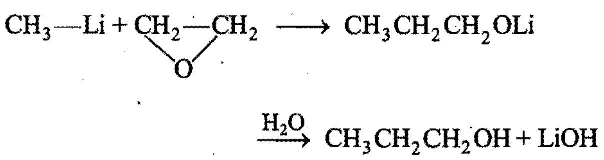
$$\underset{\text{Methyl iodide}}{CH_3I} + 2Li \xrightarrow[-10^\circ C]{\text{Ether}} \underset{\text{Methyl lithium}}{CH_3Li} + LiI$$

Alkyl iodides and alkyl bromides usually undergo Wurtz reaction. Alkyl chlorides are usually used and they give good yields.

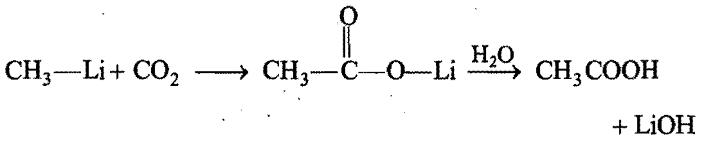
The high reactivity of organo-lithium compounds over Grignard reagent is due to the greater polar character of C—Li bond in comparison to C—Mg bond.

Generally, alkyl lithiums behave like Grignard reagents but are more reactive. They react with compounds containing active hydrogens, aldehydes, ketones, carbon dioxide, ethylene oxide, etc.

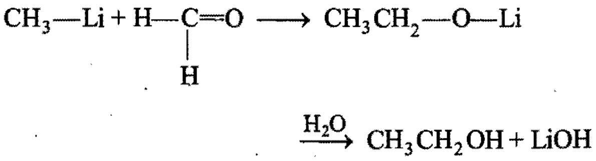
$$CH_3-Li + HOH \longrightarrow CH_4 + LiOH$$



$$CH_3-Li + \underset{O}{CH_2-CH_2} \longrightarrow CH_3CH_2CH_2OLi \xrightarrow{H_2O} CH_3CH_2CH_2OH + LiOH$$



$$CH_3-Li + CO_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-Li \xrightarrow{H_2O} CH_3COOH + LiOH$$



$$CH_3-Li + H-\underset{H}{C}{=}O \longrightarrow CH_3CH_2-O-Li \xrightarrow{H_2O} CH_3CH_2OH + LiOH$$

Unlike Grignard reagents, alkyl lithium can add to an alkenic double bond.

$$R-Li + CH_2{=}CH_2 \longrightarrow R-CH_2-CH_2-Li$$

Dialkyl zincs : These were the first organometallic compounds discovered by Frankland.

These can be prepared by heating alkyl iodide with zinc in an atmosphere of CO_2.

$$2RI + 2Zn \xrightarrow[CO_2]{\text{Heat}} \underset{\text{Alkyl zinc iodide}}{2R-Zn-I} \xrightarrow[CO_2]{\text{Heat}} \underset{\text{Dialkyl zinc}}{R_2Zn} + ZnI_2$$

Owing to the difficulty in handling and better synthetic reagents are known, their use is restricted to the following preparations:

(i) Preparation of quaternary hydrocarbon such as neopentane.

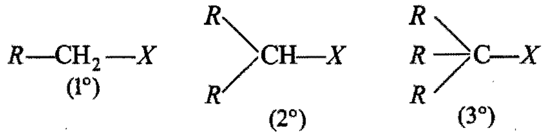
$$\underset{\textit{Tert.}\text{ butyl chloride}}{(CH_3)_3CCl} + (CH_3)_2Zn \longrightarrow \underset{\text{Neopentane}}{(CH_3)_4C} + CH_3ZnCl$$

(ii) Preparation of ketones : Acid chlorides reacts with dialkyl zinc to form ketones.

$$\underset{\text{Acid chloride}}{R'COCl} + R_2Zn \longrightarrow \underset{\text{Ketone}}{R'COR} + R-Zn-Cl$$

IMPORTANT POINTS TO REMEMBER (SUMMARY)

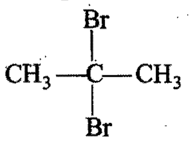
- Compounds derived from alkanes by the replacement of one or more H atoms by corresponding number of halogen atoms are termed halogen derivatives of alkanes or **haloalkanes.** They do not occur in nature.
- Haloalkanes are divided into mono, di, tri, tetra, etc. according to the number of halogen atoms in the molecule.
- **Monohalogen** derivatives are called **alkyl halides** ($R—X$) and represented by the general formula $C_nH_{2n+1}X$. They are further classified as primary (1°), secondary (2°) or tertiary (3°) depending upon whether the halogen atom is attached to 1°, 2° or 3° carbon atoms.



- **Dihaloalkanes** ($C_nH_{2n}X_2$) are mainly of three types:
- **Gem-dihalides:** In these derivatives, both the halogen atoms are attached to the same carbon atom. Their common name is **alkylidene (di)halides,** *e.g.*,

CH_3CHCl_2, Ethylidene (di)chloride

$CH_3CH_2CHBr_2$, *n*-Propylidene (di)bromide



$CH_3—C(Br)_2—CH_3$

Isopropylidene (di)bromide

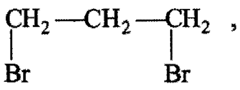
- **Vicinal-dihalides:** Both the halogen atoms are attached to adjacent (vicinal) carbon atoms. Their common name is **alkylene (di)halides,** *e.g.*,

$ClCH_2—CH_2Cl$, Ethylene (di)chloride

$CH_3CH(Br)CH_2Br$, Propylene (di)bromide

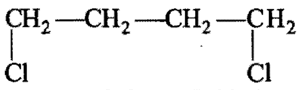
$CH_3CH(Br)CH(Br)CH_3$ Butylene (di)bromide

- **Terminal-dihalides** (α, ω)**:** In them the two halogen atoms are attached to terminal carbon atoms. Their common name is **polymethylene (di)halides,** *e.g.*,



$BrCH_2—CH_2—CH_2Br$

Trimethylene (di)bromide



$ClCH_2—CH_2—CH_2—CH_2Cl$

Tetramethylene (di)chloride

- **Trihaloalkanes (Haloforms):** Examples are,

$CHCl_3$,	$CHBr_3$,	CHI_3,	CHF_3
Chloroform	Bromoform	Iodoform	Fluoroform

- **Tetrahaloalkanes:** Examples are,

CCl_4,	CBr_4,	CCl_2F_2
Carbon tetrachloride	Carbon tetrabromide	Dichlorodifluoro methane

General methods of preparation of alkyl halides

- **By direct halogenation of alkanes:** In presence of sunlight, heat or catalyst (Free radical halogenation) gives a mixture of mono, di, tri halogen derivatives, etc.
- Replacement of H atom from hydrocarbons follows the order:

$$\text{allylic H} > 3°\text{ H} > 2°\text{ H} > 1°\text{ H} > CH_4$$

- Relative reactivity of 1°, 2°, 3° H atoms for chlorination is in the ratio 1 : 3.8 : 5.
- Chlorination of *n*-butane gives a mixture of *d*- and *l*-optical isomers, *i.e.*, racemic mixture.
- **From alkenes:** By the addition of HX ($HI > HBr > HCl > HF$). The unsymmetrical alkenes follow **Markownikoff's rule** during addition forming 2° or 3° alkyl halides predominantly through the formation of the most stable carbocation.
- The less stable intermediate carbocation changes into more stable carbocation by **1,2-hydride** or **1,2-methyl** or **phenyl** shift.
- Addition occurs through **electrophilic** attack. However, in presence of peroxide ($R—O—O—R$) the addition of HBr to unsymmetrical alkenes follows anti-Markownikoff's rule **(peroxide effect or Kharasch effect).**
- **From alcohols:** By nucleophilic substitution **(S_N) reactions.**
- Action of halogen acids, HX ($HI > HBr > HCl > HF$) on alcohols in presence of anhydrous $ZnCl_2$ yields alkyl halides. The increasing reactivity of alcohols towards HX is:

$$CH_3OH < 1° < 2° < 3° < \text{benzylic and allylic.}$$

- The mixture (1 : 1) of concentrated HCl and anhydrous $ZnCl_2$ is called **Lucas reagent.**
- Action of PX_5 or PX_3 on alcohols converts them readily into alkyl halides.
- Action of $SOCl_2$/pyridine or $SOCl_2$/ether on alcohols gives alkyl chloride.
- 1° Alcohol follows S_N2 path while 2° and 3° alcohols S_N1 path, *i.e.*, proceeds through the most stable carbocation intermediate.
- **From silver salts of carboxylic acids:** By the action of Cl_2 or Br_2 (in CCl_4). This reaction is called **Borodine-Hunsdiecker reaction** or **Hunsdiecker reaction** and the yield of halide is 1° > 2° > 3°.
- Iodine forms ester (instead of alkyl halide) with silver salt and is called **Birnbaum-Simonini reaction.**
- **By halide exchange method:** $R—Cl$ or $R—Br$ on heating with NaI in acetone or methanol solution forms $R—I$ (This reaction is called **Finkelstein reaction**).
- Alkyl fluorides can be prepared from corresponding chlorides by the action of mercurous fluoride (Hg_2F_2) or SbF_3 **(Swarts reaction).**

☐ **Physical properties:** Lower members ($CH_3F, CH_3Cl, CH_3Br, C_2H_5Cl$) are gases at room temperature while CH_3I and others are pleasant liquids and higher members are solid. *R*—Br and *R*—I are heavier than water while *R*—F and *R*—Cl are lighter than water.

☐ These are slightly soluble in water but completely soluble in organic solvents.

☐ They burn on copper wire with green edged flame **(Beilstein test for halogens).**

☐ Boiling points are in the order $RI > RBr > RCl > RF$, while in a group of isomeric halides, the order is $1° > 2° > 3°$.

☐ Boiling points of organo halogen compounds are comparatively higher than the corresponding hydrocarbons because of strong dipole-dipole and van der Waals' forces of attraction.

☐ **Chemical properties:** The high reactivity of *R*—*X* can be explained in terms of the nature of C—*X* bond which is highly polarised because the halogen is more electronegative than carbon and the dipole moment decreases as the electronegativity decreases from F to I.

☐ The polarity of C—*X* bond in alkyl halides is responsible for their **nucleophilic substitution** reactions, **elimination** reactions and the **reaction with metal** atoms to form organo metallic compounds.

☐ **Chirality** has a profound role in understanding the reaction mechanisms of S_N1 and S_N2 reactions. S_N2 reactions of chiral alkyl halides are characterised by the **inversion of configuration** while S_N1 reactions by **racemisation.**

☐ **Nucleophilic substitution (S_N) reactions of *R*—*X***

$$R—X + :Nu \longrightarrow R—Nu + X^-$$

☐ **Hydrolysis** [action of moist silver oxide (AgOH) or boiling with aqueous alkali (NaOH or KOH) solution]: Formation of alcohols.

☐ **Action with sodium alkoxide** (*R*—ONa) or dry Ag_2O : Formation of ethers with *R*ONa is known as **Williamson's synthesis.**

☐ **Action with aqueous alcoholic NaSH or KSH:** Formation of thioalcohols (alkane thiol).

☐ **Action with aqueous alcoholic KCN:** Formation of alkyl cyanides (alkane nitrile) as the major product.

☐ **Action with aqueous alcoholic AgCN:** Formation of alkyl isocyanides (carbylamines or isonitriles) as the major product.

☐ **Action of aqueous alcoholic KNO_2:** Formation of alkyl nitrite as the major product.

☐ **Action of aqueous alcoholic $AgNO_2$:** Formation of nitroalkanes as the major product.

☐ **Action of aqueous alcoholic NH_3:** Formation of a mixture of *pri-*, *sec-*, *tert-* amines along with quaternary ammonium salts.

☐ **Action with silver salt of carboxylic acids:** Formation of esters.

☐ **Action with sodium alkynide (Na—C≡C—H):** Formation of higher alkynes.

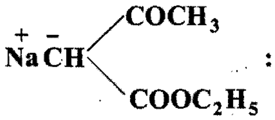
☐ **Action of alcoholic Na_2S or K_2S or NaS*R*:** Formation of thioethers (alkyl thioalkane).

☐ **Action of NaI in acetone or methanol:** Formation of alkyl iodides.

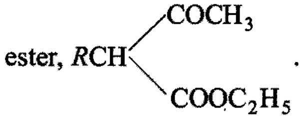
☐ **Action of alcoholic Na_2SO_3:** Formation of sodium alkyl sulphonate ($R—SO_3Na$).

☐ **Action of sodium diethyl malonate $NaCH(COOC_2H_5)_2$:** Formation of alkyl malonic ester $RCH(COOC_2H_5)_2$.

☐ **Action of sodium ethyl acetoacetate,**



$\overset{+}{Na}\overset{-}{C}H(COCH_3)(COOC_2H_5)$: Formation of alkyl acetoacetic ester,



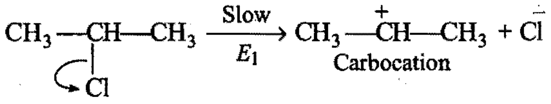
$RCH(COCH_3)(COOC_2H_5)$.

☐ **Action of sodium azide NaN_3:** Formation of alkyl azide, RN_3.

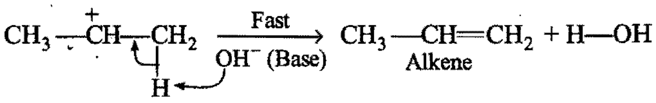
Elimination reactions

☐ **Dehydrohalogenation of alkyl halides:** On heating with alcoholic KOH, alkenes are formed. This elimination proceeds by E_1 or E_2 process.

☐ **Unimolecular elimination (E_1):** The *R*—*X* dissociates first to form carbocation and halide ion.



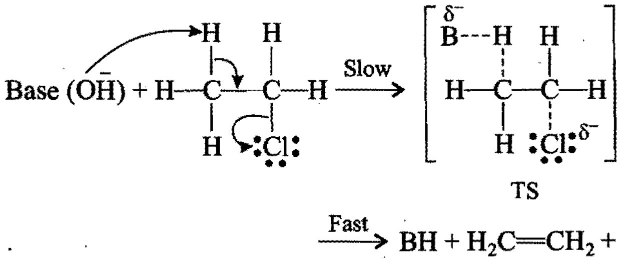
The strong nucleophile (which is also a strong base) attacks the carbocation to give alkene.



☐ E_1 involves the formation of most stable carbocation intermediate due to 1,2-hydride or methyl or phenyl shift giving unexpected products.

☐ The order of reactivity of alkyl group is $3° > 2° > 1°$ and the most substituted alkene is the Saytzeff product and the less substituted alkene is the Hofmann product.

☐ **Bimolecular elimination (E_2):** It involves the formation of intermediate TS.



☐ E_2 elimination is stereospecific and follows *trans*-elimination.

- **Action of heat:** Alkyl halides on heating above 300°C loses a molecule of HX to form an alkene. The decomposition follows the order : $I > Br > Cl$.

Miscellaneous (some other) Reactions

- **Reduction:** $R—X$ on reduction with nascent [H] obtained by Zn/HCl or Na/alcohol or $ZnCu/C_2H_5OH$ or $LiAlH_4$ etc. gives alkanes.
- **Wurtz reaction:** An etheral solution of RX (preferably bromides and iodides) forms symmetrical alkanes when heated with metallic sodium.
- Tertiary halides do not undergo this reaction.

Reaction with metals

- Alkyl halides form **Grignard reagents** when treated with Mg powder in dry ether.

$$RX + \text{Mg powder} \xrightarrow{\text{Dry ether}} R—Mg—X$$

(Reactivity order is $RI > RBr > RCl$).

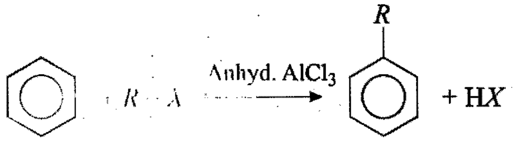
- The C—Mg bond is considered to be covalent but highly polar, the Mg—X bond is ionic ($R—\overset{+}{Mg}—\overset{-}{X}$). The Mg-metal is bonded in between X and carbon, hence nature of carbon chain does not alter.
- Grignard reagents find wide applications as the starting material for the preparation of a very large number of organic compounds.
- $R—X$ on heating with zinc powder in ether forms **dialkyl zinc.** These are called **Frankland reagents.**

$$2C_2H_5Br + 2Zn \xrightarrow{\text{Ether}} (C_2H_5)_2Zn + ZnBr_2$$

- Ethyl bromide when heated with sodium-lead alloy gives tetraethyl lead **(TEL)** which is used as **anti-knock** compound in petroleum products.

$$4C_2H_5Br + 4Na(Pb) \xrightarrow{\text{Ether}} (C_2H_5)_4Pb + 4NaBr + 3Pb$$

- $R—X$ forms **dialkyl mercury** compounds when treated with Na-Hg.
- $R—X$ forms **alkyl lithiums** when treated with lithium in dry ether.
- $R—X$ reacts with lithium dialkyl cuprate (R_2CuLi) to form alkanes **(Corey-House synthesis).**
- $R—X$ and aryl halide can react with sodium in presence of ether to form substituted (alkylated) benzene **(Wurtz-Fittig reaction).**
- **Friedel-Crafts reaction:** $R—X$ reacts with benzene in presence of anhydrous $AlCl_3$ to form alkyl benzenes.

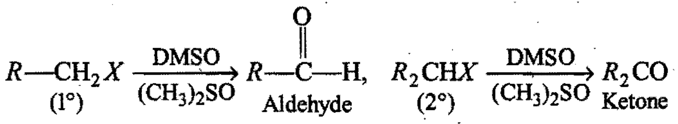


This reaction is named as Friedel-Crafts reaction.

- This reaction proceeds through the formation of an intermediate called σ-complex (a resonance stabilized carbocation). Anhydrous $AlCl_3$ (a Lewis acid) generates electrophile from the reactant. It is thus S_E reaction.
- **Halogenation (Substitution) :** Alkyl halides undergo further substitution (halogenation) in presence of sunlight, heat, etc.

$$C_2H_5Br \xrightarrow[h\nu]{Br_2} C_2H_4Br_2 \xrightarrow[h\nu]{Br_2} C_2H_3Br_3 \ldots$$

- **Oxidation reaction:** Primary alkyl halides (1°) on oxidation with dimethyl sulphoxide, $(CH_3)_2SO$ (DMSO) gives an aldehyde **(Swern oxidation)** while 2° halides give ketone.



$$\underset{(1°)}{R—CH_2X} \xrightarrow[(CH_3)_2SO]{DMSO} \underset{\text{Aldehyde}}{R—\overset{\overset{O}{\|}}{C}—H}, \quad \underset{(2°)}{R_2CHX} \xrightarrow[(CH_3)_2SO]{DMSO} \underset{\text{Ketone}}{R_2CO}$$

Oxidation can also be done with $(CH_2)_6N_4/HOH, H^+$ oxidising agent. Benzyl halide on oxidation with $(CH_2)_6N_4/HOH, H^+$ gives benzaldehyde **(Sommelet aldehyde synthesis).**

Methods of preparation of gem-dihalides (Alkylidene halides)

- **From aldehydes and ketones:** By the action of PCl_5.
- **From alkynes:** By addition of two moles of HX (HBr or HCl).

Methods of preparation of vic-dihalides (Alkylene halides)

- **From alkenes:** By the addition of halogens (Cl_2 or Br_2).
- **From glycols:** By the action of PCl_5 or HCl or $SOCl_2$.

Chemical properties of gem- and vic-dihalides

- Chemically alkylidene (gem-) dihalides are less reactive while alkylene (vic-) dihalides have nearly the same reactivity as alkyl halides.
- **Hydrolysis with aqueous KOH:** Gem-dihalides give aldehyde or ketones while vic-dihalides give glycols.
- **Action of alc. KCN followed by hydrolysis and heat:** Gem-dihalides give monocarboxylic acid while, vic-dihalides give cyclic anhydride.
  These reactions are **distinction tests** between gem- and vic-dihalides.
- **Reaction with Zn dust in methanol:** Both gem- and vic-dihalides give alkenes.
- **Reaction with alc. KOH (Dehydrohalogenation):** Both give alkynes.
- **Reaction with sodamide ($NaNH_2$) on heating:** Both give alkynes.

Trichloromethane, $CHCl_3$ (Chloroform)

- **Preparation: Lab method** and large scale preparation.
- **From ethanol:** By distilling a mixture of alcohol with a suspension of bleaching powder ($CaOCl_2$). The Cl_2 obtained from bleaching powder serves both as oxidising as well as chlorinating agent. Alcohol is first oxidised to

aldehyde by chlorine. The aldehyde then reacts with chlorine to form trichloro acetaldehyde (chloral) which on hydrolysis with $Ca(OH)_2$ yields chloroform.

- **From acetone:** Acetone first reacts with chlorine to form trichloro acetone which is then hydrolysed by $Ca(OH)_2$ to give chloroform.
- **From carbon tetrachloride:** By the partial reduction with Fe/H_2O.
- **From chloral hydrate:** Pure $CHCl_3$ is obtained by distilling chloral hydrate with concentrated NaOH solution.
- **Properties:** Chloroform is a sweet smelling liquid, b.pt. 61°C, non-inflammable but its vapour causes unconsciousness.
- **Oxidation:** When exposed to sunlight and air, it slowly decomposes into phosgene ($COCl_2$), a poisonous gas. Such chloroform cannot be used for anaesthetic purpose, so it is stored in dark blue or brown coloured bottles filled up to the neck.
- It is mixed with 1% C_2H_5OH which retards the oxidation and converts the phosgene into harmless ethyl carbonate.

$$\underset{\text{Phosgene}}{COCl_2} + 2C_2H_5OH \longrightarrow \underset{\text{Diethyl carbonate}}{(C_2H_5O)_2CO} + 2HCl$$

- **Reduction:** On reduction with Zn/HCl in presence of alcohol, chloroform forms methylene chloride (dichloromethane).
  But on reduction with Zn dust/H_2O, methane is the main product.
- **Chlorination:** Chloroform reacts with Cl_2 in presence of diffused sunlight or UV light to form CCl_4.
- **Hydrolysis with aqueous alkali:** It gives Na/K salt of formic acid.
- **Nitration:** With concentrated HNO_3, chloroform forms **chloropicrin** (nitro chloroform) which is a liquid, poisonous and used as an insecticide and a war gas (tear gas).
- **Heating with silver powder:** Acetylene is formed when chloroform is heated at high temperature with silver powder.
- **Condensation with acetone:** Chloroform condenses with acetone on heating in presence of alkali to form chloretone (1,1,1-trichloro-2-methyl propan-2-ol) which is used as a **hypnotic** (drug).
- **Reaction with sodium ethoxide:** On heating chloroform with C_2H_5ONa, it gives ethyl *ortho*-formate, $HC(OC_2H_5)_3$.
- **Reimer-Tiemann reaction:** Chloroform reacts with phenol when heated at 65°C in presence of alkali gives salicylaldehyde (*o*-hydroxy benzaldehyde) as major product.
- **Carbylamine reaction (isocyanide test):** Chloroform on heating with primary (1°) amine in presence of alcoholic KOH forms isocyanide (carbylamine) having very offensive odour (a test of $CHCl_3$ and also of primary amine).
- **Tests of chloroform:** It gives isocyanide test (pungent smell). Pure $CHCl_3$ does not give white precipitate with $AgNO_3$, but with Tollens' reagent, it gives a grey precipitate of silver. On heating with Fehling's solution, it gives brown precipitate.

Tri-iodomethane, CHI_3 (Iodoform)

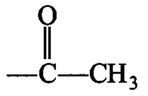
- Iodoform resembles chloroform in methods of preparation and properties.
- It is prepared by heating compounds like ethanol, 2-alkanols and methyl ketones with iodine and alkali solution or Na_2CO_3.

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\text{Heat}} CHI_3 + 5NaI + HCOONa + 5H_2O$$

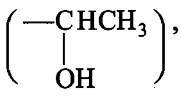
$$CH_3COCH_3 + 3I_2 + 2Na_2CO_3 \xrightarrow{\text{Heat}} CHI_3 + 3NaI + CH_3COONa + 2CO_2$$

The reactions producing iodoform are called **Iodoform reactions.**

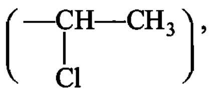
- **Properties:** It is a yellow crystalline solid, pungent characteristic odour, m.pt. 119°C and is steam volatile. It is used as an antiseptic for dressing wounds.
- Hydrolysis with KOH: Iodoform gives HCOOK.
- Reduction with red P/HI: It gives methylene iodide, CH_2I_2.
- Heating with Ag powder: Acetylene is formed.
- Carbylamine reaction: With aniline and KOH gives phenyl isocyanide, C_6H_5NC (an offensive smell).
- Heating alone: It gives I_2 vapours.
- With $AgNO_3$: It gives a yellow precipitate of AgI (difference from $CHCl_3$).
- **Tests of CHI_3:** Iodoform reaction is mainly given by CH_3CH_2OH, CH_3CHO,



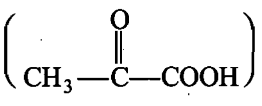
$-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ group (methyl ketones), -2-ols



$\left(-\underset{\underset{\displaystyle OH}{|}}{C}HCH_3\right)$, secondary alkyl halides



$\left(-\underset{\underset{\displaystyle Cl}{|}}{C}H-CH_3\right)$, etc. Lactic acid [($CH_3CH(OH)COOH$)] and pyruvic acid



$\left(CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-COOH\right)$ also gives iodoform reaction.

Tetrachloromethane, CCl_4 (Carbon tetrachloride):

- **Preparations—From methane:** By chlorination (excess of Cl_2) at 400°C. Methane used in this method is obtained from natural gas.

- **From CS_2:** Chlorine reacts with CS_2 in presence of catalyst $AlCl_3$ or $SbCl_5$ to form sulphur monochloride (S_2Cl_2) and then CCl_4.
- **From propane:** By reacting excess of Cl_2 at 400°C under atmospheric pressure forms liquid CCl_4.
- **Properties:** It is a liquid, b.pt. 77°C, non-inflammable, hence used as a solvent for fats, oils, waxes and resins, etc. It is used as a fire extinguisher under the name **pyrene.**

  Reaction with steam (oxidation): CCl_4 reacts with superheated steam at 500°C to form phosgene, a poisonous gas.

  Reduction: It is reduced by iron filling into chloroform.

  Hydrolysis with aqueous KOH: It gives CO_2 and then KCl and K_2CO_3.

  Reimer-Tiemann reaction: Phenol combines with CCl_4 in presence of alkali to form *o*-hydroxy benzoic acid (salicylic acid).

  Friedel-Crafts reaction: Benzene on treatment with CCl_4 in presence of anhydrous $AlCl_3$ gives dichlorodiphenyl methane which on hydrolysis forms diphenyl ketone (benzophenone).

Some important halogen derivatives

- **Chlorofluoro carbons: Freons (CFC's)**

  Freons are small organic molecules containing C, Cl and F. The most common freons are CF_2Cl_2, dichlorodifluoromethane **(freon-12)** and CF_3Cl, chlorotrifluoromethane **(freon-11).**
- **Preparation:** Action of HF on CCl_4 forms freon-12.

$$CCl_4 + 2HF \xrightarrow[\text{or SbF}_5\text{, Catalyst}]{\text{SbCl}_5\text{ or SbF}_3} \underset{\text{Freon-12}}{CCl_2F_2} + 2HCl$$

- **Freon-12** is widely used as refrigerant and propellant in aerosol sprays of all kinds. Halothane ($CF_3CHBrCl$) is used as inhalation anaesthetic.
- Action of SbF_3 on CCl_4:

$$3CCl_4 + 2SbF_3 \xrightarrow[\Delta]{SbCl_5} 3CCl_2F_2 + 2SbCl_3$$

$$6HF + 2SbCl_3 \xrightarrow{\text{Heat}} 2SbF_3 + 6HCl$$

- Freon is a gas under ordinary condition. Its b.pt. is –29.8°C and can easily be liquefied. It is chemically inert.
- **Westron** ($CHCl_2—CHCl_2$) or acetylene tetrachloride:

$$\underset{\text{Acetylene}}{HC\equiv CH} + 2Cl_2 \xrightarrow[\text{AlCl}_3\text{,Catalyst}]{\text{FeCl}_3\text{ or}} \underset{\text{1,1,2,2-Tetrachloroethane}}{CHCl_2—CHCl_2}$$

  It is non-inflammable liquid, b.pt. is 146°C and highly toxic in nature.
- **Westrosol** ($CHCl{=}CCl_2$) or Trichloroethene:

$$\underset{\text{Westron}}{CHCl_2—CHCl_2} + Ca(OH)_2 \xrightarrow{\text{Heat}} \underset{\text{Westrosol}}{2CHCl{=}CCl_2} + CaCl_2 + 2H_2O$$

- Both westron and westrosol are used as solvents for oils, fats, waxes, resins, paints and varnishes, etc.

QUESTIONS

Very Short Answer Type

1. Fill in the blanks:

(a) The compound prepared by the action of magnesium on dry ethyl bromide in ether is known as ....

(b) The interaction of elemental sulphur with Grignard reagent gives ....

$$\left[\textbf{Hint: } S + RMgX \rightarrow RSMgX \xrightarrow{H_2O} \underset{\text{Trioalcohol}}{RSH} + Mg(OH)X\right]$$

(c) Pure chloroform is obtained by heating ...... with aqueous solution of sodium hydroxide.

(d) Grignard's reagent has the general formula ....

(e) When acetone is heated with bleaching powder ...... is obtained.

(f) A sensitive test of chloroform is based on the formation of ....

(g) The yellow precipitate in the reaction of acetone with iodine in the presence of alkali is ....

(h) An alkyl halide may be converted into alcohol by ...... reaction.

(i) The most reactive alkyl halides are ....

(j) Another name of 1,1,2,2-tetrachloroethane is ....

(k) The well known refrigerant freon has the structure ....

(l) Chloropicrin is formed by the action of ...... on chloroform.

(m) Carbon tetrachloride is used as fire extinguisher under the name ....

(n) Diethyl ether is obtained from ethyl bromide by treating it with ...... and the name of the reaction is ....

(o) Chloroform when exposed to light and air forms a poisonous gas known as ....

(p) Chloroform forms a hypnotic when reacts with ....

(q) Allyl chloride is a ...... compound while vinyl chloride is inert towards nucleophilic substitution.

(r) The dihalides in which halogen atoms are attached to adjacent carbon atoms are termed as ....

(s) Alkyl halides are formed when thionyl chloride and ...... are refluxed in presence of pyridine.

(t) The order of reactivity (tertiary > secondary > primary) is due to + *I* effect of the alkyl groups which ...... the polarity of C—*X* bond.

(u) The hydrolysis of trialkyl chlorosilane, R_3SiCl, yields ....

(v) Ethylene chloride on hydrolysis with aq. KOH forms ....

(w) When chloroform is heated with primary amine and alcoholic KOH, it forms a very offensive smelling compound, the name of the compound is ...... and the reaction is known as ...... reaction.

(x) *Gem* dihalides on hydrolysis yield ....

(y) Vinyl chloride on reaction with dimethyl copper gives ....

(z) Both westron and westrosol are used as ...... for oils, fats and varnishes.

2. State, whether the following statements are **True** or **False**:

(a) Alkyl halides follow the reactivity sequence,

$$R\text{—I} > R\text{—Br} > R\text{—Cl} > R\text{—F}$$

(b) Alkyl halides when treated with dry silver oxide form alcohols.

(c) Carbon tetrachloride is inflammable.

(d) Alkyl halides are soluble in water.

(e) Chloroform gives carbylamine reaction with primary amines.

(f) Westrosol is a very good solvent for fats, oils, waxes, resins, etc.

(g) Ethyl bromide when heated with silver acetate forms ethyl alcohol.

(h) Polytetrafluoro ethylene is commercially known as teflon.

(i) Iodoform is a yellow coloured antiseptic compound.

(j) Pure chloroform gives precipitate with silver nitrate.

(k) Iodoform when heated with silver nitrate gives yellow precipitate.

(l) *Gem*-dihalides on hydrolysis yield aldehydes or ketones.

(m) The reaction of methyl magnesium iodide with acetone followed by hydrolysis, gives secondary alcohol.

(n) Chloroform is stored in dark coloured bottles.

(o) Vinyl chloride reacts with dilute NaOH to form vinyl alcohol.

(p) Allyl chloride is more reactive than vinyl chloride.

(q) CCl_4 is more reactive than $CHCl_3$.

(r) Alcohol is added to chloroform to prevent its oxidation.

(s) Alkyl iodides are less stable and thus, darken on standing.

(t) Acetaldehyde and all methyl ketones undergo haloform test.

(u) Alkyl halides react with benzene in presence of anhydrous aluminium chloride to form homologues of benzene. This reaction is called Wurtz-Fittig reaction.

(v) $(CH_3)_3CCl$ is a 3° halide.

(w) Alkyl halides being polar compounds are soluble in water.

(x) Tertiary butyl bromide undergoes S_N1 reactions.

(y) Both *vic*- and *gem*-dihalides on heating with zinc dust in presence of alcohol form same alkene.

(z) Pyruvic acid and lactic acid do not give iodoform test.

3. Match the following:

(i)	(A) Carbon tetrachloride	1. Antiseptic
	(B) Chloretone	2. Refrigerant
	(C) Westrosol	3. Chloroform
	(D) Freon	4. Polymer
	(E) Iodoform	5. Hypnotic
	(F) Teflon	6. Pyrene
	(G) Carbylamine reaction	7. Solvent
(ii)	(A) Acetone	1. Plastic
	(B) Chloropicrin	2. Gem-dihalide
	(C) PVC	3. Vic-dihalide
	(D) $RCHCl_2$	4. Iodoform test
	(E) $CH_2Cl—CH_2Cl$	5. Grignard reagent
	(F) $RMgX$	6. $CHCl_3 + HNO_3$

4. What is the final product in each reaction?

(i) $C_2H_5OH \xrightarrow[NaOH]{I_2} ?$

(ii) $CHCl_3 \xrightarrow[Heat]{Ag} ?$

(iii) $CHCl_3 \xrightarrow{HNO_3} ?$

(iv) $CCl_4 \xrightarrow{Fe/H_2O} ?$

(v) $C_6H_5NH_2 \xrightarrow[KOH]{CHCl_3} ?$

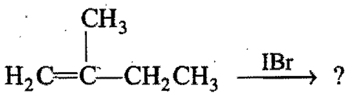
(vi) $CH_3MgBr \xrightarrow{NH_3} ?$

(vii) $H_2C{=}CH—CH_2Cl \xrightarrow{Aq.\ KOH} ?$

(viii) $H_2C{=}CHCl \xrightarrow{Aq.\ KOH} ?$

(ix) $CH_3Li \xrightarrow{CH_2{=}CH_2} ?$

(x) $(CH_3)_3CCl \xrightarrow{(CH_3)_2Zn} ?$

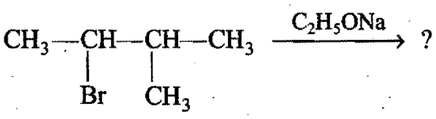
(xi) 

$H_2C{=}\underset{}{\overset{CH_3}{\overset{|}{C}}}—CH_2CH_3 \xrightarrow{IBr} ?$

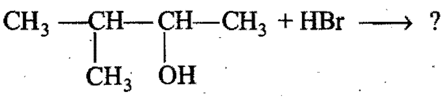
(xii) $CH_3—CH{=}CH_2 \xrightarrow{NBS} ?$

(xiii) $H_2C{=}CH—CH_2Br \xrightarrow{HBr} ?$

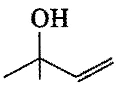
(xiv) $R_3MgX \xrightarrow{(CH_3)_2CO/H_2O} ?$

(xv) 

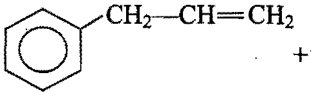
$CH_3—\underset{Br}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{CH}}—CH_3 \xrightarrow{C_2H_5ONa} ?$

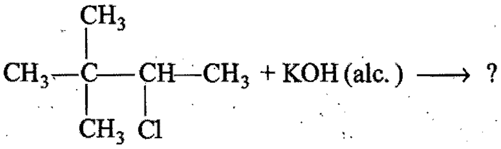
(xvi) 

$CH_3—\underset{CH_3}{\underset{|}{CH}}—\underset{OH}{\underset{|}{CH}}—CH_3 + HBr \longrightarrow ?$

(xvii)  + HBr → ?

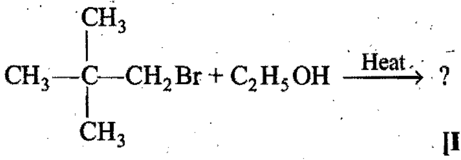
(xviii)  + NBS → ?

(ix)  + HBr → ?

(xx) 

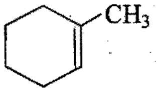
$CH_3—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—\underset{Cl}{\underset{|}{CH}}—CH_3 + KOH\,(alc.) \longrightarrow ?$

(xxi) $(CH_3)_3C—CH_2Br + KOH\,(alc.) \longrightarrow ?$

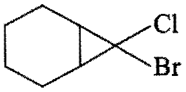
(xxii) 

$CH_3—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—CH_2Br + C_2H_5OH \xrightarrow{Heat} ?$

[IIT 2000]

(xxiii)  $+ HBr \xrightarrow{Peroxide} ?$

[Roorkee 2000]

(xxiv)  $\xrightarrow{Bu_3SnH} ?$

5. What happens when? Give equations only:
   - (i) Chlorine reacts with CS_2 in presence of anhydrous aluminium chloride.
   - (ii) Chloroform is heated with alcoholic KOH and aniline.
   - (iii) Ethyl alcohol is heated with iodine and sodium hydroxide.
   - (iv) Ethyl alcohol reacts with bleaching powder.
   - (v) Chlorine is passed through ethyl alcohol.
   - (vi) Ethyl bromide reacts with sodium ethoxide.
   - (vii) Ethyl bromide reacts with silver cyanide.
   - (viii) Chloral is treated with aqueous sodium hydroxide.
   - (ix) Carbon tetrachloride is treated with hydrogen fluoride in presence of antimony fluoride.
   - (x) Ethyl amine is heated with chloroform and alcoholic KOH.
   - (xi) Chloroform is boiled with aqueous potassium hydroxide.
   - (xii) Ethyl bromide is treated with alcoholic caustic soda.
   - (xiii) Ethyl bromide is heated with zinc.
   - (xiv) Methyl magnesium bromide is treated with formaldehyde followed by hydrolysis.
   - (xv) 2-Bromopentane is heated with alcoholic KOH.
   - (xvi) 2-Chloro-2-methylpropane is treated with potassium *tert*-butoxide in dimethyl sulphoxide.
   - (xvii) Tertiary butyl chloride reacts with ethylene in presence of $AlCl_3$.
   - (xviii) Benzene reacts with *n*-propyl chloride in presence of anhydrous $AlCl_3$.

Short Answer Type

6. How will you obtain the following compounds from ethyl bromide?
(a) Ethene, (b) *n*-Butane, (c) Ethanol,
(d) Diethyl ether, (e) Ethyl acetate, (f) Ethane.

7. Describe the action of KOH($aq.$) on:
   (a) CH_3Cl, (b) CH_2Cl_2, (c) $CHCl_3$, (d) CCl_4
8. How will you synthesise?
   (a) Isopropyl bromide from n-propyl bromide.
   (b) n-Propyl bromide from isopropyl bromide.
   (c) Propionic acid from ethyl bromide.
   (d) 1-Bromopropane from 1-chloropropane.
   (e) Ethylene glycol from ethyl chloride.
   (f) Chloroform from ethyl alcohol.
   (g) Iodoform from acetylene.
   (h) Vinyl bromide from ethyl alcohol.
   (i) Allyl chloride from propane.
   (j) Methyl iodide from methane.
9. Complete the following by providing (A), (B), (C) and (D):

(i) $CH_3CH_2CH_2OH \xrightarrow{PBr_3} (A) \xrightarrow{Alc.\ KOH}$

$(B) \xrightarrow{HBr} (C) \xrightarrow{NH_3} (D)$

(ii) $CH_3CH_2CH_2I \xrightarrow{Alc.\ KOH} (A) \xrightarrow{H^+/H_2O}$

$(B) \xrightarrow{SOCl_2} (C) \xrightarrow[LiAlH_4]{H} (D)$

(iii) $CH_3CHBrCH_3 \xrightarrow{Alc.\ KOH} (A) \xrightarrow[Peroxide]{HBr}$

$(B) \xrightarrow[Acetone]{NaI} (C) \xrightarrow[Ether]{Mg} (D)$

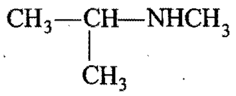
(iv) $CH_3CH_2CH{=}CH_2 \xrightarrow[Light]{NBS} (A) \xrightarrow{Alc.\ KOH} (B)$

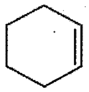
$\xrightarrow{HBr} (C)$

(v) $CH_3CH_2MgBr \xrightarrow{CH_3CHO/H_2O} (A) \xrightarrow{HBr} (B)$

$\xrightarrow{Alc.\ KOH} (C)$

(vi) $(A) \xrightarrow{NH_3} (B) \xrightarrow{CHCl_3 + KOH(alc.)} (C) \xrightarrow[C_2H_5OH]{Na}$


$CH_3-\underset{\underset{CH_3}{|}}{CH}-NHCH_3$

(vii)  $\xrightarrow[(CH_2Cl_2)]{Br_2} (A) \xrightarrow[CH_3COOH]{Zn}$

$(B) \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ (BH_3)_2} (C)$

[Roorkee 2000]

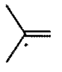
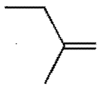
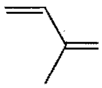
(viii) $CH_3CH_2Br \xrightarrow[(ii)\ H_2O/H^+]{(i)\ (CH_2)_6N_4} (A) \xrightarrow{NaOH} (B)$

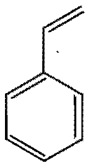
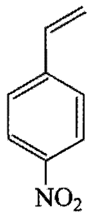
$\xrightarrow[(ii)\ Zn/HOH]{(i)\ O_3} (A) + (C) \xrightarrow{Conc.\ NaOH} (D)$

10. Give structures and IUPAC names of the products expected from reaction between 1-chlorobutane and (a) KOH (alc.), (b) NaOH($aq.$), (c) NH_3, (d) H_2S, (e) $C_6H_6 + AlCl_3$, (f) C_2H_5ONa.
11. How will you distinguish between the following?
   (a) Chloroform and carbon tetrachloride.
   [**Hint :** Chloroform gives carbylamine reaction, $i.e.$, when heated with aniline and alcoholic KOH, offensive smell of isocyanide is produced. CCl_4 does not give this test.]
   (b) Ethyl chloride and vinyl chloride.
   [**Hint :** Ethyl chloride reacts with alcoholic silver nitrate to give a white precipitate of AgCl. Vinyl chloride does not give this test.]
   (c) Alkyl halide and an alkane.
   [**Hint :** Alkyl halide gives a positive Beilstein test. Alkane does not give this test. Alkyl halide gives a ppt. of AgX when warmed with alcoholic silver nitrate solution. Alkane does not give this test.]
   (d) Ethylene bromide and ethylidene bromide.
   (e) Chloroform and iodoform.
   [**Hint :** Chloroform is a sweet smelling colourless liquid while iodoform is a yellow crystalline solid having a pungent characteristic smell. Iodoform gives yellow ppt. with $AgNO_3$ solution. This reaction is not shown by chloroform.]
12. (a) Identify the product (A), (B) and (C).

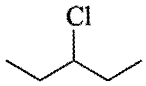
$$C_2H_4 \xrightarrow{HBr} (A) \xrightarrow{Hydrolysis} (B) \xrightarrow[I_2]{Na_2CO_3} (C)$$

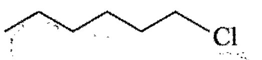
   (b) Write the structural formulae of the isomers of the alkyl halide, $C_5H_{11}Br$.
      (w) Which one undergoes E_1 elimination at the fastest rate?
      (x) Which one can give only a single alkene on E_2 elimination?
      (y) Which one gives the most complex mixture of alkenes on E_2 elimination?
      (z) Which one is incapable of reacting by the E_2 elimination?
   (c) A compound is formed by substitution of two chlorine atoms for two H-atoms in propane. What is the number of structural isomers possible?
13. Write down the IUPAC names and structures of all the possible isomers having the molecular formula $C_2H_4Cl_2$. How are these prepared and distinguished?
14. (i) State which compound has a faster rate of reaction with HCl.

(a)  or  (b)  or 

(c)  or 

(ii) In the following pairs of halogen compounds, which compound undergoes faster $S_{N}1$ reaction?

(d)  and 

(e)  and 

(iii) In the following pairs of halogen compounds, which compound undergoes faster S_N2 reaction with ^-OH?

(f) CH_3Br or CH_3I (g) $(CH_3)_3C—Cl$ or CH_3Cl

15. (a) Arrange alkyl halides, water and alkane in order of decreasing density.

(b) Arrange chloromethanes and water in order of decreasing density.

(c) Arrange Me*X* in order of decreasing bond length.

(d) Arrange Me*X* in order of decreasing bond strength.

(e) Arrange Me*X* in order of activity.

(f) Arrange alkyl halides ($1°, 2°, 3°$) in order of decreasing S_N2 reactivity.

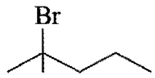
(g) Arrange the order of reactivity of alcohols towards H*X*.

(h) Arrange the decreasing order of reactivity in haloforms.

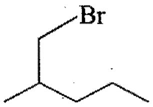
(i) Arrange the following isomeric bromides in order of decreasing reactivity in S_N2 displacement:

(a)

(I) 

(II) 

(III) 

(IV) 

(b) 2-Bromo-2-methylbutane (I), 1-Bromopentane (II), 2-Bromopentane (III)

(c) 1-Bromo-3-methylbutane (I), 2-Bromo-2-methylbutane (II), 2-Bromo-3-methylbutane (III)

(d) 1-Bromobutane (I), 1-Bromo-2-methylbutane (II), 1-Bromo-3-methylbutane (III), 1-Bromo-2,2-dimethylpropane (IV)

16. Explain the following:

(a) Carbon tetrachloride is used as fire extinguisher.

[**Solution :** The dense vapours form a protective layer on the burning objects and prevent the oxygen or air to come in contact with the burning objects.]

(b) Use of chloroform as anaesthetic is decreasing.

[**Solution :** Due to side effects, as it causes liver damage, etc., it is rarely used as anaesthetic these days.]

(c) Chloroform is kept with a little ethyl alcohol in a dark brown coloured bottle.

[**Solution :** When exposed to **sunlight** and **air**, chloroform slowly decomposes into phosgene and hydrogen chloride. Phosgene is extremely poisonous gas. As to prevent the decomposition, it is stored in dark brown coloured bottle and 1% ethyl alcohol is added. This retards the decomposition and converts phosgene into harmless ethyl carbonate.

$$CHCl_3 + [O] \longrightarrow COCl_2 + HCl;$$

$$COCl_2 + 2C_2H_5OH \longrightarrow (C_2H_5)_2CO_3 + 2HCl]$$

(d) Iodoform gives precipitate with $AgNO_3$ on heating while chloroform does not.

[**Solution :** C—I bond being less stable than C—Cl bond and thus undergoes fission on heating giving I^- ions which combine with Ag^+ ions to form a yellow ppt.]

(e) Alkyl iodides become darken on standing in presence of light.

[**Solution :** Alkyl iodides are less stable and lose free iodine. This iodine makes the remaining iodide darken.]

(f) A small amount of NaI or KI catalyses the hydrolysis of *R*Cl or the reaction,

$$RCl + R'ONa \longrightarrow ROR' + NaCl$$

[**Solution :** NaI or KI reacts with *R*Cl to form *R*I. The alkyl iodide is comparatively more reactive than alkyl chloride, it undergoes hydrolysis readily or reacts with *R*′ONa to form ether.

$$RI + HOH \longrightarrow ROH + HI;$$

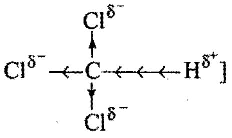
$$RI + R'ONa \longrightarrow ROR' + NaI]$$

(g) While preparing alkyl halides from alkanes, dry gaseous hydrohalogen acids are used instead of their aqueous solutions.

[**Solution :** Dry hydrohalogen acids are stronger acids and better electrophiles than H_3O^+ formed in the aqueous solutions. Furthermore, H_2O is a nucleophile and can easily react with *R*—*X* to form alcohol.]

(h) Hydrogen atom of chloroform is definitely acidic in nature.

[**Solution :** Chlorine is more electronegative than carbon. Due to three chlorine atoms, the carbon acquires partial positive charge on account of –*I* effect. The carbon atom, thus, attracts the electron pair of C—H bond towards itself making the hydrogen atom removal as proton easier

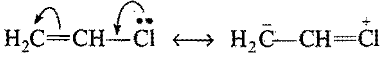


$$\begin{array}{c} Cl^{\delta-} \\ \uparrow \\ Cl^{\delta-} \leftarrow C \leftarrow\leftarrow\leftarrow H^{\delta+} \\ \uparrow \\ Cl^{\delta-} \end{array}]$$

(i) Vinyl halide is less reactive while allyl halide is more reactive than alkyl halides. **or**

Vinyl chloride does not give S_N reaction but allyl chloride gives.

[**Solution :** In vinyl chloride C—Cl bond is stable due to resonance (as in chloro benzene)



$$H_2C{=}CH{-}\ddot{Cl} \longleftrightarrow H_2\bar{C}{-}CH{=}\overset{+}{Cl}$$

Hence, Cl atom cannot be replaced. Further sp^2-hybridized carbon is more acidic than sp^3-carbon.

In allyl chloride, S_N reaction is easier since allyl carbonium ion formed after removal of Cl^- is stabilized by resonance.

$H_2C{=}CH{-}CH_2Cl \longrightarrow Cl^- + H_2C{=}CH{-}\overset{+}{C}H_2$

$\longleftrightarrow H_2\overset{+}{C}{-}CH{=}CH_2]$

(j) Why is free radical halogenation of alkanes is seldom used for laboratory preparation of alkyl halides ? Under what condition good yields of monosubstituted chlorides can be obtained?

[**Solution :** Several isomeric monosubstituted halides are formed because alkanes have different types of hydrogen atoms. Their separation is difficult. Thus, free radical halogenation method is not used unless the parent hydrocarbon possesses equivalent hydrogen atoms. Good yields are obtained in hydrocarbons such as CH_3-CH_3, $(CH_3)_4C$, cyclopropane, etc.]

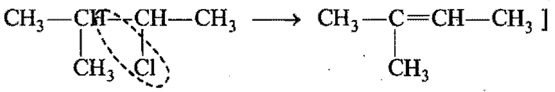
(k) What effect should the following resonance of vinyl chloride have on its dipole moment?

$$H_2C{=}\overset{\delta^+}{C}H\overset{\delta^-}{Cl} \longleftrightarrow H_2\overset{\delta^-}{C}{-}CH{=}\overset{\delta^+}{Cl}$$

[**Solution :** The dipole moment increases because the distance between positive and negative partial charges increases.]

(l) 2-Chloro-3-methylbutane on treatment with alcoholic potash gives 2-methylbut-2-ene as the major product.

[**Solution :** Elimination occurs in accordance to Saytzeff's rule, *i.e.*, elimination of hydrogen from the carbon which is attached with least number of hydrogen atoms.



$$CH_3{-}\underset{CH_3}{\underset{|}{C}H}{-}\underset{Cl}{\underset{|}{C}H}{-}CH_3 \longrightarrow CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CH{-}CH_3\ ]$$

Major product

(m) Compare the rates of (i) S_N1 and (ii) S_N2 reactions of allyl chloride and *n*-propyl chloride.

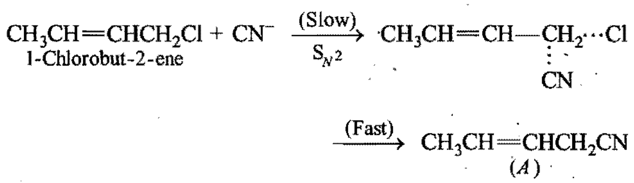
[**Solution :** (i) Allyl chloride is much more reactive than *n*-propyl chloride and the +charge of its intermediate R^+ is stabilized by resonance $(H_2C{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow H_2\overset{+}{C}{=}CH{-}CH_2)$

(ii) Allyl chloride is again more reactive but not to the extent of S_N1 reaction and stabilizes the transition state.]

(n) When $CH_3CH{=}CHCH_2Cl$ reacts with alcoholic potassium cyanide, a mixture of isomeric products is obtained.

[**Solution :** It can undergo S_N1 and S_N2 reactions.

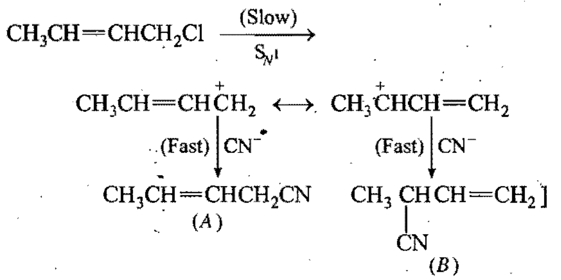
By S_N2 reaction only one product (A) is formed.



$$\underset{\text{1-Chlorobut-2-ene}}{CH_3CH{=}CHCH_2Cl} + CN^- \xrightarrow[S_N2]{(Slow)} CH_3CH{=}CH{-}\underset{CN}{\underset{\vdots}{CH_2}}\cdots Cl$$

$$\xrightarrow{(Fast)} \underset{(A)}{CH_3CH{=}CHCH_2CN}$$

By S_N1 reaction, the intermediate is carbocation (resonance stabilized) and can give a mixture of two isomeric products (A) and (B).



$$CH_3CH{=}CHCH_2Cl \xrightarrow[S_N1]{(Slow)}$$

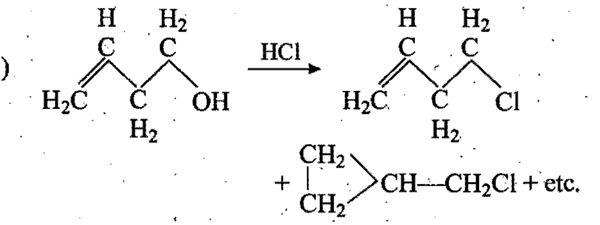
$$CH_3CH{=}CH\overset{+}{C}H_2 \longleftrightarrow CH_3\overset{+}{C}HCH{=}CH_2$$

$$\downarrow (Fast)\ CN^- \qquad \downarrow (Fast)\ CN^-$$

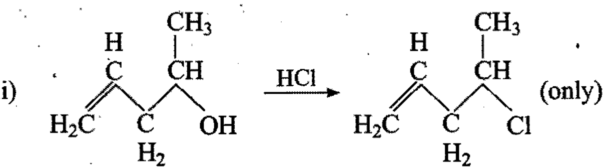
$$\underset{(A)}{CH_3CH{=}CHCH_2CN} \qquad \underset{(B)}{CH_3\underset{CN}{\underset{|}{C}H}CH{=}CH_2}\ ]$$

(o) The formation of the products giving the structures of the intermediates.

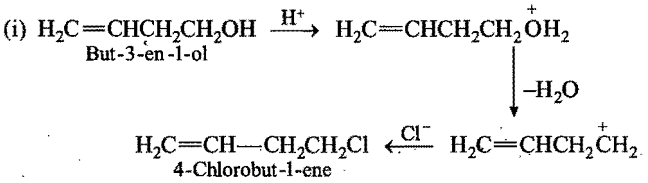
(i)



(ii)



[**Solution :**

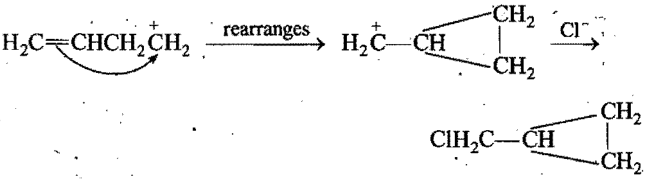


(i) $\underset{\text{But-3-en-1-ol}}{H_2C{=}CHCH_2CH_2OH} \xrightarrow{H^+} H_2C{=}CHCH_2CH_2\overset{+}{O}H_2$

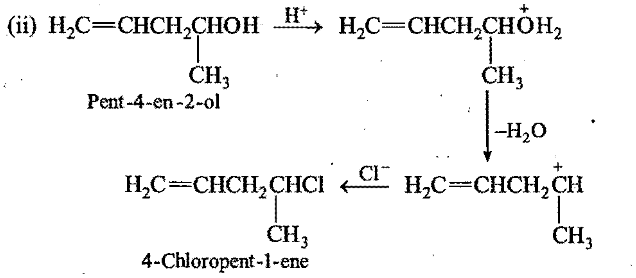
$\downarrow -H_2O$

$\underset{\text{4-Chlorobut-1-ene}}{H_2C{=}CH{-}CH_2CH_2Cl} \xleftarrow{Cl^-} H_2C{=}CHCH_2\overset{+}{C}H_2$

and for the cyclic product:



In this reaction, the major product (4-chlorobut-1-ene) is formed by S_N2 mechanism. Now the second product is formed by the initial formation of carbocation and attacked by the double bond on the +ve carbon atom to form a second (cyclic) carbocation, which eventually gives the product.]

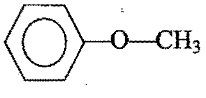


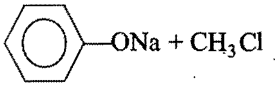
(ii) $\underset{\text{Pent-4-en-2-ol}}{H_2C{=}CHCH_2\underset{CH_3}{\underset{|}{C}H}OH} \xrightarrow{H^+} H_2C{=}CHCH_2\underset{CH_3}{\underset{|}{C}H}\overset{+}{O}H_2$

$\downarrow -H_2O$

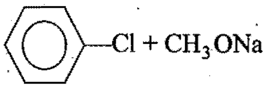
$\underset{\text{4-Chloropent-1-ene}}{H_2C{=}CHCH_2\underset{CH_3}{\underset{|}{C}H}Cl} \xleftarrow{Cl^-} H_2C{=}CHCH_2\underset{CH_3}{\underset{|}{\overset{+}{C}H}}$

In this reaction, the $+I$ effect of CH_3 — group avoids cyclisation.]

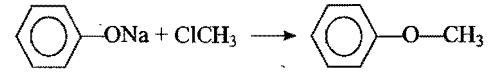
(p) Anisole  can be prepared by either of the following two reactions:

(i) 

or

(ii) 

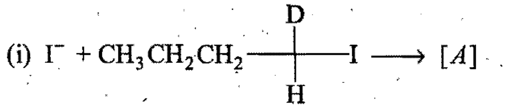
Which one (i) or (ii) is preferred?

[**Solution.**(i) 

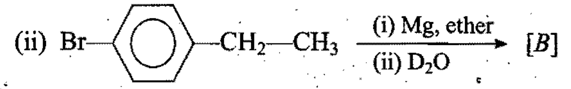
because in equation (ii) C—Cl bond is stable due to resonance hence nucleophilic attack is not preferred.]

17. Write the structural formulae of the isomers for the compound with molecular formula, $C_2BrClFI$ **[IIT 2001]**

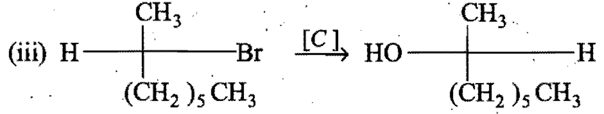
18. Give structures/configurations of the products in the following reactions: **[Roorkee 2001]**



(i) $I^- + CH_3CH_2CH_2-\overset{D}{\underset{H}{+}}-I \longrightarrow [A]$



(ii) $Br-C_6H_4-CH_2-CH_3 \xrightarrow[\text{(ii) } D_2O]{\text{(i) Mg, ether}} [B]$



(iii) $H-\overset{CH_3}{\underset{(CH_2)_5CH_3}{+}}-Br \xrightarrow{[C]} HO-\overset{CH_3}{\underset{(CH_2)_5CH_3}{+}}-H$

ANSWERS

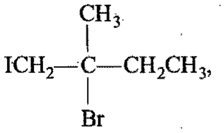
1. (a) Grignard reagent; (b) thioalcohol; (c) chloral; (d) R—Mg—X; (e) chloroform; (f) phenyl isocyanide; (g) iodoform; (h) nucleophilic substitution; (i) alkyl iodides; (j) westron; (k) CF_2Cl_2; (l) nitric acid; (m) pyrene; (n) sodium ethoxide, Williamson's synthesis; (o) phosgene; (p) acetone; (q) reactive; (r) vic-dihalides or alkylene halides; (s) alcohols; (t) increases;
(u) $R_3Si-O-SiR_3$; (v) glycol; (w) isocyanide, carbylamine;
(x) aldehydes or ketones; (y) polyvinyl chloride; (z) solvent.

2. (a) True; (b) False—form ethers; (c) False—non-inflammable; (d) False—insoluble; (e) True; (f) True; (g) False—ethyl acetate; (h) True; (i) True; (j) False—does not form precipitate; (k) True; (l) True; (m) False—tertiary butyl alcohol; (n) True;
(o) False—does not react; (p) True; (q) False—less reactive;
(r) True; (s) True; (t) True; (u) False—Friedel-Craft reaction;
(v) True; (w) False— insoluble; (x) True; (y) True;
(z) False—undergo iodoform test.

3. (i) (A—6); (B—5); (C—7); (D—2); (E—1); (F—4); (G—3).
(ii) (A—4); (B—6); (C—1); (D—2); (E—3); (F—5).

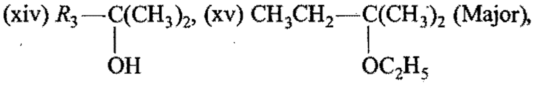
4. (i) CHI_3, (ii) $HC{\equiv}CH$, (iii) CCl_3NO_2, (iv) $CHCl_3$, (v) C_6H_5NC, (vi) CH_4, (vii) $H_2C{=}CHCH_2OH$, (viii) No reaction,

(ix) $CH_3CH_2CH_2Li$, (x) $(CH_3)_4C$, (xi)

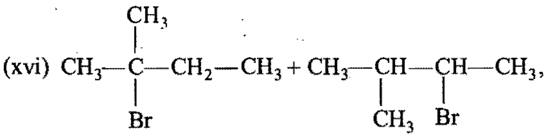


$ICH_2-\overset{CH_3}{\underset{Br}{C}}-CH_2CH_3$,

(xii) $BrCH_2HC{=}CH_2$, (xiii) $BrCH_2-CH_2-CH_2Br$,



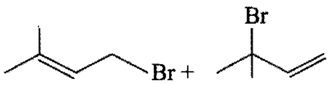
(xiv) $R_3-\underset{OH}{C}(CH_3)_2$, (xv) $CH_3CH_2-\underset{OC_2H_5}{C}(CH_3)_2$ (Major),



(xvi) $CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3 + CH_3-\underset{CH_3}{CH}-\underset{Br}{CH}-CH_3$,

(Major) (Minor)

(xvii)

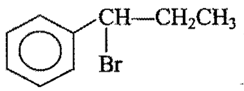


(Major) (Minor)

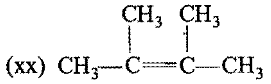
(xviii)

,

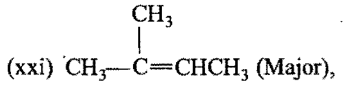
(xix)



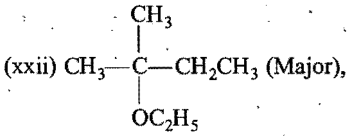
(Due to 1,2-hydride shift),



(xx) $CH_3-\overset{CH_3}{C}{=}\overset{CH_3}{C}-CH_3$ (Due to 1,2-methyl shift),

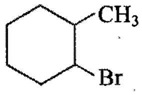


(xxi) $CH_3-\overset{CH_3}{C}{=}CHCH_3$ (Major),

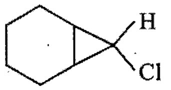


(xxii) $CH_3-\overset{CH_3}{\underset{OC_2H_5}{C}}-CH_2CH_3$ (Major),

(xxiii)



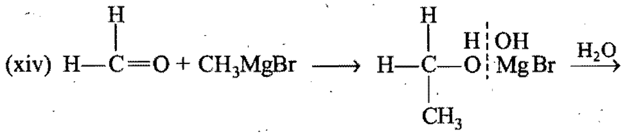
(xxiv)



5. (i) $CS_2 + 3Cl_2 \xrightarrow{AlCl_3} CCl_4 + S_2Cl_2$
(ii) $C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$
(iii) $C_2H_5OH + 4I_2 + 6KOH \longrightarrow CHI_3 + HCOOK + 5KI + 5H_2O$
(iv) $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$; $C_2H_5OH \xrightarrow[{[O]}]{Cl_2}$

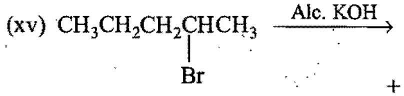
$CH_3CHO \xrightarrow{Cl_2} CCl_3CHO \xrightarrow{Ca(OH)_2} CHCl_3 + (HCOO)_2Ca$

(v) $C_2H_5OH \xrightarrow[{[O]}]{Cl_2} CH_3CHO \xrightarrow{Cl_2} CCl_3CHO$ (Chloral)
(vi) $C_2H_5Br + NaOC_2H_5 \longrightarrow C_2H_5OC_2H_5 + NaBr$
(vii) $C_2H_5Br + AgCN \longrightarrow C_2H_5NC + AgBr$
(viii) $CCl_3CHO + NaOH \longrightarrow CHCl_3 + HCOONa$
(ix) $CCl_4 + H_2F_2 \xrightarrow{SbF_3} CCl_2F_2 + 2HCl$ (Freon)
(x) $C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5NC + 3KCl + 3H_2O$
(xi) $CHCl_3 + 4KOH \longrightarrow HCOOK + 3KCl + 2H_2O$
(xii) $C_2H_5Br + \text{Alc. KOH} \longrightarrow C_2H_4 + KBr + H_2O$
(xiii) $2C_2H_5Br + 2Zn \longrightarrow (C_2H_5)_2Zn + ZnBr_2$



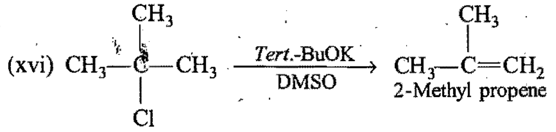
(xiv) $H-\overset{H}{C}{=}O + CH_3MgBr \longrightarrow H-\overset{H}{\underset{CH_3}{C}}-O\overset{H\,\vdots\,OH}{\vdots}MgBr \xrightarrow{H_2O}$

$CH_3CH_2OH + Mg(OH)Br$



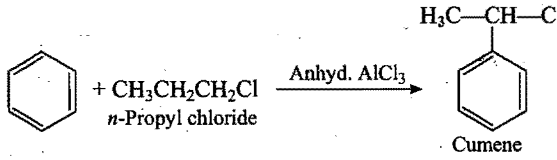
(xv) $CH_3CH_2CH_2\underset{Br}{C}HCH_3 \xrightarrow{\text{Alc. KOH}} CH_3CH_2CH_2CH{=}CH_2$ Pent-1-ene

$+ CH_3CH_2CH{=}CHCH_3$ Pent-2-ene (*cis* and *trans*)
[Pent-2-ene (*trans*-) predominates]



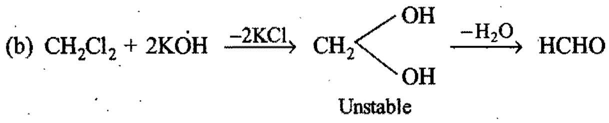
(xvi) $CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_3 \xrightarrow[\text{DMSO}]{\textit{Tert}\text{.-BuOK}} CH_3-\overset{CH_3}{C}{=}CH_2$ 2-Methyl propene

(xvii) $(CH_3)_3C-Cl + H_2C{=}CH_2 \xrightarrow{AlCl_3}$
$(CH_3)_3C-CH_2CH_2Cl$
1-Chloro-3,3-dimethylbutane

(xviii)


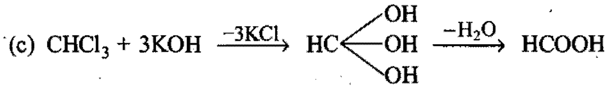
6. (a) C_2H_5Br + Alc.KOH,
(b) C_2H_5Br + Na,
(c) $C_2H_5Br + (Aq.)NaOH$ or $C_2H_5Br + AgOH$,
(d) $C_2H_5Br + NaOC_2H_5$,
(e) $C_2H_5Br + CH_3COOAg$,
(f) $C_2H_5Br + H_2(LiAlH_4)$.

7. (a) $CH_3Cl + KOH \longrightarrow CH_3OH + KCl$

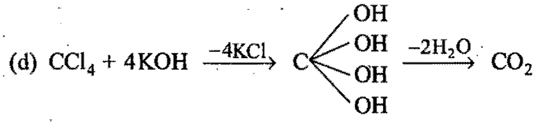
(b)


$$CH_2Cl_2 + 2KOH \xrightarrow{-2KCl} CH_2(OH)_2 \xrightarrow{-H_2O} HCHO$$

Unstable

(c)


$$CHCl_3 + 3KOH \xrightarrow{-3KCl} HC(OH)_3 \xrightarrow{-H_2O} HCOOH$$

(d)


$$CCl_4 + 4KOH \xrightarrow{-4KCl} C(OH)_4 \xrightarrow{-2H_2O} CO_2$$

8. (a) $CH_3CH_2CH_2Br \xrightarrow{\text{Alc. KOH}} CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3CHBrCH_3$

(b) $CH_3CHBrCH_3 \xrightarrow{\text{Alc. KOH}} CH_3CH{=}CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3CH_2CH_2Br$

(c) $C_2H_5Br \xrightarrow{KCN} C_2H_5CN \xrightarrow{H_2O} C_2H_5COOH$

(d) $CH_3CH_2CH_2Cl \xrightarrow{\text{Alc. KOH}} CH_3CH{=}CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3CH_2CH_2Br$

(e) $CH_3CH_2Cl \xrightarrow{\text{Alc. KOH}} CH_2{=}CH_2 \xrightarrow[KMnO_4]{\text{Alkaline}} CH_2OHCH_2OH$

(f) $C_2H_5OH + CaOCl_2$ (Bleaching powder)
$[CaOCl_2 + HOH \longrightarrow Cl_2 + Ca(OH)_2]$

$$C_2H_5OH \xrightarrow[{[O]}]{Cl_2} CH_3CHO \xrightarrow{Cl_2} CCl_3CHO \xrightarrow{Ca(OH)_2} CHCl_3 + (HCOO)_2Ca$$

(g) $HC{\equiv}CH \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO \xrightarrow[NaOH]{I_2} CHI_3 + HCOONa$

(h) $C_2H_5OH \xrightarrow[\text{Heat}]{H_2SO_4} C_2H_4 \xrightarrow[CCl_4]{Br_2} CH_2Br—CH_2Br \xrightarrow{\text{Alc. KOH}} CH_2{=}CHBr$

(i) $CH_3CH_2CH_3 \xrightarrow[UV]{Cl_2} CH_3CH_2CH_2Cl + CH_3CHClCH_3 \xrightarrow{\text{Alc. KOH}} CH_3CH{=}CH_2 \xrightarrow[500°C]{Cl_2} ClCH_2CH{=}CH_2$

(j) $CH_4 \xrightarrow[UV]{Cl_2} CH_3Cl \xrightarrow[\text{Acetone}]{NaI} CH_3I$

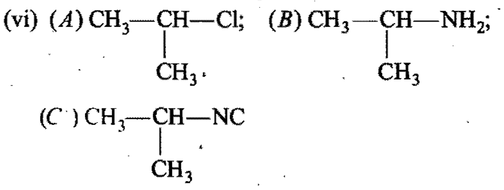
9. (i) (*A*) $CH_3CH_2CH_2Br$; (*B*) $CH_3CH{=}CH_2$; (*C*) $CH_3CHBrCH_3$; (*D*) $CH_3CHNH_2CH_3$

(ii) (*A*) $CH_3CH{=}CH_2$; (*B*) $CH_3CHOHCH_3$; (*C*) $CH_3CHClCH_3$; (*D*) $CH_3CH_2CH_3$.

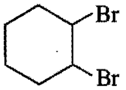
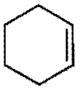
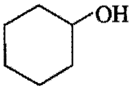
(iii) (*A*) $CH_3CH{=}CH_2$; (*B*) $CH_3CH_2CH_2Br$; (*C*) $CH_3CH_2CH_2I$; (*D*) $CH_3CH_2CH_2MgI$.

(iv) (*A*) $CH_3CH(Br)CH{=}CH_2$; (*B*) $CH_2{=}CH—CH{=}CH_2$; (*C*) $CH_3CH(Br)CH{=}CH_2$ and $CH_3CH{=}CH—CH_2Br$

(v) (*A*) $CH_3CH_2CH(OH)CH_3$; (*B*) $CH_3CH_2CH(Br)CH_3$; (*C*) $CH_3CH{=}CHCH_3$.

(vi)


(*A*) $CH_3—CH(CH_3)—Cl$; (*B*) $CH_3—CH(CH_3)—NH_2$;
(*C*) $CH_3—CH(CH_3)—NC$

(vii) (*A*)

(*Trans*-); (*B*)

; (*C*)


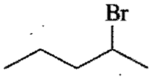
(viii) (*A*) CH_3CHO; (*B*) $CH_3CH{=}CHCHO$
(*C*) $OHC—CHO$; (*D*) $HOCH_2—COONa$

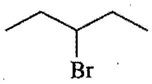
10. (a) $CH_3CH_2CH{=}CH_2$ (But-1-ene);
(b) $CH_3CH_2CH_2CH_2OH$ (Butan-1-ol);
(c) $CH_3CH_2CH_2CH_2NH_2$ (Butanamine);
(d) $CH_3CH_2CH_2CH_2SCH_2CH_2CH_2CH_3$ (1-Butylthiobutane);
(e) $C_6H_5 — C_4H_9$ (Butylbenzene;);
(f) $C_4H_9OC_2H_5$ (1-Ethoxybutane).

12. (a) (*A*) C_2H_5Br (Ethylbromide); (*B*) C_2H_5OH (Ethylalcohol); (*C*) CHI_3 (Iodoform)
(b) Eight isomers:

(i)

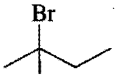
1-Bromopentane

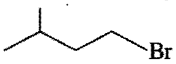
(ii)

2-Bromopentane

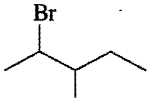
(iii)

3-Bromopentane

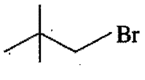
(iv)

1-Bromo-2-methyl butane

(v)

2-Bromo-2-methylbutane

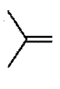
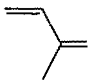
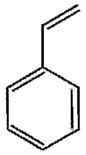
(vi)

1-Bromo-3-methylbutane

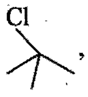
(vii)

2-Bromo-3-methylbutane

(viii)

1-Bromo-2,2-dimethyl propane

(w) (v) and (viii), (x) (i), (y) (ii) Pent-1-ene, Pent-2-ene (*cis* and *trans*), (z) (iv)
(c) Four isomers : $ClCH_2CH_2CH_2Cl$; $CH_3CHClCH_2Cl$; $CH_3CH_2CHCl_2$; $CH_3CCl_2CH_3$.

13. $C_2H_4Cl_2$—Two structural isomers CH_3CHCl_2 (1,1-dichloroethane) and CH_2ClCH_2Cl (1,2-dichloroethane).

14. (i) (a)

(b)

(c)


(ii) (d) 

, Because tertiary halide reacts faster than secondary halide due to greater stability of tertiary carbocation.

(e) 

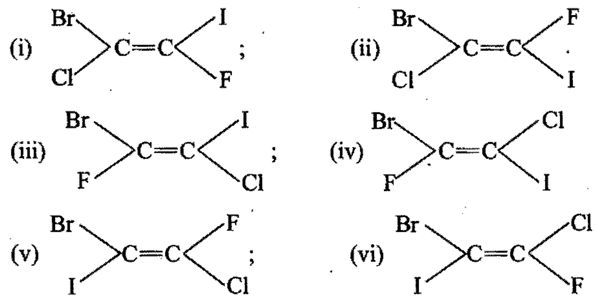
, Because of greater stability of secondary carbocation than primary.

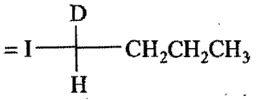
(iii) (f) CH_3I, Because I^- ion is a better leaving group than Br^- ion due to its large size.

(g) CH_3Cl, Because of stearic hindrance in $(CH_3)_3C—Cl$.

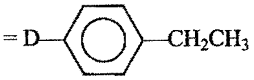
15. (a) $RI > RBr > H_2O > RCl > RF > RH$
(b) $CCl_4 > CHCl_3 > CH_2Cl_2 > H_2O > CH_3Cl$
(c) $MeI > MeBr > MeCl > MeF$
(d) $MeF > MeCl > MeBr > MeI$
(e) $MeI > MeBr > MeCl > MeF$
(f) $MeX > RCH_2—X > R_2CH—X > R_3C—X$
(g) Allyl, benzyl > 3° > 2° > 1°
(h) $CHI_3 > CHBr_3 > CHCl_3 > CH_3F$
(i) (a) I > IV > III > II (b) II > III > I
(c) I > III > II (d) I > III > II > IV

16. $C_2BrClFI$. It has six isomers:



17. (i) $[A] =$ 

$$I—\overset{D}{\underset{H}{C}}—CH_2CH_2CH_3$$

(ii) $[B] =$ 

(iii) $[C] = KOH$ or OH^- or $NaOH/CCl_4$

PROBLEMS BASED ON STRUCTURE AND PROPERTIES

1. An organic compound (*A*) $C_7H_{15}Cl$ on treatment with alcoholic caustic potash gives a hydrocarbon (*B*) C_7H_{14}. (*B*) on treatment with ozone and subsequent hydrolysis gives acetone and butyraldehyde. What are (*A*) and (*B*)?

[**Hint:** (*A*) $(CH_3)_2CClCH_2CH_2CH_2CH_3$

or

$(CH_3)_2CHCHClCH_2CH_2CH_3$

$$(B)\ (CH_3)_2C{=}CHCH_2CH_2CH_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} (CH_3)_2CO + OHCCH_2CH_2CH_3$$]

2. A chloro compound (*A*) showed the following properties: (a) decolourised bromine water, (b) absorbed hydrogen catalytically, (c) gives precipitate with ammonical cuprous chloride, (d) when vaporized 1.49 g of (*A*) gave 448 mL of vapours at STP. Identify (*A*) and write down the reactions involved.

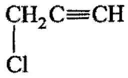
[**Hint:** First two properties indicate, the compound is unsaturated. The third property shows that the compound has $\equiv CH$ grouping.

$$\text{Molecular mass} = \frac{22400 \times 1.49}{448} = 74.5$$

Let the formula of the compound be $RClC{\equiv}CH$, *i.e.*,

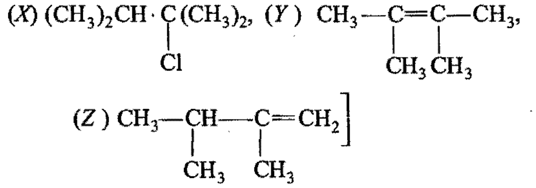
$R + 35.5 + 25 = 74.5$

$R = 14(CH_2)$

The compound is  (3-Chloropropyne)]

$$\underset{\displaystyle Cl}{CH_2}C{\equiv}CH$$

3. An alkyl halide (*X*) of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes (*Y*) and (*Z*) of formula C_6H_{12}. Both alkenes on hydrogenation give 2,3-dimethylbutane. Predict (*X*), (*Y*) and (*Z*).

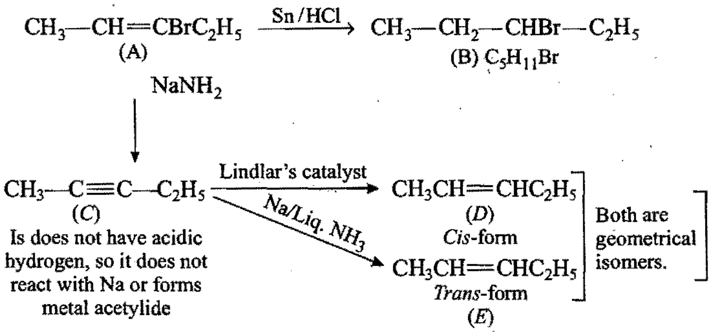
[**Ans.** 

$$(X)\ (CH_3)_2CH\cdot\underset{\displaystyle Cl}{C}(CH_3)_2,\ (Y)\ CH_3—\underset{\displaystyle CH_3}{C}{=}\underset{\displaystyle CH_3}{C}—CH_3,$$

$$(Z)\ CH_3—\underset{\displaystyle CH_3}{CH}—\underset{\displaystyle CH_3}{C}{=}CH_2$$]

4. An organic compound (*A*), C_5H_9Br which readily decolourises bromine water and $KMnO_4$ solution gives (*B*), $C_5H_{11}Br$ on treatment with Sn/HCl. The reaction of (*A*) with $NaNH_2$ produces (*C*) with evolution of ammonia. (*C*) neither reacts with sodium nor forms any metal acetylide but reacts with Lindlar catalyst to give (*D*) and on reaction with Na/liq. NH_3 produces (*E*). Both the compounds (*D*) and (*E*) are isomeric. Give structures of (*A*) to (*E*) with proper reasoning.

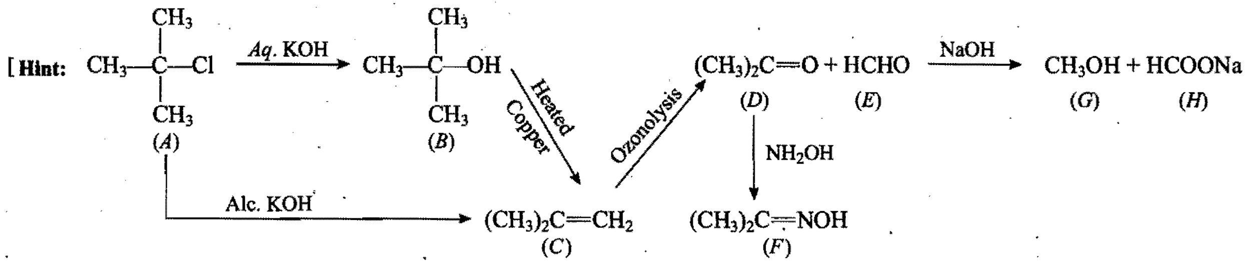
[**Hint:** Compound (*A*) is an unsaturated compound consisting a double bond as it decolourises bromine water and $KMnO_4$ solution.



5. An organic compound (*A*), C_4H_9Cl on reacting with aqueous KOH gives (*B*) and on reaction with alcoholic KOH gives (*C*) which is also formed by passing vapours of (*B*) over heated copper. The compound (*C*) readily

decolourises bromine water. Ozonolysis of (*C*) gives two compounds (*D*) and (*E*). Compound (*D*) reacts with NH_2OH to give (*F*) and the compound (*E*) reacts with NaOH to give an alcohol (*G*) and sodium salt (*H*) of an acid. (*D*) can also be prepared from propyne on treatment with water in presence of Hg^{2+} and H_2SO_4. Identify (*A*) to (*H*) with proper reasoning.

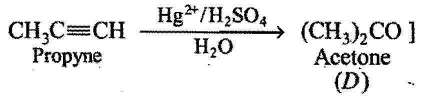
[**Hint:**



$$\underset{(A)}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl} \xrightarrow{Aq.\ KOH} \underset{(B)}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH} \xrightarrow{\text{Heated Copper}} \underset{(C)}{(CH_3)_2C{=}CH_2} \xrightarrow{\text{Ozonolysis}} \underset{(D)}{(CH_3)_2C{=}O} + \underset{(E)}{HCHO} \xrightarrow{NaOH} \underset{(G)}{CH_3OH} + \underset{(H)}{HCOONa}$$

$$(A) \xrightarrow{\text{Alc. KOH}} \underset{(C)}{(CH_3)_2C{=}CH_2}$$

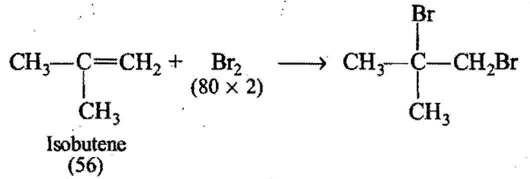
$$\underset{(D)}{(CH_3)_2C{=}O} \xrightarrow{NH_2OH} \underset{(F)}{(CH_3)_2C{=}NOH}$$



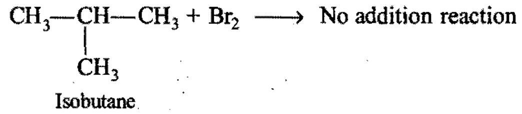
$$\underset{\text{Propyne}}{CH_3C\equiv CH} \xrightarrow[H_2O]{Hg^{2+}/H_2SO_4} \underset{\underset{(D)}{\text{Acetone}}}{(CH_3)_2CO}\ ]$$

6. A 10 g mixture of isobutane and isobutene requires 20 g of Br_2 (in CCl_4) for complete addition. If 10 g of the mixture is catalytically hydrogenated and the entire alkane is monobrominated in the presence of light at 120°C, which exclusive product and how much of it would be formed? (Atomic weight of bromine = 80)

[**Hint:** Let isobutane be a g and isobutene b g. Thus $a + b = 10$ g



$$\underset{\underset{(56)}{\text{Isobutene}}}{CH_3-\underset{\underset{CH_3}{|}}{C}{=}CH_2} + \underset{(80\times 2)}{Br_2} \longrightarrow CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Br$$

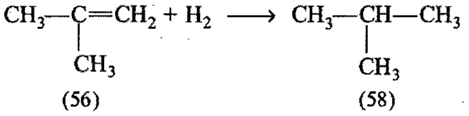


$$\underset{\text{Isobutane}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3} + Br_2 \longrightarrow \text{No addition reaction}$$

Now 160 g of Br_2 reacts with 56 g of isobutene

$\therefore$ 20 g of Br_2 reacts with $\dfrac{56 \times 20}{160} = 7$ g of isobutene (b)

Thus, amount of isobutane (a) is $(10 - 7) = 3$ g



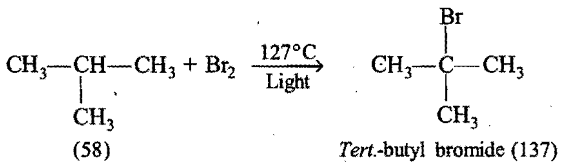
$$\underset{(56)}{CH_3-\underset{\underset{CH_3}{|}}{C}{=}CH_2} + H_2 \longrightarrow \underset{(58)}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3}$$

Now 56 g of isobutene gives 58 g of isobutane

$\therefore$ 7 g of isobutene gives $\dfrac{58 \times 7}{56} = 7.25$ g of isobutane

Total amount of isobutane available for 10 g mixture

$= (7.25 + 3)$ g $= 10.25$ g



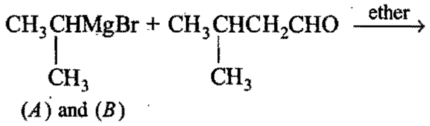
$$\underset{(58)}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3} + Br_2 \xrightarrow[\text{Light}]{127°C} \underset{\textit{Tert}\text{.-butyl bromide (137)}}{CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

Now 58 g of isobutane gives 137 g of *tert*-butyl bromide

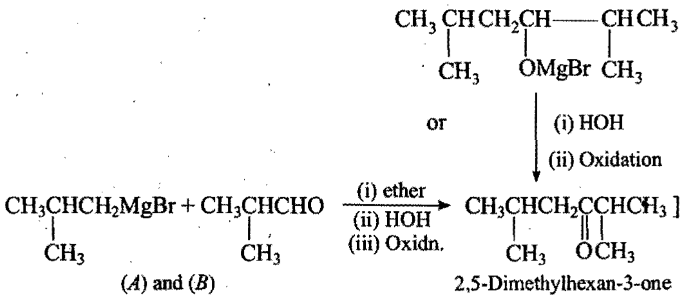
$\therefore$ 10.25 g of isobutane gives $\dfrac{13.7 \times 10.25}{58} = 24.21$ g of *tert*-butyl bromide.]

7. Compounds (A) and (B) on reaction in ether medium and subsequent acidification and oxidation give 2,5-dimethylhexan-3-one. What are (A) and (B)?

[**Hint:**



$$\underset{(A)\text{ and }(B)}{CH_3\underset{\underset{CH_3}{|}}{C}HMgBr + CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CHO} \xrightarrow{\text{ether}}$$



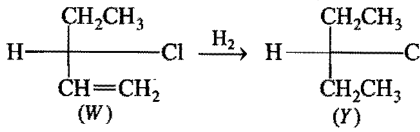
$$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2\underset{\underset{OMgBr}{|}}{C}H-\underset{\underset{CH_3}{|}}{C}HCH_3 \xrightarrow[\text{(ii) Oxidation}]{\text{(i) HOH}}$$

or

$$\underset{(A)\text{ and }(B)}{CH_3\underset{\underset{CH_3}{|}}{C}HCH_2MgBr + CH_3\underset{\underset{CH_3}{|}}{C}HCHO} \xrightarrow[\text{(iii) Oxidn.}]{\text{(i) ether; (ii) HOH}} \underset{\text{2,5-Dimethylhexan-3-one}}{CH_3\underset{\underset{CH_3}{|}}{C}HCH_2\underset{\underset{O}{\|}}{C}\underset{\underset{CH_3}{|}}{C}HCH_3}\ ]$$

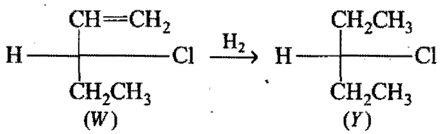
8. (W) and (X) are optically active isomers of C_5H_9Cl. (W) on treatment with 1 mol of H_2 is converted to an optically inactive compound (Y) but (X) gives an optically active compound (Z) under the same conditions. Give structure of (Y) and configurations of (W), (X) and (Z) in Fischer projections. **[Roorkee 2000]**

[**Hint:**

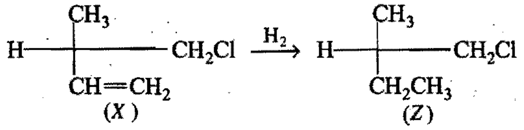


$$\underset{(W)}{H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH{=}CH_2}{|}}{C}}-Cl} \xrightarrow{H_2} \underset{(Y)}{H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-Cl}$$

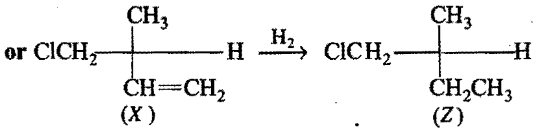
or



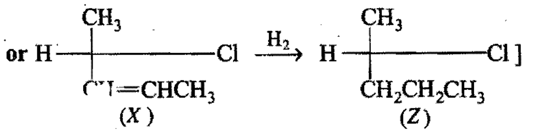
$$\underset{(W)}{H-\overset{\overset{CH{=}CH_2}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-Cl} \xrightarrow{H_2} \underset{(Y)}{H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-Cl}$$



$$H-\underset{\underset{(X)}{CH=CH_2}}{\overset{CH_3}{|}}-CH_2Cl \xrightarrow{H_2} H-\underset{\underset{(Z)}{CH_2CH_3}}{\overset{CH_3}{|}}-CH_2Cl$$



$$\text{or } ClCH_2-\underset{\underset{(X)}{CH=CH_2}}{\overset{CH_3}{|}}-H \xrightarrow{H_2} ClCH_2-\underset{\underset{(Z)}{CH_2CH_3}}{\overset{CH_3}{|}}-H$$



$$\text{or } H-\underset{\underset{(X)}{CH=CHCH_3}}{\overset{CH_3}{|}}-Cl \xrightarrow{H_2} H-\underset{\underset{(Z)}{CH_2CH_2CH_3}}{\overset{CH_3}{|}}-Cl\,]$$

9. On electrolysis, an alcoholic solution of sodium chloride gives a sweet smelling liquid (*A*) which gives carbylamine reaction and condenses with acetone to form hypnotic. What is (*A*)? Give reactions of its formation.

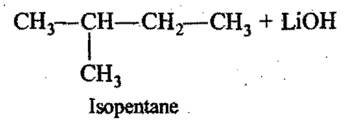
[**Hint :** $NaCl \rightleftharpoons Na^+ + Cl^-$. At anode Cl_2 is discharged and electrolytic solution contains NaOH on electrolysis. Cl_2 oxidises alcohol to acetaldehyde which is chlorinated to chloral. Chloral on hydrolysis yields chloroform.

$$C_2H_5OH \xrightarrow[{[O]}]{Cl_2} CH_3CHO \xrightarrow{Cl_2} CCl_3CHO \xrightarrow{NaOH} \underset{(A)}{CHCl_3} + HCOONa$$

$CHCl_3$ gives carbylamine reaction and condenses with acetone to form hypnotic.]

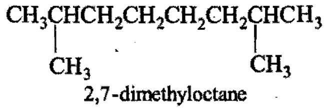
10. *R*Cl is treated with Li in ether to form *R*—Li. *R*—Li reacts with water to form isopentane. *R*—Cl also reacts with sodium to form 2,7-dimethyloctane. What is the structure of *R*—Cl?

[**Hint :** $R-Li + H_2O \longrightarrow$



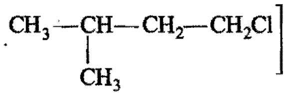
$$\underset{\text{Isopentane}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3} + LiOH$$

$R-Cl + Na + Cl-R \rightarrow$



$$\underset{\text{2,7-dimethyloctane}}{CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CH_2CH_2\underset{CH_3}{\underset{|}{C}}HCH_3}$$

The structure of *R*Cl is,



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2Cl\,]$$

11. Which hydrocarbon is consistent with the following formation? Molecular mass = 72 gives a single monochloride and two dichlorides on photochlorination.

[**Hint :** Let the hydrocarbon be C_nH_{2n+2}, *i.e.*, $12n + 2n + 2 = 72$ or $n = 5$. The hydrocarbon is C_5H_{12}. As it forms a single monochloride, all the hydrogen atoms are equivalent. The compound is $(CH_3)_4C$, *i.e.*, neopentane. Single chloro derivative is $(CH_3)_3CCH_2Cl$ and the two dichlorides are $(CH_3)_3CCHCl_2$ and $(CH_3)_2C(CH_2Cl)_2$]

12. With alkali $C_3H_6Cl_2$ (*A*) gives C_3H_6O(*B*) or C_3H_4 (*C*). (*C*) reacts with dilute H_2SO_4 containing mercuric sulphate to give C_3H_6O (*D*) which gives iodoform test.

[**Ans.** (*A*) is $CH_3CH_2CHCl_2$ (1,1-Dichloropropane)
(*B*) is CH_3CH_2CHO (Propanal)
(*C*) is $CH_3-C\equiv CH$ (Propyne)
(*D*) is CH_3COCH_3 (Acetone)]

OBJECTIVE QUESTIONS

SET I : This set contains the questions with single correct answer.

1. The derivatives not found in nature are:
(a) alkanes ☐ (b) carbohydrates ☐
(c) fats ☐ (d) alkyl halides ☐

2. C_2H_5Br can be obtained in the laboratory by the action of ethyl alcohol with:
(a) KBr ☐
(b) NH_4Br ☐
(c) Br_2 ☐
(d) KBr and conc. H_2SO_4 ☐

3. The reaction,

$$\text{Alcohol} + HCl \rightleftharpoons \text{Alkyl halide} + H_2O$$

is reversible. For the completion of the reaction ...... is used.
(a) anhydrous zinc chloride ☐
(b) concentrated H_2SO_4 ☐
(c) excess of water ☐
(d) calcium chloride ☐

4. Which one is an organometallic compound?
(a) C_2H_5ONa ☐ (b) C_2H_5SNa ☐
(c) C_2H_5MgI ☐ (d) All of these ☐

5. A Grignard reagent is prepared by the action of magnesium in dry ether on: **[EAMCET (Med.) 2006; CPMT 2008]**
(a) C_2H_5OH ☐ (b) C_2H_6 ☐
(c) C_2H_5Cl ☐ (d) C_2H_5CN ☐

6. Iodoform is formed on warming iodine and sodium hydroxide with:
(a) CH_3OH ☐ (b) C_2H_5OH ☐
(c) HCOOH ☐ (d) C_2H_6 ☐

7. Ozone in stratosphere is depleted by: **[AIIMS 2004]**
(a) C_6F_6 ☐ (b) CF_2Cl_2 ☐
(c) C_7F_{16} ☐ (d) $C_6H_6Cl_6$ ☐

8. Chloral is:
(a) CCl_3CHO ☐ (b) CCl_3CH_3 ☐
(c) CCl_3COCH_3 ☐ (d) CCl_3CH_2OH ☐

9. The poisonous gas obtained by exposing chloroform to air and sunlight is: **[CPMT 2004]**
(a) CH_2Cl_2 ☐ (b) $COCl_2$ ☐
(c) CH_2O ☐ (d) CH_3Cl ☐

10. Which is the correct formula of bleaching powder? **[BHU 2005]**
(a) Ca(OCl)Cl ☐ (b) CaO(OCl) ☐
(c) $Ca(OCl)_2$ ☐ (d) $Ca(OCl)_2Cl$ ☐

11. When chloroform is treated with aniline and potassium hydroxide we get:
(a) sweet odour ☐
(b) bitter almond odour ☐
(c) very repulsive characteristic odour ☐
(d) none of the above ☐

12. When the reaction between methyl iodide and sodium ethoxide occurs, we get:
(a) methyl acetate ☐ (b) ethyl methyl ketone ☐
(c) ethyl acetate ☐ (d) ethyl methyl ether ☐

13. The bad smelling substance formed by the action of alcoholic caustic potash on chloroform and aniline is:
(a) phenyl isocyanide ☐ (b) nitrobenzene ☐
(c) chloropicrin ☐ (d) acetylene ☐

14. ..... would be obtained by boiling $CHCl_3$ with caustic soda.
(a) Sodium acetate ☐ (b) Sodium formate ☐
(c) Sodium oxalate ☐ (d) Methyl alcohol ☐

15. Heating together of sodium ethoxide and ethyl iodide will give:
(a) ethyl alcohol ☐ (b) acetaldehyde ☐
(c) diethyl ether ☐ (d) acetic acid ☐

16. Chloropicrin is:
(a) picric derivative ☐ (b) nitrochloroform ☐
(c) nitromethane ☐ (d) nitroethyl chloride ☐

17. $CH_3OH \xrightarrow{PI_3} (A) \xrightarrow{KCN} (B) \xrightarrow{\text{Hydrolysis}} (C)$

The compound (*C*) is:
(a) CH_3OH ☐ (b) HCOOH ☐
(c) CH_3CHO ☐ (d) CH_3COOH ☐

18. $C_2H_5Br \xrightarrow{KCN} (A) \xrightarrow[HCl]{\text{Hydrolysis}} (B)$

The compound (*B*) in above reaction is:
(a) ethylene chloride ☐ (b) acetic acid ☐
(c) propionic acid ☐ (d) ethyl cyanide ☐

19. Which of the following reactions is an example of nucleophilic substitution reaction? **[CBSE (Med.) 2009]**
(a) $RX + Mg \longrightarrow RMgX$ ☐
(b) $RX + KOH \longrightarrow ROH + KX$ ☐
(c) $2RX + 2Na \longrightarrow R{-}R + 2NaX$ ☐
(d) $RX + H_2 \longrightarrow RH + HX$ ☐

20. Chloroform can be obtained from:
(a) methanol ☐ (b) methanal ☐
(c) propan-1-ol ☐ (d) propan-2-ol ☐

21. When iodoform is heated with Ag powder it forms:
(a) acetylene ☐ (b) ethylene ☐
(c) methane ☐ (d) ethane ☐

22. Which one of the following is gem-dihalide?
(a) $CH_3CH_2Br_2$ ☐ (b) $CH_2Br \cdot CH_2Br$ ☐
(c) $CH_3CHBrCH_2Br$ ☐ (d) $CH_3CHBrCH_2CH_2Br$ ☐

23. Ethylene dichloride and ethylidene chloride are isomeric compounds. Identify the statement which is not applicable to both of them:

(a) they react with alcoholic KOH ☐
(b) they are dihalides ☐
(c) they react with aq. KOH and give the same product ☐
(d) they respond to Beilstein's test ☐

24. A sample of chloroform before using as an anaesthetic, is tested by: **[JIPMER 2003]**
(a) Fehling's solution ☐
(b) ammoniacal cuprous chloride ☐
(c) ammoniacal silver nitrate solution ☐
(d) silver nitrate solution after boiling with alcoholic KOH ☐

25. Ethyl alcohol is obtained when ethyl chloride is boiled with:
(a) alcoholic KOH ☐ (b) aqueous KOH ☐
(c) water ☐ (d) H_2O_2 ☐

26. Which one of the following statements is wrong?
(a) Lower alkyl halides are either colourless gases or volatile liquids ☐
(b) Alkyl halides are very soluble in water ☐
(c) Alkyl halides burn easily with green edged flame ☐
(d) The higher alkyl halides are colourless solids ☐

27. Alkyl halides are used for the preparation of:
(a) alkanes ☐ (b) alkenes ☐
(c) alcohols ☐ (d) all of these ☐

28. A silver salt of fatty acid on heating with alkyl halide gives:
(a) ether ☐ (b) alcohol ☐
(c) ester ☐ (d) aldehyde ☐

29. The product obtained when ethyl alcohol is distilled with bleaching powder is:
(a) chloroform ☐ (b) ethyl chloride ☐
(c) acetaldehyde ☐ (d) chloral ☐

30. Chlorination of CS_2 gives:
(a) carbon tetrachloride ☐ (b) chloroform ☐
(c) both of these ☐ (d) none of these ☐

31. Which will be obtained by boiling CH_2Cl_2 with caustic soda?
(a) Sodium oxalate ☐ (b) Sodium acetate ☐
(c) Sodium formate ☐ (d) Ethyl alcohol ☐
[**Hint :** Formaldehyde is the first product which undergoes Cannizzaro's reaction to form methyl alcohol and sodium formate]

32. When CCl_4 is boiled with hot ethanolic KOH, the product formed is KCl and:
(a) formic acid ☐ (b) methyl alcohol ☐
(c) formaldehyde ☐ (d) potassium carbonate ☐

33. Which one of the following statement is wrong?
(a) Iodoform is used as an antiseptic ☐
(b) Chloroform can be used as an anaesthetic ☐
(c) Chloropicrin is used as an insecticide ☐
(d) Chloretone is used as an antiseptic ☐

34. In the reaction, $CH{\equiv}CH + 2Cl_2 \longrightarrow CHCl_2{-}CHCl_2$, the product is:
(a) called westrosol ☐
(b) used as a solvent ☐
(c) used as a fire-extinguisher ☐
(d) used as an anaesthetic ☐

35. The compound $CCl_2{=}CHCl$ is known as westrosol. Which one of the following statements is wrong regarding this compound?
(a) It is obtained by treating westron with $Ca(OH)_2$ ☐
(b) It is used as a solvent ☐
(c) It is used in refrigerators ☐
(d) It is used as a degreasing agent ☐

36. Alcoholic solution of KOH is used for:
(a) dehalogenation ☐ (b) dehydrohalogenation ☐
(c) dehydration ☐ (d) dehydrogenation ☐

37. The reaction,
$R{-}Br + NaCN \longrightarrow R{-}CN + NaBr$, is an example of:
(a) elimination reaction ☐
(b) nucleophilic substitution ☐
(c) electrophilic substitution ☐
(d) oxidation reduction ☐

38. ...... is usually added to chloroform to retard its decomposition.
(a) Ethanol ☐ (b) Sodium carbonate ☐
(c) Ethyl chloride ☐ (d) Ethyl borate ☐

39. $AgNO_3$ does not give precipitate with $CHCl_3$ because: **[BCECE (Med.) 2008]**
(a) $AgNO_3$ is chemically inert ☐
(b) $CHCl_3$ is chemically inert ☐
(c) $CHCl_3$ does not ionise in water ☐
(d) none of the above ☐

40. Teflon is a polymer of:
(a) ethylene ☐ (b) vinyl chloride ☐
(c) acetonitrile ☐ (d) tetrafluoro ethene ☐

41. Which alkyl halide has maximum reactivity?
(a) CH_3CH_2Br ☐ (b) CH_3Br ☐
(c) $CH_3CH_2CH_2Br$ ☐ (d) $CH_3CH_2CH_2CH_2Br$ ☐

42. Decreasing order of reactivity of alkyl halide is:
(a) $RI > RCl > RBr$ ☐ (b) $RBr > RCl > RI$ ☐
(c) $RI > RBr > RCl$ ☐ (d) $RCl > RBr > RI$ ☐

43. *n*-Propyl bromide reacts with ethanolic KOH to form: **[CET (Karnataka) 2008]**
(a) propane ☐ (b) propene ☐
(c) propyne ☐ (d) propanol ☐

44. The bond angle in carbon tetrachloride is approximately:
(a) 180° ☐ (b) 120° ☐
(c) 109° ☐ (d) 90° ☐

45. Ethylidene chloride on hydrolysis with aq. KOH gives: **[JIPMER 2004]**
(a) CH_3CHO ☐ (b) CH_3COOH ☐
(c) $CHCl_3$ ☐ (d) CH_3CH_2OH ☐

46. Chloroform on reaction with acetone yields:
(a) insecticide ☐ (b) analgesic ☐
(c) isocyanide ☐ (d) hypnotic ☐

47. The chloro compound which is used as a fire extinguisher is:
(a) CCl_4 ☐ (b) $CHCl_3$ ☐
(c) CH_3Cl ☐ (d) $COCl_2$ ☐

48. 1-Chlorobutane when treated with alcoholic potash gives:
(a) 1-butene ☐ (b) 1-butanol ☐
(c) 2-butene ☐ (d) 2-butanol ☐

49. Which of the following is obtained when chloral is boiled with NaOH?
(a) CH_3Cl ☐ (b) $CHCl_3$ ☐
(c) CCl_4 ☐ (d) None of these ☐

50. Which of the following will not give iodoform test? **[CPMT 2004; UGET (Med.) 2007]**
(a) HCHO ☐ (b) C_2H_5OH ☐
(c) CH_3CHO ☐ (d) CH_3COCH_3 ☐

51. Butanenitrile may be prepared by heating:
(a) propyl alcohol with KCN ☐
(b) butyl alcohol with KCN ☐
(c) butyl chloride with KCN ☐
(d) propyl chloride with KCN ☐

52. A mixture of 1-chlorobutane and 2-chlorobutane when treated with alcoholic KOH, gives: **[UGET (Med.) 2008]**
(a) 1-butene ☐
(b) 2-butene ☐
(c) isobutylene ☐
(d) a mixture of 1-butene and 2-butene ☐

53. The reagent used in the conversion of 1-butanol to 1-bromobutane is:
(a) $CHBr_3$ ☐ (b) Br_2 ☐
(c) CH_3Br ☐ (d) PBr_3 ☐

54. Which reagent cannot be used to prepare an alkyl halide from an alcohol?
(a) NaCl ☐ (b) PCl_5 ☐
(c) $SOCl_2$ ☐ (d) $ZnCl_2 + HCl$ ☐

55. Ethyl bromide reacts with lead-sodium alloy to form:
(a) tetraethyl lead ☐
(b) tetraethyl lead bromide ☐
(c) both (a) and (b) ☐
(d) none of the above ☐

56. The nature of hydrogen atom in chloroform molecule is:
(a) neutral ☐ (b) acidic ☐
(c) basic ☐ (d) cannot be predicted ☐

57. How many structural isomers are possible for $C_2H_4Br_2$?
(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) 4 ☐

58. In the preparation of $CHCl_3$ from ethanol and bleaching powder, the latter provides:
(a) Cl_2 ☐ (b) $Ca(OH)_2$ ☐
(c) both (a) and (b) ☐ (d) none of these ☐

59. Which of the following processes does not occur during formation of $CHCl_3$ from ethyl alcohol and bleaching powder?
(a) Oxidation ☐ (b) Chlorination ☐
(c) Hydrolysis ☐ (d) Reduction ☐

60. Which of the following is 2° chloride?
(a) Isopropyl chloride ☐ (b) Isobutyl chloride ☐
(c) *n*-Propyl chloride ☐ (d) *n*-Butyl chloride ☐

61. Which one of the following will produce a primary alcohol by reacting with CH_3MgI?
(a) Acetone ☐ (b) Methyl cyanide ☐
(c) Ethylene oxide ☐ (d) Ethyl acetate ☐

62. Grignard reagent adds to:
(a) $>C{=}O$ ☐ (b) $-C{\equiv}N$ ☐
(c) $>C{=}S$ ☐ (d) all of these ☐

63. For the reaction,

$$C_2H_5OH + HX \xrightarrow{ZnX_2} C_2H_5X$$

The decreasing order of reactivity of halogen acids is:
(a) $HI > HCl > HBr$ ☐ (b) $HI > HBr > HCl$ ☐
(c) $HCl > HBr > HI$ ☐ (d) $HBr > HI > HCl$ ☐

64. Which of the following alkyl halide is hydrolysed by S_N1 mechanism?
(a) $(CH_3)_2CHX$ ☐ (b) CH_3CH_2X ☐
(c) $CH_3CH_2CH_2X$ ☐ (d) $(CH_3)_3CX$ ☐

65. S_N1 reaction is favoured by:
(a) non-polar solvents ☐
(b) bulky groups on the carbon atom attached to halogen atom ☐
(c) small groups on the carbon atom attached to halogen atom ☐
(d) none of the above ☐

66. Only two isomeric monochloro derivatives are possible from:
(a) ethane ☐ (b) 2,2-dimethylpentane ☐
(c) neopentane ☐ (d) 2-methylpropane ☐

67. An organic halide with formula $C_6H_{13}Br$ on heating with alc. KOH gives two isomeric alkenes (*A*) and (*B*) with formula C_6H_{12}. On reductive ozonolysis of mixture (*A*) and (*B*), the following compounds are obtained:

CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2CHCHO$

The organic halide is:
(a) 2-bromohexane ☐
(b) 3-bromo-2-methylpentane ☐
(c) 1-bromo-2,2-dimethylhexane ☐
(d) none of the above ☐

68. $(CH_3)_2CHCl + NaI \longrightarrow (CH_3)_2CHI + NaCl$
The above reaction is known as:
(a) Finkelstein reaction ☐ (b) Stephen's reaction ☐
(c) Kolbe's reaction ☐ (d) Wurtz reaction ☐

69. In elimination reactions, the reactivity of alkyl halides is in decreasing order:
(a) $T > S > P$ ☐ (b) $P > S > T$ ☐
(c) $S > P > T$ ☐ (d) none of these ☐

70. Which of the following alkyl halides is hydrolysed by S_N2 mechanism?
(a) $H_2C{=}CHCH_2Br$ ☐ (b) $(CH_3)_3CBr$ ☐
(c) CH_3Br ☐ (d) None of these ☐

71. Ethene on treatment with bromine in presence of NaCl solution gives:
(a) 1,2-dibromoethane ☐
(b) 1,2-dichloroethane ☐
(c) a mixture of 1,2-dibromo and 2-bromo-1-chloroethanes ☐
(d) no reaction occurs ☐

72. The non-reactivity of chlorine atom in $H_2C{=}CH{-}Cl$ is due to:
(a) inductive effect ☐ (b) resonance stabilization ☐
(c) electromeric effect ☐ (d) electronegativity ☐

73. Ethyl orthoformate is formed by heating ...... with sodium ethoxide. **[DCE 2008]**
(a) HCOOH ☐ (b) C_2H_5OH ☐
(c) $CHCl_3$ ☐ (d) CH_3CHO ☐

74. What happens when CCl_4 is treated with $AgNO_3$ solution?
(a) NO_2 will be evolved ☐
(b) A white ppt. will be formed ☐
(c) CCl_4 will dissolve in $AgNO_3$ solution ☐
(d) No reaction takes place ☐

75. Iodoform can be prepared in the laboratory by the action of iodine on sodium carbonate solution having:
(a) ethanol ☐ (b) ether ☐
(c) acetone ☐ (d) acetic acid ☐

76. Haloform reaction is used for preparing:
(a) halogens ☐ (b) alkyl halides ☐
(c) CCl_4 ☐ (d) $CHCl_3$ ☐

77. Upon reduction, iodoform yields as the first product:
(a) methane ☐ (b) methylene iodide ☐
(c) ethane ☐ (d) mono-iodomethane ☐

78. Chloroform on reduction with zinc and water gives:
(a) acetylene ☐ (b) ethylene ☐
(c) ethane ☐ (d) methane ☐

79. When carbon tetrachloride is reduced with Zn and H_2SO_4 in alcoholic solution, it forms:
(a) CH_3Cl ☐ (b) $CHCl_3$ ☐
(c) C_2H_5Cl ☐ (d) Cl_2 ☐

80. Pure chloroform may be prepared by:
(a) chlorination of methane ☐
(b) partial reduction of CCl_4 ☐
(c) the action of bleaching powder and alkali on ethanol ☐
(d) distilling chloral hydrate with conc. aqueous alkali solution ☐

81. When iodoform is heated with silver nitrate solution, we get:
(a) a yellow ppt. of AgI ☐ (b) a white ppt. of AgCl ☐
(c) silver mirror ☐ (d) no precipitate ☐

82. When pure chloroform is shaken with silver nitrate solution, we get:
(a) no precipitate ☐ (b) a yellow ppt. of AgI ☐
(c) a white ppt. of AgCl ☐ (d) acetylene is liberated ☐

83. When alkyl halide is heated with an aqueous ethanolic solution of silver nitrite, it gives:
(a) nitroalkane only ☐
(b) alkylnitrite only ☐
(c) a mixture of nitroalkane and alkylnitrite ☐
(d) acetylene ☐

84. When ethyl chloride is heated with AgCN, the main product is:
(a) ethyl cyanide ☐ (b) ethyl isocyanide ☐
(c) ethyl amine ☐ (d) ethyl nitrate ☐

85. When a solution of sodium chloride containing ethyl alcohol is electrolysed, it forms:
(a) ethyl chloride ☐ (b) chloral ☐
(c) chloroform ☐ (d) acetaldehyde ☐

86. When ethyl alcohol is heated with a paste of bleaching powder, we get a compound in which the function of bleaching powder is:
(a) as an oxidising agent ☐
(b) as a chlorinating agent ☐
(c) as a hydrolysing agent ☐
(d) as chlorinating, oxidising and hydrolysing agent ☐

87. Which of the following will not give iodoform test? **[UPSEAT 2004]**
(a) Isopropyl alcohol ☐ (b) Ethanol ☐
(c) Ethanal ☐ (d) Benzyl alcohol ☐

88. Which is detected by carbylamine test?
(a) H_2NCONH_2 ☐ (b) CH_3CONH_2 ☐
(c) $C_2H_5NH_2$ ☐ (d) All of these ☐

89. Terminal dihalides on heating with zinc and methanol, we get:
(a) alkenes ☐ (b) cycloalkanes ☐
(c) alkynes ☐ (d) alkanes ☐

90. When an alkyl halide reacts with alcoholic potassium hydroxide to form an alkene, the reaction is called as:
(a) dehydrohalogenation reaction ☐
(b) elimination reaction ☐
(c) increase in unsaturation ☐
(d) all of the above ☐

91. *Tert.* butyl chloride preferably undergoes hydrolysis by: **[DCE 2008]**
(a) S_N1 mechanism ☐ (b) S_N2 mechanism ☐
(c) any of (a) and (b) ☐ (d) none of these ☐

92. Alkyl halide reacts with alcoholic potassium hydrogen sulphide to form:
(a) alkanethiol ☐ (b) thioether ☐
(c) thioacid ☐ (d) alkane ☐

93. Alkyl halide when heated with alcoholic solution of potassium sulphide, it forms:
(a) thioalcohol ☐ (b) thioether ☐
(c) thioacid ☐ (d) alkane ☐

94. The aliphatic halide which is used for the preparation of synthetic rubber, plastics and resins is:
(a) chloroform ☐ (b) carbon tetrachloride ☐
(c) allyl iodide ☐ (d) vinyl chloride ☐

95. The antiseptic action of CHI_3 is due to:
(a) iodoform itself ☐
(b) liberation of free iodine ☐

(c) partially due to iodine and partially due to CHI_3 itself ☐
(d) none of the above ☐

96. Which of the following is not an industrial solvent?
(a) $CHCl_3$ ☐ (b) CHI_3 ☐
(c) CCl_4 ☐ (d) $(C_2H_5)_2O$ ☐

97. The reaction conditions leading to the best yield of C_2H_5Cl are:
(a) $C_2H_6\,(\text{excess}) + Cl_2 \xrightarrow{\text{UV light}}$ ☐
(b) $C_2H_6 + Cl_2 \xrightarrow{\text{Dark, Room temp.}}$ ☐
(c) $C_2H_6 + Cl_2\,(\text{excess}) \xrightarrow{\text{UV light}}$ ☐
(d) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$ ☐

98. Arrange the following in order of their decreasing acid strength:
(a) $HClO > HClO_2 > HClO_3 > HClO_4$ ☐
(b) $HClO_4 > HClO_3 > HClO_2 > HClO$ ☐
(c) $HClO > HClO_4 > HClO_3 > HClO_2$ ☐
(d) $HClO_4 > HClO > HClO_2 > HClO_3$ ☐

99. With conc. nitric acid, the chloroform forms a compound which is used as an:
(a) anaesthetic ☐ (b) antiseptic ☐
(c) insecticide ☐ (d) antiknock compound ☐

100. The order of reactivity of alkyl halides depends upon:
(a) nature of alkyl group ☐
(b) nature of halogen atom ☐
(c) nature of both alkyl group and halogen atom ☐
(d) none of the above ☐

101. 1-Bromopropane and 2-bromopropane on treatment with sodium in presence of ether gives:
(a) *n*-hexane ☐
(b) 2,3-dimethylbutane ☐
(c) 2-methylpentane ☐
(d) a mixture of all these different alkanes ☐

102. Compound $C_4H_8Cl_2$ (A) on hydrolysis gives a compound C_4H_8O (B) which reacts with hydroxylamine and does not give any test with Tollens' reagent. What are (A) and (B)?
(a) 1,1-Dichlorobutane and butanal ☐
(b) 2,2-Dichlorobutane and butanal ☐
(c) 1,1-Dichlorobutane and butan-2-one ☐
(d) 2,2-Dichlorobutane and butan-2-one ☐

103. Secondary butyl chloride on boiling with alcoholic potash gives:
(a) only 1-butene ☐
(b) only 2-butene ☐
(c) isobutylene ☐
(d) a mixture of 1-butene and 2-butene ☐

104. Which one of the following compounds is stable?
(a) $CH_3CH(OH)_2$ ☐ (b) $(CH_3)_2CH(OH)_2$ ☐
(c) $CCl_3CH(OH)_2$ ☐ (d) None of these ☐

105. Chloroform on treatment with phenol in presence of caustic alkali forms salicylaldehyde. This reaction is known as:
(a) Carbylamine reaction ☐
(b) Cannizzaro's reaction ☐
(c) Wurtz-Fittig reaction ☐
(d) Reimer-Tiemann reaction ☐

106. Which of the following compounds will give a yellow precipitate with I_2 and alkali? **[UPSEAT 2003]**
(a) Acetophenone ☐ (b) Benzophenone ☐
(c) Methyl acetate ☐ (d) Propionaldehyde ☐

107. $CCl_3CHO \xrightarrow{NaOH} (A) \xrightarrow[\text{Sun light}]{+\,Cl_2} (B)$

The product (B) can be used as a:
(a) fire extinguisher ☐ (b) solvent ☐
(c) insecticide ☐ (d) all of these ☐

108. $CH_3C{\equiv}CH \xrightarrow[(HgSO_4)]{\text{Dil. } H_2SO_4} (B) \xrightarrow[(NaOH)]{CHCl_3} (C)$

Compound (C) can be used as:
(a) an anaesthetic ☐ (b) an insecticide ☐
(c) a solvent ☐ (d) a hypnotic ☐

109. Treatment of NH_3 with excess of ethyl chloride gives:
(a) diethylamine ☐
(b) ethane ☐
(c) tetraethylammonium chloride ☐
(d) methylamine ☐

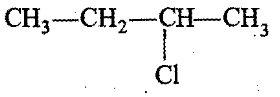
110. Chloropicrin is obtained by the reaction of: **[CBSE (Med.) 2004; UGET (Med.) 2007]**
(a) steam on carbon tetrachloride ☐
(b) nitric acid on chlorobenzene ☐
(c) chlorine on picric acid ☐
(d) nitric acid on chloroform ☐

111. Isobutyl magnesium bromide with dry ether and absolute alcohol gives:
(a) $(CH_3)_2CHCH_2OH$ and CH_3CH_2MgBr ☐
(b) $(CH_3)_2CHCH_2CH_2CH_3$ and $Mg(OH)Br$ ☐
(c) $(CH_3)_3CH$ and CH_3CH_2OMgBr ☐
(d) $(CH_3)_3CH$, $H_2C{=}CH_2$ and $Mg(OH)Br$ ☐

112. Which of the following is an organometallic compound?
(a) Lithium methoxide ☐
(b) Lithium acetate ☐
(c) Lithium dimethylamide ☐
(d) Methyl lithium ☐

113. Which of the following will give a yellow precipitate with $I_2/NaOH$?
(a) $ICH_2COCH_2CH_3$ ☐
(b) $CH_3COOCOCH_3$ ☐
(c) CH_3CONH_2 ☐
(d) $CH_3CH(OH)CH_2CH_3$ ☐

114. Which of the following will react with water?
(a) $CHCl_3$ ☐ (b) Cl_3CCHO ☐
(c) CCl_4 ☐ (d) $ClCH_2CH_2Cl$ ☐

115. 
$CH_3—CH_2—\underset{\displaystyle Cl}{\underset{|}{CH}}—CH_3$ obtained by chlorination of *n*-butane will be: **[CBSE (Med.) 2001]**

(a) meso form ☐ (b) racemic mixture ☐
(c) *d*-form ☐ (d) *l*-form ☐

116. Isopropyl chloride undergoes hydrolysis by: **[CBSE (Med.) 2001]**

(a) S_N1 mechanism ☐
(b) S_N2 mechanism ☐
(c) S_N1 and S_N2 mechanism ☐
(d) Neither S_N1 nor S_N2 mechanism ☐

117. The number of isomers for the compound with molecular formula $C_2BrClFI$ is: **[IIT 2001]**

(a) 3 ☐ (b) 4 ☐
(c) 5 ☐ (d) 6 ☐

118. Which one of the following is most reactive towards nucleophilic substitution? **[SCRA 2001]**

(a) $H_2C=CH—Cl$ ☐ (b) C_6H_5Cl ☐
(c) $CH_3—CH=CH—Cl$ ☐ (d) $ClCH_2—CH=CH_2$ ☐

119. Match List I (Compound) with List II (Use) and select the correct answer using the codes given below in the lists: **[SCRA 2001]**

List I (Compound)	**List II (Use)**
I. Acetyl salicylic acid	A. Insecticide
II. DDT	B. Drug
III. Naphthalene	C. Moth repellent
IV. Carbon tetrachloride	D. Fire extinguisher
	E. Refrigerant

Codes:

(a) I—B, II—A, III—C, IV—D ☐
(b) I—E, II—C, III—D, IV—A ☐
(c) I—B, II—C, III—D, IV—A ☐
(d) I—E, II—A, III—C, IV—D ☐

120. The order of reactivities of the following alkyl halides for a S_N2 reaction is: **[IIT 2000]**

(a) $RF > RCl > RBr > RI$ ☐ (b) $RF > RBr > RCl > RI$ ☐
(c) $RCl > RBr > RF > RI$ ☐ (d) $RI > RBr > RCl > RF$ ☐

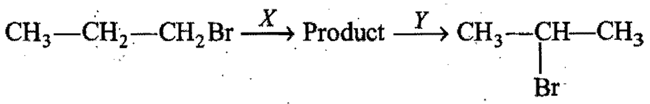
121. The reactivity order of halides for dehydrohalogenation is: **[CBSE (Med.) 2002]**

(a) $R—F > R—Cl > R—Br > R—I$ ☐
(b) $R—I > R—Br > R—Cl > R—F$ ☐
(c) $R—I > R—Cl > R—Br > R—F$ ☐
(d) $R—F > R—I > R—Br > R—Cl$ ☐

122. Among the following the molecule with highest dipole moment is: **[IIT (S) 2003]**

(a) CH_3Cl ☐ (b) CH_2Cl_2 ☐
(c) $CHCl_3$ ☐ (d) CCl_4 ☐

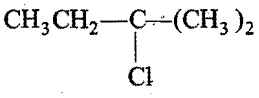
123. Identify the set of reagent and reaction conditions '*X*' and '*Y*' in the following set of transformations,


$$CH_3—CH_2—CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3$$

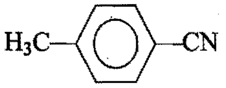
[IIT (S) 2002]

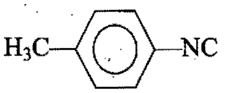
(a) X = Dilute aqueous NaOH, 20° C
Y = HBr/acetic acid, 20°C ☐
(b) X = Concentrated alcoholic NaOH, 80° C
Y = HBr/acetic acid, 20°C ☐
(c) X = Dilute aqueous NaOH, 20° C
$Y = Br_2/CHCl_3$, 0°C ☐
(d) X = Concentrated alcoholic NaOH, 80° C
$Y = Br_2/CHCl_3$, 0°C ☐

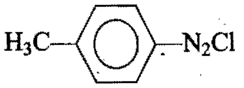
124. Which chlorine atom is more electronegative in the following? **[UPSEAT 2004]**

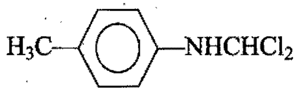
(a) CH_3Cl ☐
(b) CH_3CH_2Cl ☐
(c) $(CH_3)_2CHCl$ ☐
(d) 
$CH_3CH_2—\underset{\displaystyle Cl}{\underset{|}{C}}—(CH_3)_2$ ☐

125. The reaction of chloroform with alcoholic KOH and *p*-toluidine forms: **[AIEEE 2003]**

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

126. When an alkyl halide is heated with dry Ag_2O, it produces: **[BHU 2004]**

(a) ester ☐ (b) ether ☐
(c) ketone ☐ (d) alcohol ☐

127. The formula of freon-12 is: **[PMT (MP) 2004]**

(a) $CClF_3$ ☐ (b) CH_2Cl_2 ☐
(c) CCl_2F_2 ☐ (d) CH_2F_2 ☐

128. Which one of the following will not form a yellow precipitate on heating with an alkaline solution of iodine? **[CBSE (Med.) 2004; UGET (Med.) 2007]**

(a) $CH_3CH(OH)CH_3$ ☐
(b) $CH_3CH_2CH(OH)CH_3$ ☐
(c) CH_3OH ☐
(d) CH_3CH_2OH ☐

129. Among the following the most reactive towards alcoholic KOH is: **[AIIMS 2004]**

(a) CH_3CH_2Br ☐ (b) $(CH_3)_2CHBr$ ☐
(c) $CH_3CH_2CH_2Br$ ☐ (d) $CH_3COCH_2CH_2Br$ ☐

130. Acetone is mixed with bleaching powder to give: **[AFMC 2004]**
(a) chloroform ☐ (b) acetaldehyde ☐
(c) ethanol ☐ (d) phosgene ☐

131. Debromination of mesodibromobutane will give the product as: **[MGIMS (Wardha) 2003]**
(a) *n*-butane ☐ (b) 2-butyne ☐
(c) *cis*-2-butene ☐ (d) *trans*-2-butene ☐

132. At higher temperature, iodoform reaction is given by: **[AIIMS 2003]**
(a) CH_3COOCH_3 ☐ (b) $CH_3COOC_2H_5$ ☐
(c) $C_6H_5COOCH_3$ ☐ (d) $CH_3COOC_6H_5$ ☐

133. Alkyl halides react with dialkyl copper reagents to give : **[AIEEE 2005; JCECE (Med.) 2008]**
(a) alkenes ☐ (b) alkyl copper halides ☐
(c) alkanes ☐ (d) alkenyl halides ☐

134. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of: **[AIEEE 2005]**
(a) insolubility ☐ (b) instability ☐
(c) inductive effect ☐ (d) steric hindrance ☐

135. Which of the following is liquid at room temperature? **[AFMC 2005]**
(a) CH_3I ☐ (b) CH_3Br ☐
(c) C_2H_5Cl ☐ (d) CH_3F ☐

136. The product obtained on reaction of C_2H_5Cl with hydrogen over palladium carbon is: **[AFMC 2005]**
(a) C_3H_8 ☐ (b) C_4H_{10} ☐
(c) C_2H_6 ☐ (d) C_2H_4 ☐

137. The major product obtained on treatment of $CH_3CH_2CH(F)CH_3$ with CH_3O^-/CH_3OH is: **[AFMC 2005]**
(a) $CH_3CH_2CH(OCH_3)CH_3$ ☐
(b) $CH_3CH{=}CHCH_3$ ☐
(c) $CH_3CH_2CH{=}CH_2$ ☐
(d) $CH_3CH_2CH_2CH_2OCH_3$ ☐

138. Which of the following gives iodoform test? **[DCE 2005]**
(a) CH_3CH_2OH ☐ (b) C_2H_5CHO ☐
(c) $(CH_2OH)_2$ ☐ (d) None of these ☐

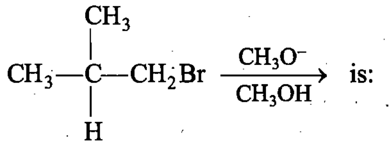
139. Which among the following is a catalyst for the preparation of Grignard reagent? **[UPSEE (Engg.) 2010]**
(a) Iodine powder ☐ (b) Iron powder ☐
(c) Activated charcoal ☐ (d) Manganese dioxide ☐

140. Consider the following reaction:

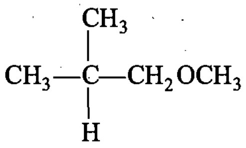
$$C_2H_5OK + C_2H_5I \xrightarrow{\Delta} X \text{ (Pleasant smelling liquid)}$$

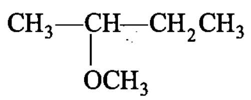
Which of the following reagents converts ethyl bromide to X? **[EAMCET (Med.) 2005]**
(a) Sodium ☐ (b) Dry silver oxide ☐
(c) Ethyl chloride ☐ (d) Dry silver powder ☐

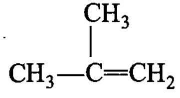
141. The major product formed in the following reaction, **[AIIMS 2005]**

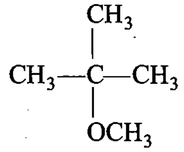


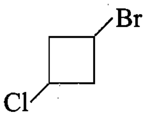
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large H}{|}}{C}}-CH_2Br \xrightarrow[CH_3OH]{CH_3O^-}$$ is:

(a) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_2OCH_3$ ☐

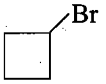
(b) 
$CH_3-\underset{\underset{OCH_3}{|}}{CH}-CH_2CH_3$ ☐

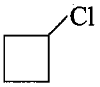
(c) 
$CH_3-\overset{\overset{CH_3}{|}}{C}{=}CH_2$ ☐

(d) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OCH_3}{|}}{C}}-CH_3$ ☐

142. 

, when treated with two equivalents of sodium in dry ether gives: **[IIT 2005]**

(a) 

☐ (b) 

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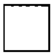
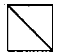
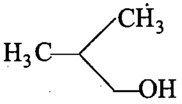
(c)  ☐ (d)  ☐

143. $CH_3Br + \bar{Nu} \longrightarrow CH_3-Nu + \bar{Br}$
The decreasing order of the rate of the above reaction with nucleophile (Nu^-) A to D is:
$[Nu^- = (A)\, PhO^-,\ (B)\, AcO^-,\ (C)\, HO^-,\ (D)\, CH_3O^-]$ **[AIEEE 2006]**
(a) $D > C > A > B$ ☐ (b) $D > C > B > A$ ☐
(c) $A > B > C > D$ ☐ (d) $B > D > C > A$ ☐

144. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is: **[AIEEE 2006]**
(a) $CH_3CH_2CH(OH)CH_2CH_3$ ☐
(b) $C_6H_5CH_2CH_2OH$ ☐
(c) 

☐
(d) $PhCHOHCH_3$ ☐

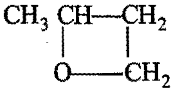
145. Which of the following compounds has the highest boiling point? **[AIIMS 2006; BCECE (Med.) 2007]**
(a) $CH_3CH_2CH_2Cl$ ☐ (b) $CH_3CH_2CH_2CH_2Cl$ ☐
(c) $CH_3CH(CH_3)CH_2Cl$ ☐ (d) $(CH_3)_3C-Cl$ ☐

146. The catalyst used in the preparation of an alkyl chloride by the action of dry HCl on an alcohol is: **[KCET 2006; AFMC 2008]**

(a) anhyd. $AlCl_3$ ☐ (b) $FeCl_3$ ☐
(c) anhyd. $ZnCl_2$ ☐ (d) Cu ☐

147. The major product in the following reaction is:

$$CH_3CH(Cl)CH_2CH_2OH \xrightarrow{\text{Aq. KOH}}$$ **[AIIMS 2006]**

(a) $CH_3CH{=}CHCH_2OH$ ☐
(b) $H_2C{=}CHCH_2CH_2OH$ ☐
(c)  ☐
(d) $CH_3CH(OH)CH_2CH_2OH$ ☐

148. Which can undergo haloform reaction? **[DCE 2006]**
(a) $(CH_3)_3C{-}OH$ ☐ (b) $(C_2H_5)_2C{=}O$ ☐
(c) Acetophenone ☐ (d) Benzophenone ☐

149. Which of the following is a primary halide? **[PMT (Haryana) 2006; AIIMS 2008]**
(a) Isopropyl iodide ☐
(b) Secondary butyl iodide ☐
(c) Tertiary butyl bromide ☐
(d) Neo hexyl chloride ☐

150. Among the halogens, the one which is oxidised by nitric acid is: **[AMU (Engg.) 2006]**
(a) fluorine ☐ (b) iodine ☐
(c) chlorine ☐ (d) bromine ☐

151. Freon used as refrigerant is: **[BHU (Screening) 2006; AFMC 2006]**
(a) $F_2C{=}CF_2$ ☐ (b) CH_2F_2 ☐
(c) CCl_2F_2 ☐ (d) CF_4 ☐

152. Which of the following is formed when the product of oxidation of chloroform is treated with ethyl alcohol? **[EAMCET (Med.) 2006]**
(a) Ethyl chloride ☐ (b) Ethyl carbonate ☐
(c) Chloral hydrate ☐ (d) Chloral ☐

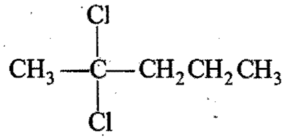
153. Which of the following is added to chloroform to slow down its aerial oxidation in presence of light? **[EAMCET (Engg.) 2006; AFMC 2008]**
(a) Carbonyl chloride ☐ (b) Ethyl alcohol ☐
(c) Sodium hydroxide ☐ (d) Nitric acid ☐

154. Ethyl chloride reacts with sodium ethoxide to form a compound '*A*'. Which of the following reactions also yields '*A*'? **[EAMCET (Engg.) 2006; AFMC 2008]**
(a) $C_2H_5Cl, KOH\,(alc.), \Delta$ ☐
(b) $2C_2H_5OH, conc.\ H_2SO_4, 140°\,C$ ☐
(c) C_2H_5Cl, Mg (dry ether) ☐
(d) C_2H_2, dil. H_2SO_4, $HgSO_4$ ☐

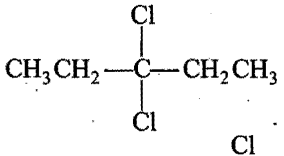
155. Maximum number of molecules of CH_3I that can react with a molecule of CH_3NH_2 is: **[MGIMS (Med.) 2008]**
(a) 3 ☐ (b) 4 ☐
(c) 2 ☐ (d) 1 ☐

156. $HC{\equiv}CH \xrightarrow[H_2SO_4]{HgSO_4} \xrightarrow[HOH]{CH_3MgBr} \xrightarrow{P/Br_2} (X)$; (X) is: **[MGIMS (Wardha) 2006]**
(a) $CH_3CH(Br)CH_3$ ☐ (b) $CH_3CH_2CH_2Br$ ☐
(c) $H_2C{=}CH{-}Br$ ☐ (d) $BrCH{=}CH{-}CH_3$ ☐

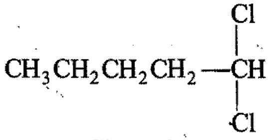
157. A compound (*A*) $C_5H_{10}Cl_2$ on hydrolysis gives $C_5H_{10}O$ which reacts with NH_2OH, forms iodoform, but does not give Fehling test; (*A*) is: **[DPMT 2005; MGIMS (Wardha) 2006]**

(a)  ☐

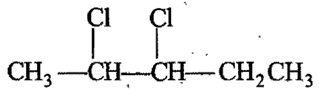
$CH_3{-}CCl_2{-}CH_2CH_2CH_3$

(b)  ☐

$CH_3CH_2{-}CCl_2{-}CH_2CH_3$

(c)  ☐

$CH_3CH_2CH_2CH_2{-}CHCl_2$

(d)  ☐

$CH_3{-}CH(Cl){-}CH(Cl){-}CH_2CH_3$

158. Match List I with List II and pick the correct matching from the codes given below: **[PMT (Kerala) 2006]**

List I (Haloalkane/arene)	**List II (Applications)**
A. Iodoform	1. CF_4
B. BHC	2. Antiseptic
C. Freon-14	3. Moth repellent
D. Halothanes	4. Inhalative anaesthetic
E. *p*-Dichlorobenzene	5. Termite pesticide

(a) A–2, B–4, C–5, D–3, E–1 ☐
(b) A–2, B–5, C–1, D–4, E–3 ☐
(c) A–3, B–4, C–2, D–1, E–5 ☐
(d) A–1, B–3, C–5, D–2, E–4 ☐
(e) A–5, B–4, C–3, D–2, E–1 ☐

159. In the reaction, $RX \xrightarrow{\text{Alc. KCN}} (A) \xrightarrow{\text{Dil. HCl}} (B)$; the product (*B*) is: **[KCET 2006]**
(a) alkyl chloride ☐ (b) aldehyde ☐
(c) carboxylic acid ☐ (d) ketone ☐

160. A compound called chloral whose formula is C_2Cl_3OH is a/an: **[BHU (S) 2006]**
(a) aldehyde ☐ (b) alcohol ☐
(c) ketone ☐ (d) alkanoyl chloride ☐

161. Which of the following haloalkanes is most reactive? **[GGS Indraprastha Univ. (Engg.) 2006]**
(a) 1-Chloropropane ☐ (b) 1-Bromopropane ☐
(c) 2-Chloropropane ☐ (d) 2-Bromopropane ☐

162. In the chemical reaction,

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow (A) + (B) + 3H_2O$$

the compounds (*A*) and (*B*) are respectively: **[AIEEE 2007]**

(a) C_2H_5NC and 3KCl ☐
(b) C_2H_5CN and 3KCl ☐
(c) $CH_3CH_2CONH_2$ and 3KCl ☐
(d) C_2H_5NC and K_2CO_3 ☐

163. $(X) + KCN \longrightarrow CH_3CN \xrightarrow{2H_2/Ni} CH_3CH_2NH_2$
what is (*X*)? **[DCE (Engg.) 2007]**
(a) CH_3CH_2Cl ☐ (b) CH_3Cl ☐
(c) $CH_3CH_2CH_2Cl$ ☐ (d) $(CH_3)_2CHCl$ ☐

164. $C_2H_5Cl \xrightarrow[Ag_2O]{Moist} (A) \xrightarrow[360°C]{Al_2O_3} (B) \xrightarrow{S_2Cl_2} (C)$
In the above sequence of reactions, identify (*C*): **[EAMCET (Med.) 2007]**
(a) chloretone ☐ (b) chloropicrin ☐
(c) mustard gas ☐ (d) lewisite gas ☐

165. $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + X$
$X + CH_3CHO \longrightarrow Y$
$Y + Ca(OH)_2 \longrightarrow CHCl_3$
what is '*Y*'? **[EAMCET (Engg.) 2007]**
(a) $CH_3CH(OH)_2$ ☐ (b) CH_2Cl_2 ☐
(c) CCl_3CHO ☐ (d) CCl_3COCH_3 ☐

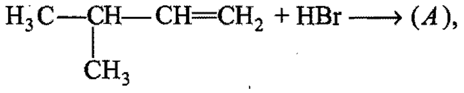
166. Ethyl chloride on reduction with $LiAlH_4$ gives compound '*X*' as an important product. '*X*' on chlorination with one mole of Cl_2 in the presence of light at ordinary temperature gives '*Y*'. What is '*Y*'? **[EAMCET (Med.) 2007]**
(a) C_2H_5OH ☐ (b) C_2H_5Cl ☐
(c) C_2H_6 ☐ (d) C_2H_4 ☐

167. Chloroform gives a trichloro derivative of an alcohol on reaction with: **[PMT (Kerala) 2007; Punjab CET (Engg.) 2008]**
(a) conc. HNO_3 ☐ (b) aq. alkali ☐
(c) acetone and alkali ☐ (d) sodium ethoxide ☐
(e) a primary amine and an alkali ☐

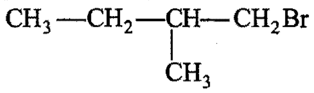
168. In a group of isomeric alkyl halides, the order of boiling point is: **[CET (J&K) 2007]**
(a) $P < S < T$ ☐ (b) $P > S < T$ ☐
(c) $P < S > T$ ☐ (d) $P > S > T$ ☐

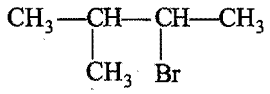
169. Which one of the following is not the correct order of boiling points of alkyl/aryl halides? **[PMT (Kerala) 2007]**
(a) $CHCl_3 > CH_2Cl_2$ ☐
(b) $CH_3(CH_2)_3Cl > CH_3(CH_2)_2Cl$ ☐
(c) $(CH_3)_3CCl > (CH_3)_2CHCH_2Cl$ ☐
(d) $CH_3(CH_2)_3Cl > CH_3CH_2CHClCH_3$ ☐
(e) $C_6H_5Br > C_6H_5Cl$ ☐

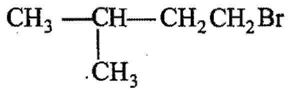
170. What is the product obtained when chlorine reacts with ethyl alcohol in the presence of NaOH? **[AIIMS 2007]**
(a) CH_3Cl ☐ (b) C_2H_5Cl ☐
(c) CCl_3CHO ☐ (d) $CHCl_3$ ☐

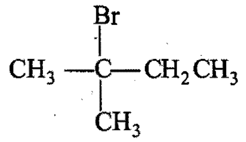
171. 
$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2 + HBr \longrightarrow (A),$

(*A*) predominantly is: **[CBSE (Med.) 2008]**

(a) 
$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2Br$ ☐

(b) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$ ☐

(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_2Br$ ☐

(d) 
$CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2CH_3$ ☐

172. A dihalogen derivative '*X*' of a hydrocarbon with three carbon atoms reacts with alcoholic KOH and produces another hydrocarbon which forms a red precipitate with ammoniacal Cu_2Cl_2. '*X*' gives an aldehyde on reaction with aqueous KOH. The compound '*X*' is: **[PET (Kerala) 2008]**
(a) 1,3-dichloropropane ☐ (b) 1,2-dichloropropane ☐
(c) 2,2-dichloropropane ☐ (d) 1,1-dichloropropane ☐
(e) 1,3-dichloropropene ☐

173. The IUPAC name of Westron is: **[BHU (Mains) 2008]**
(a) 1,1,2,2-tetrachloroethane ☐
(b) 1,1,2,2-tetrachloroethene ☐
(c) 1,2-dichloroethyne ☐
(d) 1,3,3,3-tetrachloroprop-1-yne ☐

174. CCl_4 is a well known fire extinguisher. However after using it to extinguish fire, the room should be well ventilated. This is because: **[PMT (Kerala) 2008]**
(a) it is inflammable at higher temperatures ☐
(b) it is toxic ☐
(c) it produces phosgene by reaction with water vapours at higher temperatures ☐
(d) it is corrosive ☐
(e) it is an anaesthetic ☐

175. Which of the following will be least reactive in nucleophilic substitution? **[PMT (Kerala) 2008]**
(a) $CH_3CH_2CH_2Cl$ ☐ (b) $(CH_3)_3C-Cl$ ☐
(c) $CH_3-CHClCH_3$ ☐ (d) $H_2C=CHCH_2Cl$ ☐
(e) $H_2C=CHCl$ ☐

176. The chemical formula of tear gas is: **[AIIMS 2008]**
(a) $COCl_2$ ☐ (b) CO_2 ☐
(c) Cl_2 ☐ (d) CCl_3NO_2 ☐

177. When 2-chloro-2-methylbutane is heated with alcoholic KOH, the possible product/s is/are: **[PMT (Kerala) 2008]**
(i) $(CH_3)_2C=CHCH_3$ (ii) $H_2C=C(CH_3)CH_2CH_3$
(iii) $(CH_3)_2CHCH=CH_2$

(a) (i), (ii) and (iii) ☐ (b) (i) and (iii) ☐
(c) (ii) and (iii) ☐ (d) (i) only ☐
(e) (i) and (ii) ☐

178. The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with: **[CET (Karnataka) 2009]**
(a) PCl_5 ☐
(b) $SOCl_2$ in presence of pyridine ☐
(c) PCl_3 ☐
(d) dry HCl in presence of anhydrous $ZnCl_2$ ☐

179. Which of the following on heating with aqueous KOH produces acetaldehyde? **[AIEEE 2009]**
(a) CH_3COCl ☐ (b) CH_3CH_2Cl ☐
(c) CH_2ClCH_2Cl ☐ (d) CH_3CHCl_2 ☐

180. Consider the following reaction:

$$C_2H_5Cl + AgCN \xrightarrow{EtOH/H_2O} X \text{ (major)}$$

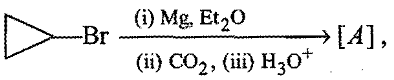
which one of the following statements is true for X? **[EAMCET (Engg.) 2009]**
(a) It gives propionic acid on hydrolysis ☐
(b) It has an ester function ☐
(c) It has a nitrogen linked to ethyl carbon ☐
(d) It has a cyanide group ☐

181. An organic compound on heating with CuO produces CO_2 but no water. The organic compound may be: **[CET (Karnataka) 2009]**
(a) chloroform ☐ (b) ethyl chloride ☐
(c) methane ☐ (d) carbon tetrachloride ☐

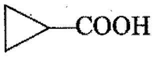
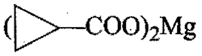
182. Which one of the following does not undergo iodoform reaction? **[CET (J&K) 2009]**
(a) Secondary butyl alcohol ☐
(b) Iso propyl alcohol ☐
(c) Diethyl ketone ☐
(d) Ethyl alcohol ☐

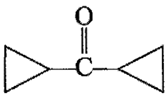
183. An ethereal solution of alkyl halide is heated with sodium metal. The reaction is known as: **[PMT (AMU) 2009]**
(a) Frankland's reaction ☐ (b) Sandmeyer's reaction ☐
(c) Wurtz-Fittig reaction ☐ (d) Wurtz reaction ☐

184. For the following reaction,



product [*A*] is: **[PMT (AMU) 2009]**

(a)  ☐ (b)  ☐

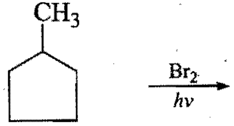
(c)  ☐ (d)  ☐

185. Which of the following is the least reactive towards nucleophile? **[PMT (Kerala) 2010]**
(a) CH_3CH_2Cl ☐ (b) CH_3Cl ☐
(c) $H_2C{=}CH{-}CH_2Cl$ ☐ (d) C_6H_5Cl ☐
(e) $CH_3CH(Cl)CH_3$ ☐

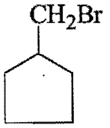
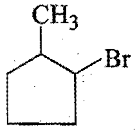
186. Methyl bromide reacts with AgF to give methyl fluoride and AgBr. This reaction is called : **[PMT (Kerala) 2010]**
(a) Finkelstein reaction ☐ (b) Fittig reaction ☐
(c) Swarts reaction ☐ (d) Wurtz reaction ☐
(e) Wurtz-Fittig reaction ☐

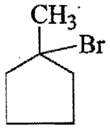
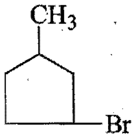
187. Chemical formula of phosgene is : **[AFMC 2010]**
(a) $COCl_2$ ☐ (b) $CaOCl_2$ ☐
(c) $CaCO_3$ ☐ (d) COCl ☐

188. In the following reaction,



The major product obtained is : **[AMU (Med.) 2010]**

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

189. If 1,3-dibromopropane reacts with zinc and NaI, the product obtained is : **[AFMC 2010]**
(a) propene ☐ (b) propane ☐
(c) cyclopropane ☐ (d) hexane ☐

190. Chronic chloroform exposure may cause damage to liver and kidney, due to the formation of : **[PMT (Kerala) 2010]**
(a) phosgene ☐ (b) methylene chloride ☐
(c) methyl chloride ☐ (d) carbon tetrachloride ☐
(e) phosphoryl chloride ☐

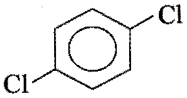
191. The correct order of reactivity of the halides, ethyl chloride (I), *iso*-propyl chloride (II) and benzyl chloride (III) in S_N1 reactions is: **[PMT (Kerala) 2010]**
(a) III > II > I ☐ (b) I > II > III ☐
(c) II > I > III ☐ (d) I > III > II ☐
(e) III > I > II ☐

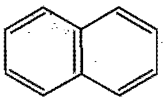
192. The order of rate of hydrolysis of alkyl halides 1°, 2°, 3° and CH_3X by the S_N2 pathway is : **[DUMET 2010]**
(a) $1° > 2° > 3° > CH_3X$ ☐ (b) $CH_3X > 3° > 2° > 1°$ ☐
(c) $CH_3X > 1° > 2° > 3°$ ☐ (d) $3° > 2° > 1° > CH_3X$ ☐

Set II. This set contains questions with two or more correct answers.

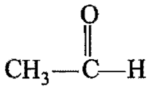
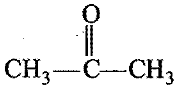
193. The compounds used as refrigerant are:
(a) NH_3 ☐ (b) CCl_4 ☐
(c) CF_4 ☐ (d) CF_2Cl_2 ☐
(e) CH_2F_2 ☐

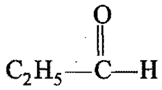
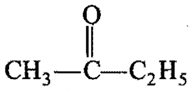
194. Which of the following chemicals are used as moth repellents?

(a)  ☐ (b) Perchloroethane ☐

(c) $CHCl_3$ ☐ (d)  ☐

195. Which of the following compounds will give iodoform test with $I_2/NaOH$?

(a)  $CH_3-\overset{O}{\overset{\|}{C}}-H$ ☐ (b)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ ☐

(c)  $C_2H_5-\overset{O}{\overset{\|}{C}}-H$ ☐ (d)  $CH_3-\overset{O}{\overset{\|}{C}}-C_2H_5$ ☐

196. Select the correct addition products among the following:

(a) $H_2C{=}CHCH_3 + HCl(aq.) \longrightarrow CH_3CHClCH_3$ ☐

(b) $H_2C{=}CHCH_3 + HBr(aq.) \longrightarrow CH_3CHBrCH_3$ ☐

(c) $H_2C{=}CHCH_3 + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2Br$ ☐

(d) $H_2C{=}CHCH_3 + HI \xrightarrow{\text{Peroxide}} CH_3CHICH_3$ ☐

197. What are the intermediate products involved in the following reaction?

$$CHCl_3 \xrightarrow{4OH^-} HCOO^- + 3Cl^- + 2H_2O$$

(a) CCl_3^- ☐ (b) CCl_2 ☐

(c) $CH(OH)_3$ ☐ (d) $COCl_2$ ☐

198. Ethyl alcohol, on treatment with bleaching powder gives chloroform. Which of the following is/are the function of bleaching powder?

(a) Chlorinating agent ☐ (b) Oxidising agent ☐

(c) Hydrolysing agent ☐ (d) None of these ☐

199. Select the correct statement among the following:

(a) S_N1 reactions involve two steps ☐

(b) S_N2 reactions involve single step ☐

(c) S_N1 reaction involves transition state intermediate ☐

(d) S_N2 reaction involves carbonium ion intermediate ☐

200. Which of the following reaction products are correct?

(a) $CH_3-Cl + Ag-CN \longrightarrow CH_3-CN + AgCl$ ☐

(b) $CH_3-Cl + Na^+CN^- \longrightarrow CH_3-NC + NaCl$ ☐

(c) $CH_3-Cl + Ag-NO_2 \longrightarrow CH_3-NO_2 + AgCl$ ☐

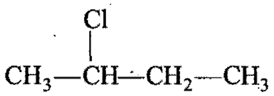
(d) $CH_3-Cl + NaNO_2 \longrightarrow CH_3-O-N{=}O + NaCl$ ☐

201. Isobutene will be obtained on treatment of which of the following compounds, by alcoholic KOH ?

(a) $(CH_3)_3C-Cl$ ☐

(b) $(CH_3)_2CH-CH_2Cl$ ☐

(c) $CH_3-(CH_2)_2-CH_2Cl$ ☐

(d)  $CH_3-\underset{}{\overset{Cl}{\overset{|}{C}H}}-CH_2-CH_3$ ☐

202. Which compounds among the following gives a positive iodoform test ? **[PET (Kerala) 2010]**

(a) Ethanol ☐ (b) Ethanal ☐

(c) 1-Butanol ☐ (d) 2-Butanol ☐

(e) Phenylethanal ☐

ASSERTION-REASON TYPE QUESTIONS

Following questions consist of an **Assertion (A)** and **Reason (R).** Use the following keys to select appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A).

(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).

(c) If (A) is correct but (R) is incorrect.

(d) If (A) is incorrect but (R) is correct.

(e) If both (A) and (R) are incorrect.

1. (A) The dipole moment of CH_3F is greater than CH_3Cl.
(R) C—F bond is more polar than C—Cl bond.

2. (A) The dipole moment of CH_3Cl is greater than CH_3F.
(R) Bond length C—Cl bond is greater than C—F bond.

3. (A) S_N2 reaction takes place in single step.
(R) S_N2 reaction involves the reactivity order of alkyl halides as 1° > 2° > 3° halides.

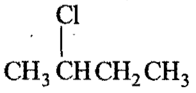
4. (A) Nucleophilic substitution of iodoethane is easier than chloroethane.
(R) Bond energy of C—I bond is less than that of C—Cl bond.

5. (A) Optically active 2-iodobutane on treatment with NaI in acetone undergoes racemization.
(R) Reaction involves multiple Walden inversion and the product contains mixture of dextro and laevo isomer.

6. (A) Nucleophilic substitution reaction on an optically active halide gives a mixture of enantiomers.
(R) Reaction should be in accordance with S_N1 mechanism.

7. (A) Ethyl chloride is more reactive than vinyl chloride towards nucleophilic substitution reactions.
(R) In vinyl chloride, the —Cl is bonded to *sp*-hybridized carbon of an alkene.

8. (A) $CH_3CH_2Br + AgCN \longrightarrow \underset{\text{(Major)}}{CH_3CH_2NC} + \underset{\text{(Minor)}}{CH_3CH_2CN}$
(R) ^-CN is an ambident nucleophile, therefore, reaction gives both cyanide and isocyanide.

9. (A)  $CH_3\overset{Cl}{\overset{|}{C}H}CH_2CH_3 \xrightarrow{\text{Alc. KOH}} CH_3CH{=}CHCH_3 + KCl + H_2O$

Dehydrohalogenation reaction of 2-chlorobutane gives 2-butene.
(R) Elimination reaction takes place according to Saytzeff's rule.

10. (A) Addition of HBr to alkene in presence of peroxide gives anti-Markownikoff product.
(R) This addition follows ionic mechanism.

11. (A) 2-Bromobutane, on reaction with sodium ethoxide in ethanol gives 1-butene as a major product.
(R) 1-Butene is less stable than 2-butene.

12. (A) Isobutanal does not give iodoform test.
(R) It does not have α-hydrogen. **[AIIMS 2004]**

13. (A) Styrene on reaction with HBr, gives 2-bromo-2-phenyl ethane.
(R) Benzyl radical is more stable than alkyl radical. **[AIIMS 2004]**

14. (A) *Tert.* butyl methyl ether is not prepared by the reaction of *tert.* butyl bromide with sodium methoxide.
(R) Sodium methoxide is a strong nucleophile. **[AIIMS 2005]**

15. (A) Addition of HBr on but-2-ene gives two isomeric products.
(R) Addition of HBr on but-2-ene follows Markownikoff's rule. **[AIIMS 2006]**

ANSWERS

OBJECTIVE QUESTIONS

1.	(d)	**2.**	(d)	**3.**	(a)	**4.**	(c)	**5.**	(c)	**6.**	(b)	**7.**	(b)	**8.**	(a)	**9.**	(b)	**10.**	(a)
11.	(c)	**12.**	(d)	**13.**	(a)	**14.**	(b)	**15.**	(c)	**16.**	(b)	**17.**	(d)	**18.**	(c)	**19.**	(b)	**20.**	(d)
21.	(a)	**22.**	(a)	**23.**	(c)	**24.**	(c)	**25.**	(b)	**26.**	(b)	**27.**	(d)	**28.**	(c)	**29.**	(a)	**30.**	(a)
31.	(c)	**32.**	(d)	**33.**	(d)	**34.**	(b)	**35.**	(c)	**36.**	(b)	**37.**	(b)	**38.**	(a)	**39.**	(c)	**40.**	(d)
41.	(b)	**42.**	(c)	**43.**	(b)	**44.**	(c)	**45.**	(a)	**46.**	(d)	**47.**	(a)	**48.**	(a)	**49.**	(b)	**50.**	(a)
51.	(d)	**52.**	(d)	**53.**	(d)	**54.**	(a)	**55.**	(a)	**56.**	(b)	**57.**	(b)	**58.**	(c)	**59.**	(d)	**60.**	(a)
61.	(c)	**62.**	(d)	**63.**	(b)	**64.**	(d)	**65.**	(b)	**66.**	(d)	**67.**	(b)	**68.**	(a)	**69.**	(a)	**70.**	(c)
71.	(c)	**72.**	(b)	**73.**	(c)	**74.**	(d)	**75.**	(a,c)	**76.**	(d)	**77.**	(b)	**78.**	(d)	**79.**	(b)	**80.**	(d)
81.	(a)	**82.**	(a)	**83.**	(c)	**84.**	(b)	**85.**	(c)	**86.**	(d)	**87.**	(d)	**88.**	(c)	**89.**	(b)	**90.**	(d)
91.	(a)	**92.**	(a)	**93.**	(b)	**94.**	(d)	**95.**	(b)	**96.**	(b)	**97.**	(a)	**98.**	(b)	**99.**	(c)	**100.**	(c)
101.	(d)	**102.**	(d)	**103.**	(d)	**104.**	(c)	**105.**	(d)	**106.**	(a)	**107.**	(d)	**108.**	(d)	**109.**	(c)	**110.**	(d)
111.	(c)	**112.**	(d)	**113.**	(a,d)	**114.**	(b)	**115.**	(b)	**116.**	(c)	**117.**	(d)	**118.**	(d)	**119.**	(a)	**120.**	(d)
121.	(b)	**122.**	(a)	**123.**	(b)	**124.**	(d)	**125.**	(b)	**126.**	(b)	**127.**	(c)	**128.**	(c)	**129.**	(d)	**130.**	(a)
131.	(c)	**132.**	(b)	**133.**	(c)	**134.**	(d)	**135.**	(a)	**136.**	(c)	**137.**	(b)	**138.**	(a)	**139.**	(a)	**140.**	(b)
141.	(d)	**142.**	(d)	**143.**	(a)	**144.**	(d)	**145.**	(b)	**146.**	(c)	**147.**	(d)	**148.**	(c)	**149.**	(d)	**150.**	(b)
151.	(c)	**152.**	(b)	**153.**	(b)	**154.**	(b)	**155.**	(a)	**156.**	(a)	**157.**	(a)	**158.**	(b)	**159.**	(c)	**160.**	(a)
161.	(d)	**162.**	(a)	**163.**	(b)	**164.**	(c)	**165.**	(c)	**166.**	(b)	**167.**	(c)	**168.**	(d)	**169.**	(c)	**170.**	(d)
171.	(d)	**172.**	(d)	**173.**	(a)	**174.**	(c)	**175.**	(e)	**176.**	(d)	**177.**	(e)	**178.**	(b)	**179.**	(d)	**180.**	(c)
181.	(d)	**182.**	(c)	**183.**	(d)	**184.**	(a)	**185.**	(d)	**186.**	(c)	**187.**	(a)	**188.**	(c)	**189.**	(c)	**190.**	(a)
191.	(a)	**192.**	(c)	**193.**	(a,d)	**194.**	(a,b,d)	**195.**	(a,b,d)	**196.**	(a,b,c,d)	**197.**	(a,b)	**198.**	(a,b,c)	**199.**	(a,b)	**200.**	(c,d)
201.	(a,b)	**202.**	(a,b,d)																

ASSERTION-REASON TYPE QUESTIONS

1.	(d)	**2.**	(a)	**3.**	(a)	**4.**	(a)	**5.**	(a)	**6.**	(a)	**7.**	(c)	**8.**	(a)	**9.**	(a)	**10.**	(c)
11.	(d)	**12.**	(c)	**13.**	(e)	**14.**	(b)	**15.**	(e)										

BRAIN STORMING PROBLEMS

1. An alkyl bromide (*A*) on treatment with Na and ether gives a hydrocarbon (*B*). (*B*) on treatment with HBr and peroxide gives Br—$(CH_2)_6$—Br. Compound (*A*) is:

(a) $CH_3CH_2CH_2Br$ ☐

(b) $H_2C{=}CH{-}CH_2Br$ ☐

(c) $CH_3{-}CH{=}CHBr$ ☐

(d) $CH_3{-}CH_2{-}CH_2{-}CH_2Br$ ☐

2. The number of monochloro product obtained during the reaction of 2,3-dimethyl butane with Cl_2 in presence of sunlight is (do not consider optical isomers):

(a) 2 ☐ (b) 3 ☐

(c) 4 ☐ (d) 5 ☐

3. In which of the following pairs, the bromination of first member is easier than the second member?

(a) Isobutane, butane ☐ (b) *n*-Butane, isobutane ☐

(c) Methane, ethane ☐ (d) None of these ☐

4. *Tert.*-alkyl halide is obtained as major product in:

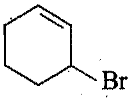
(a) $(CH_3)_3CH \xrightarrow[h\nu]{Br_2}$ ☐

(b) $(CH_3)_2CH{-}CH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr}$ ☐

(c) $(CH_3)_2CH{-}CH{=}CH_2 \xrightarrow{HBr}$ ☐

(d) both (a) and (c) ☐

5. Which of the following is fast de-brominated?

(a) 

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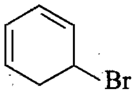
(b) 

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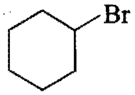
(c) 

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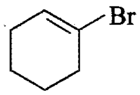
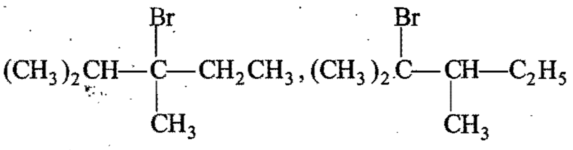
(d) 

☐

6. In which of the following pairs both members on heating with alc. KOH result in the formation of same alkene as major product?

(a) $(CH_3)_3C{-}Br, (CH_3)_2CHCH_2Br$ ☐

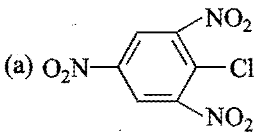
(b) *n*-Propyl iodide, isopropyl iodide ☐

(c) 

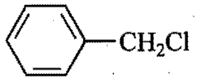
$(CH_3)_2CH{-}\underset{CH_3}{\overset{Br}{C}}{-}CH_2CH_3, (CH_3)_2\overset{Br}{C}{-}\underset{CH_3}{CH}{-}C_2H_5$ ☐

(d) All of the above ☐

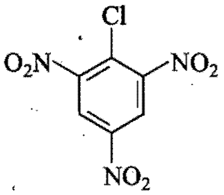
7. Detection of chlorine is possible without preparing sodium extract in:

(a) 

☐ (b) $H_2C{=}CH{-}CH_2Cl$ ☐

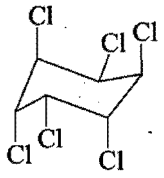
(c) 

☐ (d) $CHCl_3$ ☐

[**Hint:** In 

, three nitro groups weaken the C—Cl bond, hence, it gives test without preparing sodium extract].

8. Dehydrohalogenation by strong base is slowest in:

(a) 

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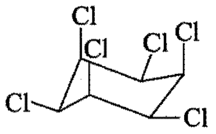
(b) 

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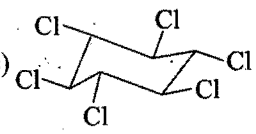
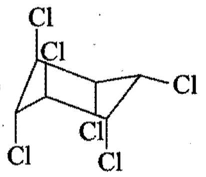
(c) 

☐

(d) 

☐

[**Hint:** Compound (c) has all equitorial substituent, hence, it is most stable and undergo elimination with slowest state.]

9. Consider the structures of the following two molecules:

X : $F_2C{=}C{=}CF_2$

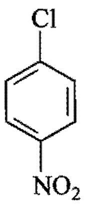
Y : $F_2B{-}C{\equiv}C{-}BF_2$

In which of these two, it is impossible for all the four F-atoms to lie in the same plane?

(a) *X* ☐ (b) *Y* ☐

(c) Both *X* and *Y* ☐ (d) None of these ☐

10. Which of the following is least reactive towards nucleophilic substitution with aqueous KOH?

(a) 

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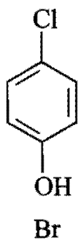
(b) 

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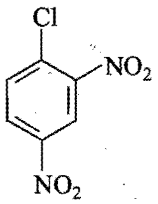
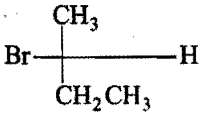
(c) 

☐

(d) 

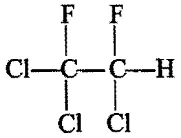
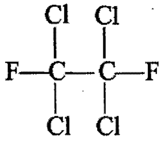
☐

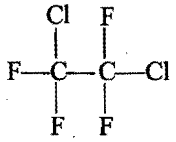
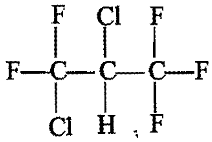
11. When  $\mathrm{Br-C(CH_3)(CH_2CH_3)-H}$ reacts with KOH in presence of water (through S_N2 reaction mechanism) then stereochemistry of product so formed will be:

(a) *R* ☐
(b) *S* ☐
(c) mixture of *R* and *S* ☐
(d) Partial *S* + racemic mixture ☐

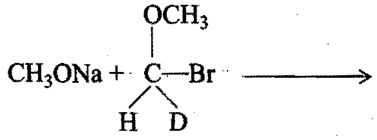
[**Hint:** Original compound is (*R*), hence, the product formed will be (*S*) due to inversion of configuration.]

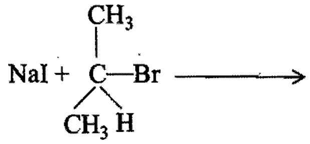
12. Which of the following molecules represents freon-1,14?

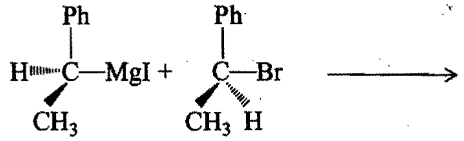
(a)  $\mathrm{Cl-CF(Cl)-CF(Cl)-H}$ ☐ (b)  $\mathrm{F-CCl_2-CCl_2-F}$ ☐

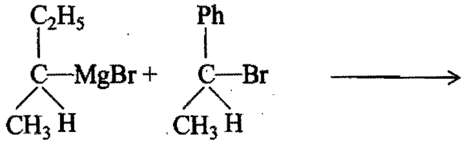
(c)  $\mathrm{F-CClF-CF_2-Cl}$ ☐ (d)  $\mathrm{F-CF_2-CClH-CF_2-F}$ ☐

13. In which of the following reactions, an optically active single product is formed?

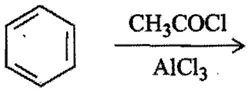
(a)  ☐

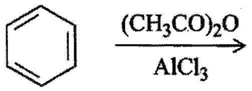
(b)  ☐

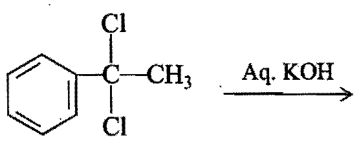
(c)  ☐

(d)  ☐

14. Which of the following will give acetophenone as a product?

(a)  ☐

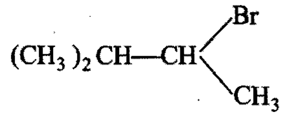
(b)  ☐

(c)  ☐

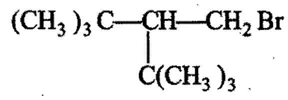
(d) All of the above ☐

15. Most reactive alkyl halide towards E_2 mechanism is:

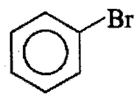
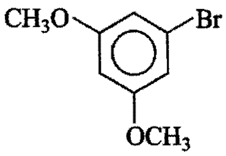
(a) $\mathrm{(CH_3)_3C-CH_2Br}$ ☐

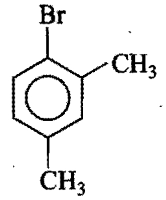
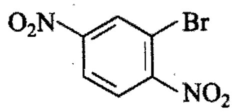
(b)  $\mathrm{(CH_3)_2CH-CH(Br)CH_3}$ ☐

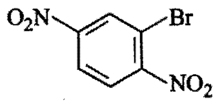
(c) $\mathrm{(CH_3)_3C-CH_2CH_2Br}$ ☐

(d)  $\mathrm{(CH_3)_3C-CH(C(CH_3)_3)-CH_2Br}$ ☐

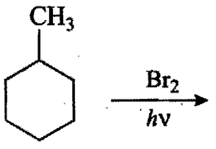
16. Which of the following compounds is the most likely to undergo a bimolecular nucleophilic substitution reaction with aqueous NaOH?

(a)  ☐ (b)  ☐

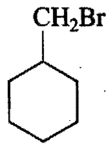
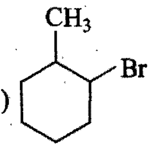
(c)  ☐ (d)  ☐

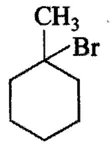
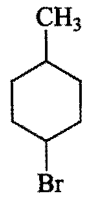
[**Hint:** In  is activated for nucleophilic substitution by electron withdrawing group present at *ortho*- position.]

17. The major product obtained in the reaction,



is:

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

18. The reaction,

$$\mathrm{H_2C{=}CH{-}CH_3 + Cl_2 \xrightarrow{400^\circ C} H_2C{=}CH{-}CH_2Cl}$$

proceeds through the intermediate formation of a:

(a) carbene ☐ (b) carbocation ☐
(c) free radical ☐ (d) carbanion ☐

19. Iodoform is used as an:

(a) anaesthetic ☐ (b) analgesic ☐
(c) antiseptic ☐ (d) antifebrin ☐

20. The trade name of trichloroethylene is:
(a) freon ☐ (b) westron ☐
(c) westrosol ☐ (d) DDT ☐

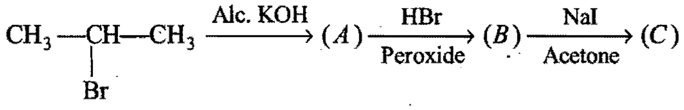
21. In the reaction,

$$R\text{—}Br + Cl^- \longrightarrow R\text{—}Cl + Br^-$$

the rates of reaction of ethyl bromide (I), *n*-propyl bromide (II), isobutyl bromide (III) and neopentyl bromide (IV) follow the order:
(a) IV > III > II > I ☐ (b) I > II > III > IV ☐
(c) I > III > II > IV ☐ (d) III > II > IV > I ☐

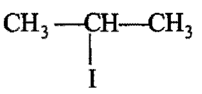
22. Arrange the following compounds in the decreasing order of the boiling point:
CH_3Br (I) CH_3CH_2Br (II) $CH_3CH_2CH_2Br$ (III)
$CH_3CH_2CH_2CH_2Br$ (IV)
(a) I > II > III > IV ☐ (b) IV > III > II > I ☐
(c) I > III > II > IV ☐ (d) III > IV > I > II ☐

23. In the reaction,



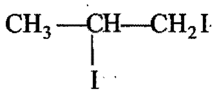
$$CH_3\text{—}\underset{\displaystyle Br}{\underset{|}{CH}}\text{—}CH_3 \xrightarrow{\text{Alc. KOH}} (A) \xrightarrow[\text{Peroxide}]{\text{HBr}} (B) \xrightarrow[\text{Acetone}]{\text{NaI}} (C)$$

the compound (*C*) is:
(a) $CH_3\text{—}CH_2CH_2I$ ☐ (b) ☐



$CH_3\text{—}\underset{\displaystyle I}{\underset{|}{CH}}\text{—}CH_3$

(c) ☐ (d) $CH_3\text{—}CH{=}CHI$ ☐



$CH_3\text{—}\underset{\displaystyle I}{\underset{|}{CH}}\text{—}CH_2I$

24. CCl_4 is used as fire extinguisher because:
(a) of its covalent bond ☐
(b) of its low b.pt. ☐
(c) of its high m.pt. ☐
(d) it gives incombustible vapours ☐

25. The correct order of reactivity of alkyl halides for S_{N^1} reaction is:
(a) $RI > RBr > RCl > RF$ ☐ (b) 3° > 2° > 1° ☐
(c) 3° < 2° < 1° ☐ (d) $RF < RCl < RBr < RI$ ☐

26. Match List I with List II and select the correct answer using the codes given below the lists:

List I Compound	List II Use
(A) Chloretone	(i) Monomer
(B) Chloropicrin	(ii) In war and as insecticide
(C) Lindane	(iii) Insecticide
(D) Teflon	(iv) Hypnotic

Codes:

	A	B	C	D	
(a)	(iii)	(i)	(iv)	(ii)	☐
(b)	(i)	(ii)	(iii)	(iv)	☐
(c)	(iv)	(iii)	(ii)	(i)	☐
(d)	(ii)	(iv)	(i)	(iii)	☐

27. Match List I with List II and select the correct answer using the codes given below the lists:

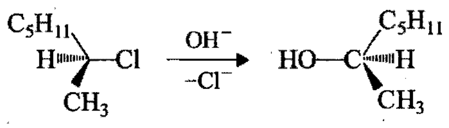
List I Compound	List II Action
(A) Teflon	(i) Ozone layer depletion
(B) Pyrene	(ii) Non-biodegradable insecticide
(C) DDT	(iii) Non-stick cookwares and insulator
(D) Freon	(iv) Fire extinguisher

Codes:

	A	B	C	D	
(a)	(i)	(ii)	(iii)	(iv)	☐
(b)	(iv)	(iii)	(i)	(ii)	☐
(c)	(iii)	(iv)	(ii)	(i)	☐
(d)	(ii)	(i)	(iv)	(iii)	☐

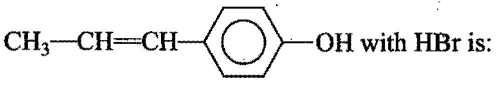
28. The intermediate compound formed in Frankland's reaction is:
(a) $RZnI_2$ ☐ (b) R_2Zn ☐
(c) $RZnI$ ☐ (d) R_2ZnI ☐

29. The reaction given

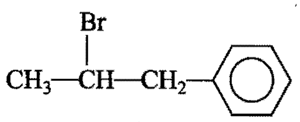


is:
(a) S_{N^1} ☐ (b) S_{N^2} ☐
(c) E_1 ☐ (d) E_2 ☐

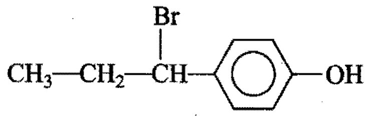
30. The major product of the reaction,



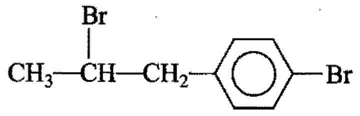
(a) ☐



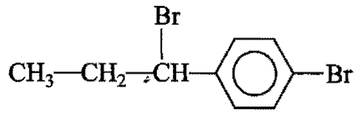
(b) ☐



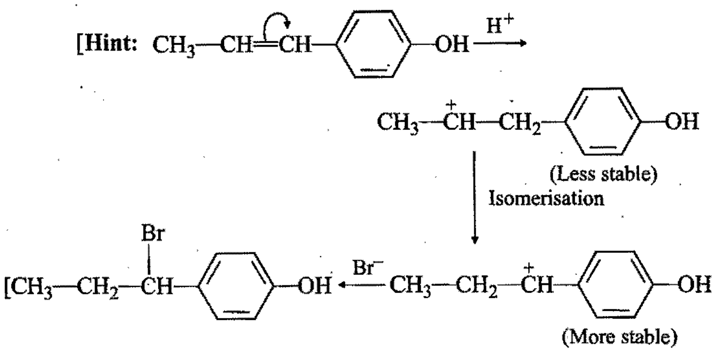
(c) ☐



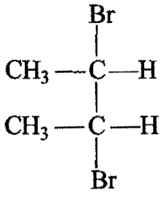
(d) ☐



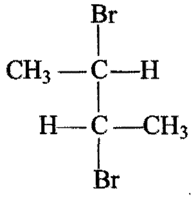
[**Hint:**



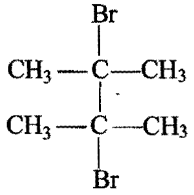
31. Which among the following on dehalogenation will give *trans*-alkene?

(a)


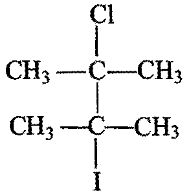
$$\begin{array}{c} Br \\ | \\ CH_3-C-H \\ | \\ CH_3-C-H \\ | \\ Br \end{array}$$
☐

(b)


$$\begin{array}{c} Br \\ | \\ CH_3-C-H \\ | \\ H-C-CH_3 \\ | \\ Br \end{array}$$
☐

(c)


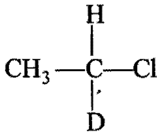
$$\begin{array}{c} Br \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ Br \end{array}$$
☐

(d)


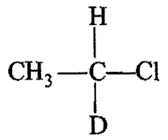
$$\begin{array}{c} Cl \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ I \end{array}$$
☐

32. Which of the following combinations is correctly matched?

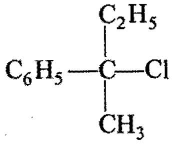
Compound **Reaction** **Stereochemistry**

(a)


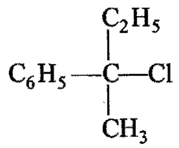
$$\begin{array}{c} H \\ | \\ CH_3-C-Cl \\ | \\ D \end{array}$$
S_N2 Walden inversion ☐

(b)


$$\begin{array}{c} H \\ | \\ CH_3-C-Cl \\ | \\ D \end{array}$$
S_N1 Walden inversion ☐

(c)


$$\begin{array}{c} C_2H_5 \\ | \\ C_6H_5-C-Cl \\ | \\ CH_3 \end{array}$$
S_N1 Retention in configuration ☐

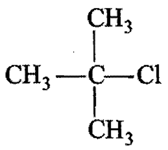
(d)


$$\begin{array}{c} C_2H_5 \\ | \\ C_6H_5-C-Cl \\ | \\ CH_3 \end{array}$$
S_N1 Inversion in configuration ☐

33. For the given reaction,

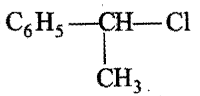
$$R-Cl + NaI \xrightarrow{\text{Acetone}} R-I + NaCl$$

Which of the following alkyl halides will give the maximum yield?

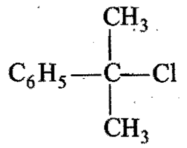
(a)


$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-Cl \\ | \\ CH_3 \end{array}$$
☐

(b) $CH_3-CH_2-CH_2-Cl$ ☐

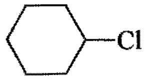
(c)


$$\begin{array}{c} C_6H_5-CH-Cl \\ | \\ CH_3 \end{array}$$
☐

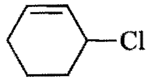
(d)


$$\begin{array}{c} CH_3 \\ | \\ C_6H_5-C-Cl \\ | \\ CH_3 \end{array}$$
☐

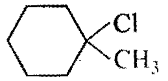
34. Which among the following compounds will be most reactive for S_N1 reaction?

(a)


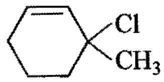
☐

(b)


☐

(c)


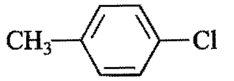
☐

(d)


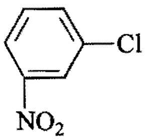
☐

35. Ullmann reaction is given by:

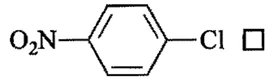
(a) C_6H_5-Cl ☐

(b)


☐

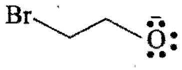
(c)


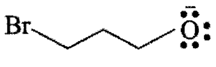
☐

(d)


☐

36. In the following compounds, nucleophile and the leaving groups are in the same molecule:

I.


II.


III.


IV.

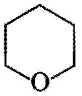

These dual nature species can undergo intramolecular and intermolecular nucleophilic substitution. Intramolecular substitution reaction is possible in:

(a) I, II ☐ (b) II, III ☐

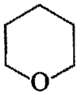
(c) III, IV ☐ (d) IV ☐

[**Hint:** In I and II, intramolecular reaction will not be possible because they will give strained ring.]

37. Compound  undergoes intramolecular nucleophilic substitution of the type .... giving .....

(a) S_N1;


☐

(b) S_N2;


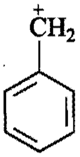
☐

(c) both of the above are correct ☐

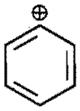
(d) intramolecular reaction is not possible ☐

38. Which is the most stable carbocation formed as intermediate in nucleophilic substitution reaction?

(a) $CH_2{=}\overset{+}{C}H$ ☐

(b)  ☐

(c) $(CH_3)_3\overset{+}{C}$ ☐

(d)  ☐

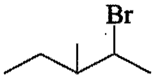
39. Transition state is accompanied by the formation of which of the following species in S_{N2} reaction?

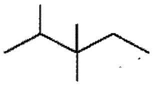
(a) Carbocation ☐ (b) Carbanion ☐

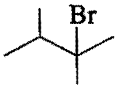
(c) Free radical ☐ (d) A dianion ☐

40. Only one of the following alkyl halides can be prepared as the major product of the addition of HBr to an alkene:

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

ANSWERS : BRAIN STORMING PROBLEMS

1. (b)	2. (a)	3. (a)	4. (d)	5. (b)	6. (d)	7. (a)	8. (c)	9. (a)	10. (b)
11. (a)	12. (c)	13. (d)	14. (d)	15. (b)	16. (d)	17. (c)	18. (c)	19. (c)	20. (c)
21. (b)	22. (b)	23. (a)	24. (d)	25. (b)	26. (c)	27. (c)	28. (c)	29. (a)	30. (b)
31. (a)	32. (a)	33. (b)	34. (d)	35. (d)	36. (c)	37. (a)	38. (b)	39. (a)	40. (d)

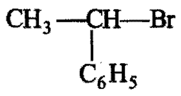
LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

The high reactivity of alkyl halides can be explained in terms of nature of C—*X* bond which is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atom. This polarity is responsible for the nucleophilic substitution reactions of alkyl halides which mostly occur by S_N1 and S_N2 mechanisms. S_N1 reaction is a two step process and in the first step, *R*—*X* ionises to give carbocation (slow process). In the second step, the nucleophile attacks the carbocation from either side to form the product (fast process). In S_N1 reaction, there can be racemization and inversion. S_N1 reaction is favoured by heavy (bulky) groups on the carbon atom attached to halogens. *i.e.*, $R_3C-X > R_2CH-X > R-CH_2X > CH_3X$. In S_N2 reaction, the strong nucleophile OH^- attacks from the opposite side of the chlorine atom to give an intermediate (transition state). which breaks to yield the product (alcohol) and leaving (X^-) group. The alcohol has a configuration opposite to that of the bromide and is said to proceed with inversion of configuration. S_N2 reaction is favoured by small groups on the carbon atom attached to halogen *i.e.*, $CH_3-X > R-CH_2X > R_2CHX > R_3C-X$.

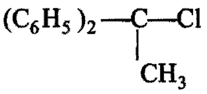
Answer the following questions:

1. Which among the following will not give S_N1 reaction?

(a) 
$CH_3-\underset{C_6H_5}{\underset{|}{CH}}-Br$

(b) $(CH_3)_3C-Br$

(c) CH_3CH_2I

(d) 
$(C_6H_5)_2-\underset{CH_3}{\underset{|}{C}}-Cl$

2. S_N1 reaction of optically active alkyl halide leads to:

(a) retention of configuration (b) racemisation

(c) inversion of configuration (d) none of these

3. An S_N2 reaction at an asymmetric carbon of a compound always gives: [IIT 2001]

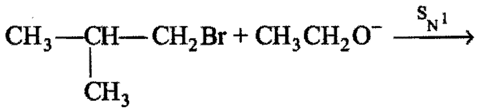
(a) an enantiomer of the substrate

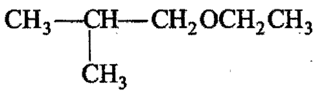
(b) a product with opposite optical rotation

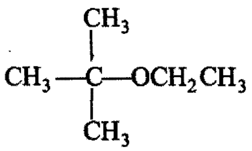
(c) a mixture of diastereomers

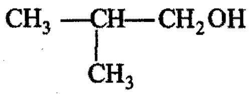
(d) a single stereoisomer

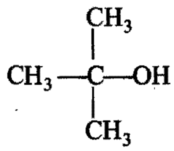
4. The main product formed in the following reaction is:


$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2Br + CH_3CH_2O^- \xrightarrow{S_N1}$

(a) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2OCH_2CH_3$

(b) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OCH_2CH_3$

(c) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2OH$

(d) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH$

5. Which of the following is an example of S_N2 reaction?

(a) $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

(b) $CH_3CH_2OH \xrightarrow{-H_2O} CH_2{=}CH_2$

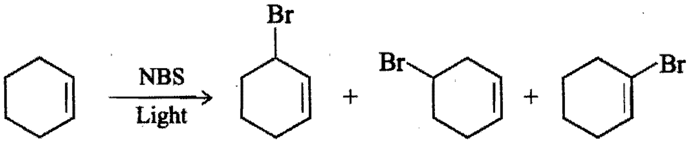
(c) $(CH_3)_2CHBr + OH^- \longrightarrow (CH_3)_2CHOH + Br^-$

(d) $(CH_3)_3C-Br + OH^- \longrightarrow (CH_3)_3C-OH + Br^-$

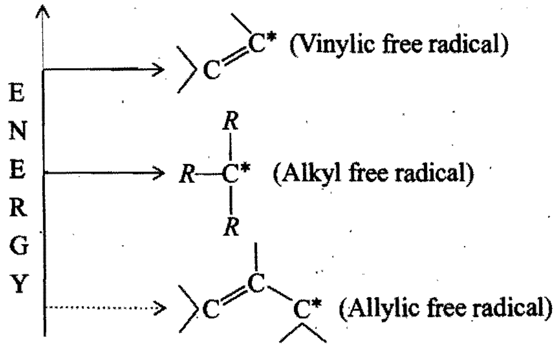
Passage 2

Karl Ziegler reported that alkenes react with N-bromosuccinimide (NBS) in presence of light to give products resulting from substitution of hydrogen by bromine at the allylic position, *i.e.*, the position next to the double bond.

Let us consider the halogenation of cyclohexene.

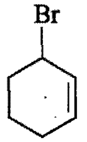


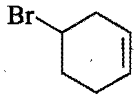
Energy level diagram for allylic, vinylic and alkylic free radicals is given below:

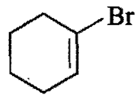


Answer the following questions:

1. In the treatment of cyclohexene with NBS, which of the following products will be least stable?

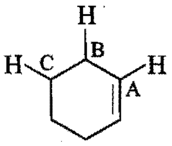
(a) 

(b) 

(c) 

(d) Cannot be predicted

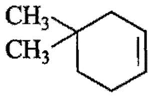
2. Consider the three types of C—H bonds in cyclohexene.



Which of the following is/are correctly matched?
(a) A—Vinylic C—H bond (b) B—Allylic C—H bond
(c) C—Alkylic C—H bond (d) All of these

3. Which of the following sequences is correct about C—H bond energy?
(a) (C—H) Vinylic > (C—H) Alkylic > (C—H) Allylic
(b) (C—H) Vinylic < (C—H) Alkylic < (C—H) Allylic
(c) (C—H) Alkylic < (C—H) Vinylic < (C—H) Allylic
(d) (C—H) Vinylic = (C—H) Alkylic = (C—H) Allylic

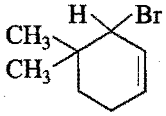
4. Select the correct statement(s) among the following:
(a) Allylic free radical is stabilised by delocalisation
(b) Vinylic free radical is stabilised by hyperconjugation
(c) Alkyl free radicals are stabilised by hyperconjugation
(d) Allylic free radical is stabilised by hyperconjugation

5. 

(4,4-Dimethyl cyclohexene)

Above compound on treatment with NBS gives allylic bromides. How many product(s) will be obtained in this reaction?
(a) One (b) Two
(c) Three (d) Four

[**Hint:** Three products will be obtained, whose structures are:



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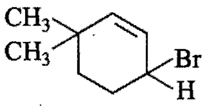

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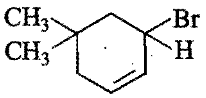

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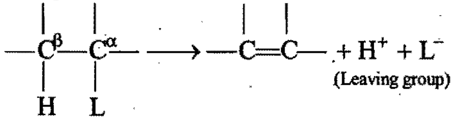
Passage 3

The removal of two atoms or groups, one generally hydrogen (H^+) and the other a leaving group (L^-) resulting in the formation of unsaturated compound is known as elimination reaction.

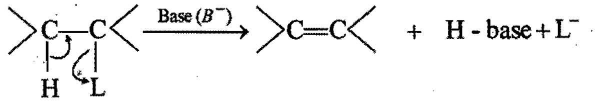


$$-\underset{H}{\underset{|}{\overset{|}{C^{\beta}}}}-\underset{L}{\underset{|}{\overset{|}{C^{\alpha}}}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}- + H^+ + L^-$$

(Leaving group)

In E_1 (elimination) reactions, the C—L bond is broken heterolytically (in step 1) to form a carbocation (as in S_N1 reaction) in which (L^-) is lost (rate determining step). The carbocation (in step 2) loses a proton from the β-carbon atom by a base (nucleophile) to form an alkene. E_1 reaction is favoured in compounds in which the leaving group is at secondary (2°) or tertiary (3°) position.

In E_2 (elimination) reactions, two sigma bonds are broken and a π-bond is formed simultaneously. E_2 reactions occur in one step through a transition state.



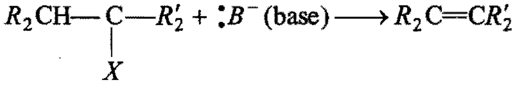
E_2 reactions are most common in haloalkanes (particularly 1°) and better the leaving group higher is the E_2 reaction. In E_2 reactions, both the leaving groups should be antiplanar.

E_1 ***cb*** (Elimination unimolecular conjugate base) reaction involves the removal of proton by a conjugate base (step 1) to produce carbanion which loses a leaving group to form an alkene (step 2) and is a slow step.

Answer the following questions:

1. Isopropyl chloride on heating with concentrated solution of ethanolic KOH gives mainly:
(a) propan-1-ol (b) propan-2-ol
(c) propene (d) isopropyl ethyl ether

2. 2-Bromobutane on heating with concentrated solution of alcoholic KOH gives major product as:
(a) but-1-ene (b) but-2-ene
(c) butan-2-ol (d) 2-methyl propene

3. 

$$R_2CH-\underset{X}{\underset{|}{C}}-R'_2 + :B^-(\text{base}) \longrightarrow R_2C{=}CR'_2 + H{-}B + X^-$$

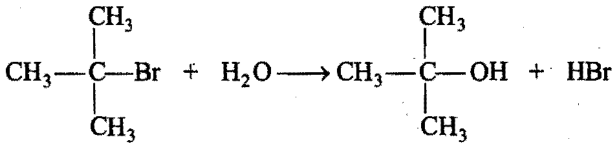
This reaction is an example of:
(a) E_1 reaction (b) E_2 reaction
(c) E_1cb reaction (d) first order reaction

4. 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is:
(a) pent-1-ene (b) 2-Ethoxy pentane
(c) *cis*-pent-2-ene (d) *trans*-pent-2-ene

5. Neopentyl bromide undergoes dehydrohalogenation to give alkene even though it has no β-hydrogen. This is due to:
[PMT (Kerala) 2006]
(a) E_2 mechanism
(b) E_1 mechanism
(c) due to rearrangement of carbocation by E_1 mechanism
(d) E_1 *cb* mechanism
(e) Hofmann elimination

Passage 4

S_N1 reaction is a first order nucleophilic substitution, *e.g.*,



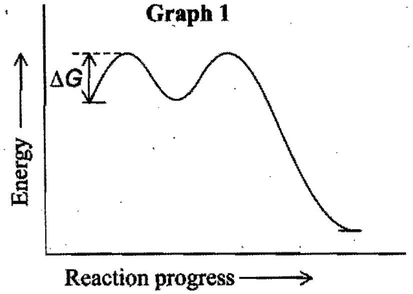
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + H_2O \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + HBr$$

The concentration of nucleophile does not appear in the rate law expression:

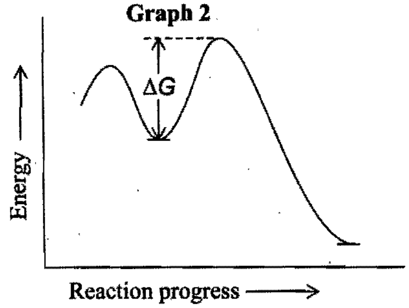
$$\text{Reaction rate} = k[RX]$$

In a multistep organic reaction, the rate-limiting step is the slowest step. Rate determining step is represented by the following energy level diagram:

Graph 1

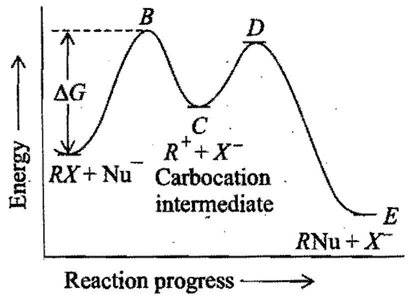


Graph 2



A reaction energy level diagram for an S_N1 reaction. The rate limiting step is spontaneous dissociation of an alkyl halide to give a carbocation intermediate.

Graph 3



Answer the following questions:

1. In S_N1 reaction, the hybridization changes in rate determination step. Select the correct change among the following:
   (a) from sp^3 to sp^2 (b) from sp^2 to sp^3
   (c) from sp^2 to sp (d) from sp to sp^2
2. Select the correct statement(s) about the graph 1:
   (a) first step is rate determining and it is endothermic
   (b) first step is rate determining and it is exothermic
   (c) second step is rate determining and it is exothermic
   (d) second step is rate determining and it is endothermic
3. Select the correct statement(s) about the graph 2:
   (a) first step is rate determining and it is endothermic
   (b) first step is rate determining and it is exothermic
   (c) second step is rate determining and it is exothermic
   (d) second step is rate determining and it is endothermic
4. In the graph 3 for S_N1 reaction, the rate limiting step is the spontaneous dissociation of alkyl halide and is given by:
   (a) *AB* (b) *AC*
   (c) *AD* (d) *DE*
5. S_N1 reaction is:
   (a) single step reaction
   (b) two step reaction
   (c) a reaction involving free radical intermediate
   (d) a reaction involving carbocation intermediate

Passage 5

Free radical halogenation takes place in the presence of light or at high temperature (above 773K). Formation of halogen free radical intermediate takes place in first step called chain initiation step.

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$$

This reaction is mainly given by those compounds which have atleast one hydrogen atom present at sp^3-hybrid carbon. Reactivity of sp^3-hybrid carbon depends on the reactivity of reaction intermediate.

The relative rate of formation of alkyl radicals by a chlorine radical is :

$$\underset{(5)}{\text{Tertiary}} > \underset{(3.8)}{\text{Secondary}} > \underset{(1)}{\text{Primary}}$$

$$\text{Percentage yield of the product} = \frac{\text{Relative amount} \times 100}{\text{Sum of relative amounts}}$$

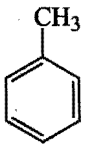
Relative amount = Number of hydrogen atoms on the respective carbon × relative reactivity.

NBS (*N*-bromo succinimide) is used for bromination at allylic and benzylic carbon, whereas $Br_2/h\nu$ gives bromination at benzylic, allylic and alkyl carbon.

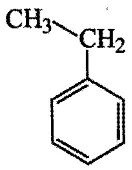
Answer the following questions:

1. Select most reactive compound for chlorination in presence of light:

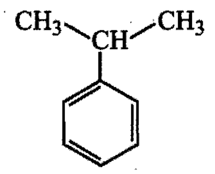
(a)



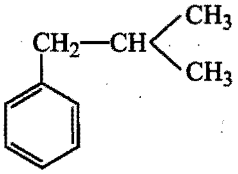
(b)



(c)

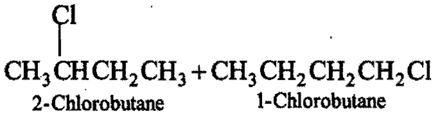


(d)



2. Chlorination of butane takes place as:

$CH_3CH_2CH_2CH_3 + Cl_2 \xrightarrow[\text{Light}]{hv}$



$CH_3\overset{Cl}{C}HCH_2CH_3 + CH_3CH_2CH_2CH_2Cl$

2-Chlorobutane 1-Chlorobutane

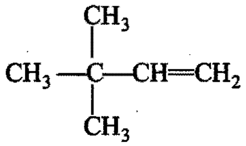
Percentage yield of 2-chlorobutane will be:

(a) $\frac{15}{21}\times100$ (b) $\frac{21}{21}\times100$

(c) $\frac{6}{21}\times100$ (d) $\frac{3}{21}\times100$

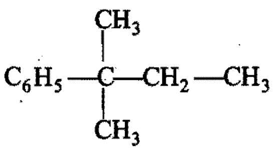
3. Which one of the following compounds will react with NBS?

(a)



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2$

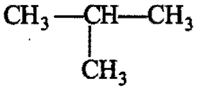
(b)



$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_3$

(c) $C_6H_5-CH_2-CH=CH_2$

(d)



$CH_3-\underset{CH_3}{CH}-CH_3$

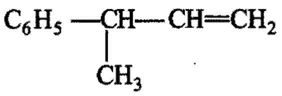
4. Arrange decreasing order of reactivity of given compounds with NBS: (N-bromo succinimide)

I. $C_6H_5-CH_3$

II. $C_6H_5-CH_2-CH_2-CH_3$

III. $C_6H_5-CH_2-CH=CH_2$

IV.



$C_6H_5-\underset{CH_3}{CH}-CH=CH_2$

Select the correct answer from the codes given below:

Codes:

(a) IV, III, I, II (b) IV, III, II, I

(c) I, II, III, IV (d) I, III, II, IV

5. Chlorinating agent for free radical chlorination may be taken as:

(a) Cl_2 (b) SO_2Cl_2

(c) $(CH_3)_3C-O-Cl$ (d) PCl_5

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1.	1. (c)	2. (b)	3. (d)	4. (b)	5. (a)
Passage 2.	1. (c)	2. (d)	3. (a)	4. (a,c)	5. (c)
Passage 3.	1. (a)	2. (b)	3. (b)	4. (d)	5. (c)
Passage 4.	1. (a)	2. (a)	3. (c)	4. (a)	5. (d)
Passage 5.	1. (c)	2. (a)	3. (c)	4. (b)	5. (a,b,c)

9

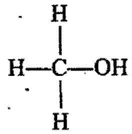
ALCOHOLS OR ALKANOLS

9.1 INTRODUCTION

Alcohols are regarded as hydroxy derivatives of alkanes. These are formed by the replacement of one, two or more hydrogen atoms of a hydrocarbon by a corresponding number of hydroxyl groups (—OH).

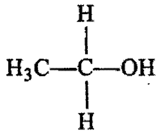
$$\underset{\text{Hydrocarbon}}{R{—}H} \xrightarrow[+OH]{-H} \underset{\text{Alcohol}}{R{—}OH}$$

Note: In alcohols, the valencies of the carbon atoms linked to the hydroxyl group are either satisfied by hydrogen atoms only or by other carbon atoms only or by both hydrogen and carbon atoms only and not by any other atom or group. For example, the compounds (i), (ii) and (iii) are alcohols but (iv) and (v) are not alcohols although they contain a hydroxyl group.



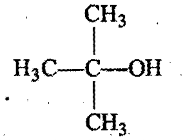
$$H{—}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{—}OH$$

(i) Methyl alcohol



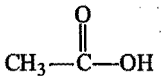
$$H_3C{—}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{—}OH$$

(ii) Ethyl alcohol



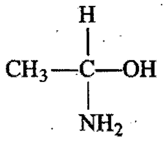
$$H_3C{—}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{—}OH$$

(iii) Tertiary butyl alcohol



$$CH_3{—}\overset{\overset{O}{\|}}{C}{—}OH$$

(iv) Acetic acid



$$CH_3{—}\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}{—}OH$$

(v) Acetaldehyde ammonia

These are not alcohols as carbon bearing —OH group is attached to =O in compound (iv) and to $—NH_2$ in compound (v).

Classification

Alcohols are classified according to the number of hydroxyl groups present in their molecules. **Monohydric** alcohols contain one hydroxyl group, **dihydric** two and **trihydric** three, respectively. However, if an alcohol contains two or more hydroxyl groups, it is generally called as a **polyhydric alcohol.**

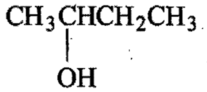
Monohydric Alcohols

CH_3OH Methyl alcohol

CH_3CH_2OH Ethyl alcohol

$CH_3CH_2CH_2OH$ *n*-Propyl alcohol

$(CH_3)_2CHOH$ Isopropyl alcohol

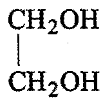


$$CH_3\underset{\underset{OH}{|}}{C}HCH_2CH_3$$

Sec. butyl alcohol

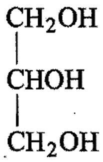
$(CH_3)_3COH$ *Tert.* butyl alcohol

Polyhydric Alcohols



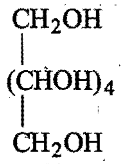
$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

Glycol
(Dihydric)



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

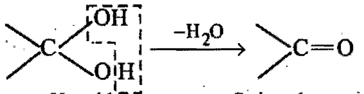
Glycerol
(Trihydric)



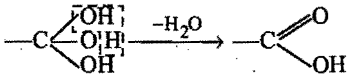
$$\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Sorbitol or
Mannitol (Hexahydric)

Note: When two or more hydroxyl groups are attached to the same carbon atom, the compound is usually unstable. The compound loses a water molecule and is converted into a stable compound.



Unstable — Carbonyl compound (Stable)



Unstable — Acid (Stable)

[However, chloral hydrate is a stable compound although two hydroxyl groups are attached to the same carbon atom. This is due to intramolecular hydrogen bonding.]

9.2 MONOHYDRIC ALCOHOLS

Alcohols containing one hydroxyl group are known as monohydric alcohols. These alcohols may be saturated or unsaturated depending on the nature of hydrocarbon groups. Saturated monohydric alcohols form a homologous series of the general formula $C_nH_{2n+1}OH$. They are also represented as R—OH where R represents an alkyl group. They may be regarded as derivatives of water, *i.e.*, one hydrogen atom of the water molecule is replaced by an alkyl group.

$$\underset{\text{Water}}{HOH} \xrightarrow[+R]{-H} \underset{\text{Alcohol}}{ROH}$$

Monohydric alcohols are further classified according to the hybridisation of carbon atom to which the hydroxyl group is attached.

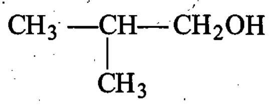
(a) Compounds containing C_{sp^3}—OH bond: In these alcohols, the —OH group is attached to a sp^3-hybridized carbon atom of an alkyl group. These are further subdivided as follows:

(i) Primary alcohols (1°) : In these alcohols, the hydroxyl group is attached with primary (1°) carbon atom. They possess a characteristic group $—CH_2OH$ and their general formula is RCH_2OH. R may be H in the first member and alkyl group in the rest of the members.

Examples :

HCH_2OH ; CH_3CH_2OH ;
Methyl alcohol, Ethyl alcohol

$CH_3CH_2CH_2OH$;
n-Propyl alcohol

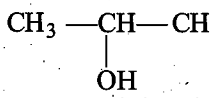


$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

Isobutyl alcohol

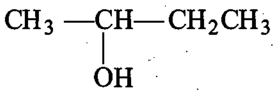
(ii) Secondary alcohols (2°) : In these monohydric alcohols, the hydroxyl group is attached with secondary (2°) carbon atom. They possess a characteristic group $>CHOH$ and the general formula $\genfrac{}{}{0pt}{}{R}{R'}\!\!>CHOH$ (R and R' may be same or different).

Examples :



$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$;

Isopropyl alcohol

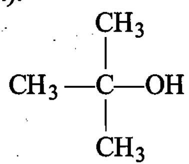


$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2CH_3$

Sec. butyl alcohol

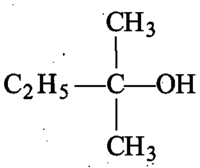
(iii) Tertiary alcohols (3°) : In these monohydric alcohols, the hydroxyl group is attached with tertiary (3°) carbon atom. They contain a characteristic group $>COH$ and have the general formula $R'\!\overset{R''}{\underset{R}{>}}C—OH$ (R, R' and R'' may be same or different).

Examples :



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-OH$;

Tert. butyl alcohol



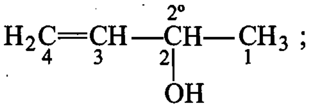
$C_2H_5-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-OH$

Tert. amyl alcohol

(iv) Allylic alcohols: In these alcohols, the —OH group is attached to a sp^3-hybridized carbon next to the carbon-carbon double bond, *i.e.*, to an allylic carbon. For example,

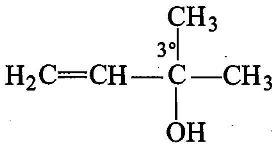
$H_2C=CH-\overset{1°}{CH_2}OH$;

Prop-2-en-1-ol
(Allyl alcohol)
Primary (1°)



$\underset{4}{H_2C}=\underset{3}{CH}-\overset{2°}{\underset{\underset{\displaystyle OH}{|}}{\underset{2}{CH}}}-\underset{1}{CH_3}$;

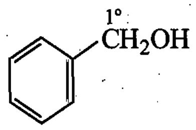
But-3-en-2-ol
Secondary (2°)



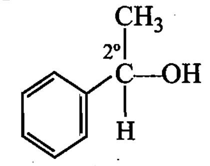
$H_2C=CH-\overset{\displaystyle CH_3}{\overset{3°|}{\underset{\underset{\displaystyle OH}{|}}{C}}}-CH_3$

2-Methyl but-3-en-2-ol
Tertiary (3°)

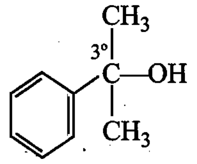
(v) Benzylic alcohols: In these alcohols, the —OH group is attached to a sp^3-hybridized carbon atom next to an aromatic ring. For example,



Primary



Secondary



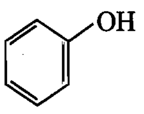
Tertiary

So, allylic and benzylic alcohols may be primary, secondary or tertiary.

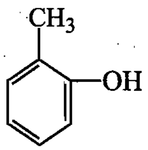
- **(b) Compounds containing C_{sp^2}—OH bond:** In these alcohols, the —OH group is attached to a carbon atom of the double bond, *i.e.*, vinylic carbon or to an aryl carbon. For example,

Vinylic alcohol: $H_2C=CH-OH$, vinyl alcohol (unstable)

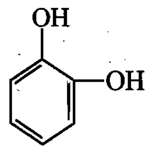
Phenols:



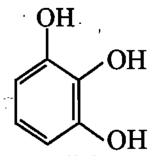
Phenol



o-Cresol



Catechol



Pyrogallol

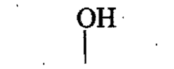
9.3 NOMENCLATURE

There are three systems for naming the alcohols.

1. Common system : In this system, alcohols (R—OH) are named as alkyl alcohols, *i.e.*, the word alcohol is added to the name of alkyl group. In higher members, it is always indicated whether the —OH group is attached to primary, secondary or tertiary carbon atom by prefixing *n* for primary, *sec.* for secondary and *tert.* for tertiary.

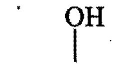
CH_3OH ; CH_3CH_2OH ;
Methyl alcohol, Ethyl alcohol

$CH_3CH_2CH_2OH$;
n-Propyl alcohol

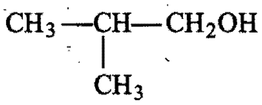


$CH_3-\overset{OH}{\overset{|}{C}H}-CH_3$;
Isopropyl alcohol

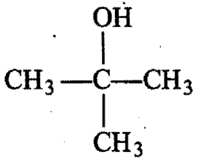
$CH_3CH_2CH_2CH_2OH$;
n-Butyl alcohol



$CH_3CH_2\overset{OH}{\overset{|}{C}H}-CH_3$;
Sec. butyl alcohol



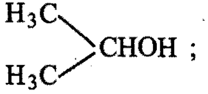
$CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_2OH$;
Isobutyl alcohol



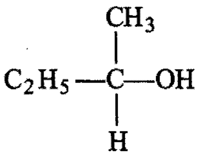
$CH_3-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$
Tert. butyl alcohol

2. Carbinol system : The simplest monohydric alcohol, CH_3OH, is called carbinol. All other members are considered its alkyl derivatives. The alkyl groups attached to the carbon atom carrying —OH group are named in alphabetical order.

CH_3OH ; CH_3CH_2OH ;
Carbinol; Methyl carbinol

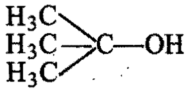


Dimethyl carbinol

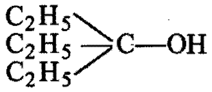


$C_2H_5-\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OH$;
Ethyl methyl carbinol

Isopropyl carbinol



Trimethyl carbinol



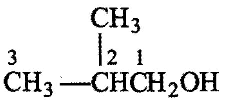
Triethyl carbinol

3. IUPAC system : According to this system, the alcohols are called alkanols, *i.e.*, by replacing -e from the name of alkane by -ol, *i.e.*,

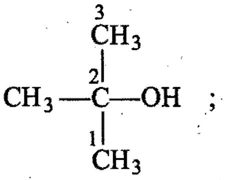
Alkane (– e) + ol = Alkanol

Examples :

CH_3OH ; CH_3CH_2OH ; $CH_3CH_2CH_2OH$;
Methanol; Ethanol; Propan-1-ol

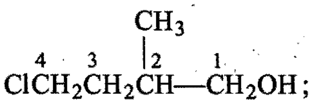


$\overset{3}{C}H_3-\overset{CH_3}{\overset{|}{\overset{2}{C}}}H\overset{1}{C}H_2OH$;
2-Methyl propan-1-ol



$CH_3-\overset{\overset{3}{CH_3}}{\overset{|}{\underset{CH_3}{\underset{|}{\overset{2}{C}}}}}-OH$;
2-Methyl propan-2-ol

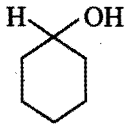
$\overset{3}{C}H_3-\overset{OH}{\overset{|}{\overset{2}{C}}}H-\overset{1}{C}H_3$;
Propan-2-ol



$Cl\overset{4}{C}H_2\overset{3}{C}H_2\overset{CH_3}{\overset{|}{\overset{2}{C}}}H-\overset{1}{C}H_2OH$;
4-Chloro-2-methyl butan-1-ol

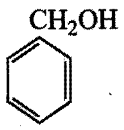
$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2OH$;
Butan-1-ol

$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{OH}{\overset{|}{\overset{2}{C}}}H-\overset{1}{C}H_3$;
Butan-2-ol



Cyclohexanol

;



Phenylmethanol
(Benzyl alcohol)

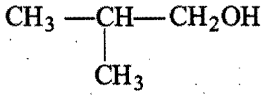
9.4 ISOMERISM

Monohydric saturated alcohols show following three types of isomerism:

1. Chain isomerism : Chain isomerism exists due to difference in the structure of the chain containing four or more carbon atoms attached to the hydroxyl group.

Examples :

$CH_3CH_2CH_2CH_2OH$ and
Butan-1-ol
(n-Butyl alcohol)



$CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_2OH$
2-Methyl propan-1-ol
(Isobutyl alcohol)

are chain isomers.

2. Position isomerism : This isomerism is due to the difference in the position of the hydroxyl group when the carbon chain of three or more carbon atoms is the same.

Examples :

$CH_3CH_2CH_2OH$ Propan-1-ol (n-Propyl alcohol)	and	$CH_3CHOHCH_3$ Propan-2-ol (Isopropyl alcohol)

are position isomers.

$CH_3CH_2CH_2CH_2OH$ Butan-1-ol (n-Butyl alcohol)	and	$CH_3CH_2CHOHCH_3$ Butan-2-ol (*Sec.* butyl alcohol)

are position isomers.

3. Functional isomerism : Saturated monohydric alcohols containing two or more carbon atoms show functional isomerism with ethers. Both have the general formula $C_nH_{2n+2}O$. The alcohols contain a hydroxyl group whereas ethers have ethereal oxygen (—O—).

Examples :

C_2H_5OH Ethyl alcohol	and	CH_3OCH_3 Dimethyl ether

are functional isomers.

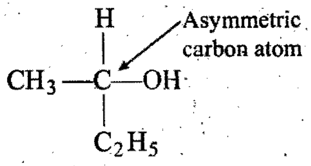
$CH_3CH_2CH_2OH$ Propan-1-ol	and	$C_2H_5OCH_3$ Ethyl methyl ether (Methoxy ethane)

are functional isomers.

Besides the structural isomerism, alcohols having asymmetric carbon atom exhibit optical isomerism (enantiomerism) also.

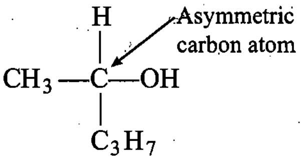
Examples :

Butan - 2 - ol
(*Sec.* butyl alcohol) ;



$CH_3-\overset{H}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}-OH$

Pentan-2-ol (*Sec.* amyl alcohol) ;


$$CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle C_3H_7}{|}}{C}}-OH$$

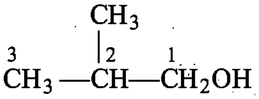
SOME SOLVED PROBLEMS

Problem 1. *Write the structural formulae and give* IUPAC *names for all isomeric alcohols of the molecular formula* $C_4H_{10}O$.

Solution : $C_4H_{10}O$ is a monohydric alcohol, *i.e.*, C_4H_9OH. It can have four isomeric alcohols.

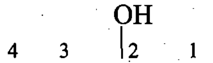
$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2OH$
Butan-1-ol

and


$$\overset{3}{C}H_3-\overset{\overset{\displaystyle CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}H_2OH$$

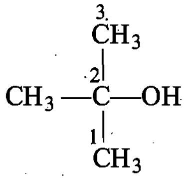
2-Methyl propan-1-ol

are primary alcohols.


$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{\overset{\displaystyle OH}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$$

Butan-2-ol
(Secondary alcohol)

and


$$CH_3-\overset{\overset{\displaystyle \overset{3}{C}H_3}{|}}{\underset{\underset{\displaystyle \overset{1}{C}H_3}{|}}{\overset{2}{C}}}-OH$$

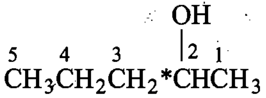
2-Methyl propan-2-ol
(Tertiary alcohol)

Problem 2. (*a*) *Write the structural formulae and give* IUPAC *names for all the isomeric alcohols of the molecular formula* $C_5H_{12}O$. *Indicate any chirality.*

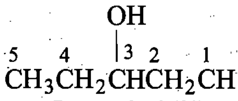
(*b*) *Write the structures and name all the cyclic* C_4H_7OH *isomers.*

Solution : (a) $C_5H_{12}O$ is a monohydric alcohol, *i.e*, $C_5H_{11}OH$. It can have the following eight isomers:

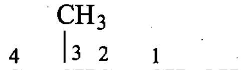
(1) $\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2OH$
Pentan-1-ol (1°)

(2)

$$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2{}^*\overset{\overset{\displaystyle OH}{|}}{\overset{2}{C}H}\overset{1}{C}H_3$$

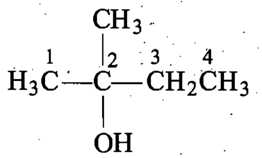
Pentan-2-ol (2°)

(3)

$$\overset{5}{C}H_3\overset{4}{C}H_2\overset{\overset{\displaystyle OH}{|}}{\overset{3}{C}H}\overset{2}{C}H_2\overset{1}{C}H_3$$

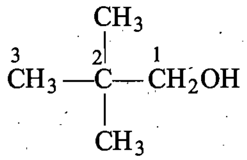
Pentan-3-ol (2°)

(4)

$$\overset{4}{C}H_3\overset{\overset{\displaystyle CH_3}{|}}{\overset{3}{C}H}\overset{2}{C}H_2\overset{1}{C}H_2OH$$

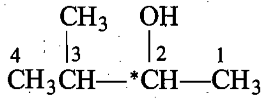
3-Methyl butan-1-ol (1°)

(5)

$$H_3\overset{1}{C}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{\overset{2}{C}}}-\overset{3}{C}H_2\overset{4}{C}H_3$$

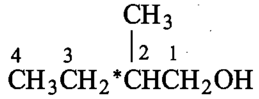
2-Methyl butan-2-ol (3°)

(6)

$$\overset{3}{C}H_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{C}}}-\overset{1}{C}H_2OH$$

2,2-Dimethyl propan-1-ol (1°)

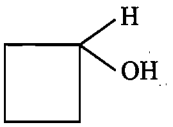
(7)

$$\overset{4}{C}H_3\overset{\overset{\displaystyle CH_3}{|}}{\overset{3}{C}H}-{}^*\overset{\overset{\displaystyle OH}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$$

3-Methyl butan-2-ol (2°)

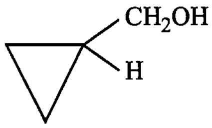
(8)

$$\overset{4}{C}H_3\overset{3}{C}H_2{}^*\overset{\overset{\displaystyle CH_3}{|}}{\overset{2}{C}H}\overset{1}{C}H_2OH$$

2-Methyl butan-1-ol (1°)

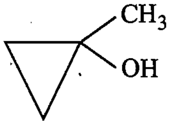
*Isomers (2), (7) and (8) containing chiral centres can exhibit enantiomerism.

(b) (1)


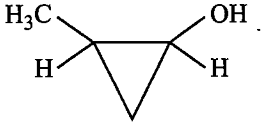
Cyclobutanol

(2)


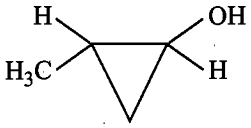
Cyclopropyl methanol

(3)


1-Methyl cyclopropanol

(4)


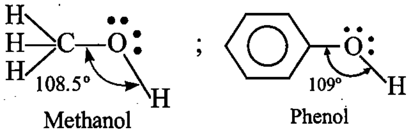
2-Methyl cyclopropanol
(*Cis*-) chiral

(5)


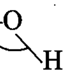
2-Methyl cyclopropanol
(*Trans*-) chiral

Electronic structures of the functional groups (Alcohols and Phenols)

The general formula of alcohols is R—OH, where R is some alkyl or substituted alkyl group and the —OH group in alcohols is attached to sp^3-hybridized carbon of —CH_3 by a sigma (σ) bond formed by the overlap of sp^3-hybrid orbital of oxygen. The structure of the simplest alcohol is:



Methanol ; Phenol or (C_6H_5—$\ddot{\underset{\cdot\cdot}{O}}$—H)

The oxygen atom of the hydroxyl group has two bond pairs and two lone pairs of electrons, so the C—O—H bonds in alcohols (as well as in phenols) are not linear and the bond angle  in alcohols is 108.5° which is slightly less than tetrahedral angle (109.5°) due to the repulsion between the unshared electron pairs of oxygen.

Since, the oxygen atom is more electronegative than both carbon and hydrogen, the electrons of C—O and the O—H bonds are a little more displaced towards the oxygen atom. As a result, the oxygen has partial negative charge (δ^-) and carbon and hydrogen each have a partial positive charge (δ^+) and so alcohols (and phenols) possess a net dipole moment. Methanol has a dipole moment of 1.71D.

$$[H_3C^{\delta^+}—O^{\delta^-}—H^{\delta^+}]$$

Phenol on the other hand has a dipole moment 1.54 D. The smaller dipole moment of phenol is due to the electron attracting effect of phenyl group in contrast to the electron releasing effect of methyl (or alkyl) group in alcohols.

Due to this **dipolar nature,** alcohols and phenols form intermolecular hydrogen bonding.

In phenols, the —OH group is attached to sp^2-hybrid carbon of an aromatic ring and oxygen atom of the hydroxyl group has two lone pairs of electrons and the bond angle in phenol is 109°. The C—O bond length in phenol (136 pm) is slightly less than in methanol (142 pm) due to resonance in aromatic ring of phenol.

9.5 GENERAL METHODS OF PREPARATION OF MONOHYDRIC ALCOHOLS

1. By the hydrolysis of alkyl halides with aqueous alkali or moist silver oxide : Alkyl halides undergo hydrolysis when heated with aqueous NaOH or KOH or moist silver oxide. The hydrolysis occurs by a nucleophilic substitution reaction.

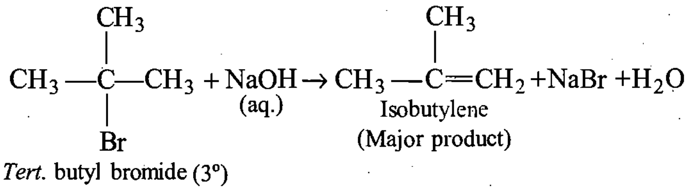
$$\underset{\text{Alkyl halide}}{RX} + KOH(aq.) \xrightarrow{\Delta} \underset{\text{Alcohol}}{ROH} + KX$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + KOH(aq.) \xrightarrow{\Delta} \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KBr$$

This method is not satisfactory as olefins (alkenes) are formed as side products. However, satisfactory results are obtained by using moist silver hydroxide (AgOH) or aqueous potassium carbonate (K_2CO_3).

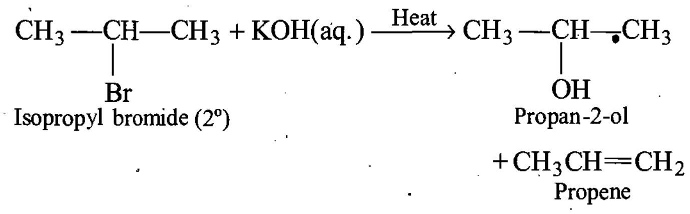
$$\underset{\text{Alkyl iodide}}{RI} + \underset{\text{Moist silver oxide}}{AgOH} \longrightarrow \underset{\text{Alkyl alcohol}}{ROH} + AgI$$

The method is applicable for the preparation of primary, secondary or tertiary alcohols, but primary alkyl halides give good yield of alcohols, while tertiary butyl halides mainly give alkenes due to dehydrohalogenation.



$$\underset{\text{Tert. butyl bromide (3°)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3} + \underset{(aq.)}{NaOH} \rightarrow \underset{\text{Isobutylene (Major product)}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} + NaBr + H_2O$$

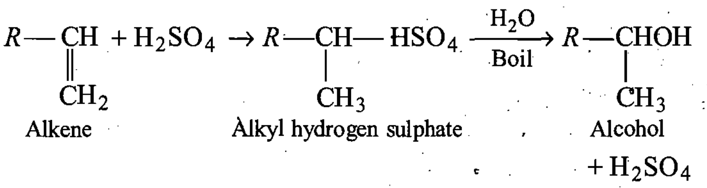
Secondary alkyl halides give a mixture of alcohol and alkene.



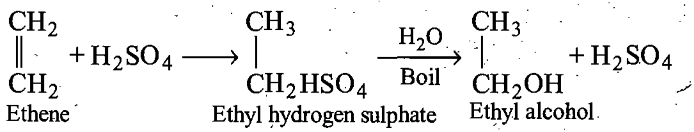
$$\underset{\text{Isopropyl bromide (2°)}}{CH_3-\underset{\underset{Br}{|}}{CH}-CH_3} + KOH(aq.) \xrightarrow{\text{Heat}} \underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} + \underset{\text{Propene}}{CH_3CH=CH_2}$$

Hydrolysis of 1° halides proceeds by S_N2 mechanism while those of 3° halides by S_N1 mechanism. The hydrolysis of 2° alkyl halides may proceed by S_N1 or S_N2 reaction.

2. Hydration of alkenes : Alkenes are absorbed in cold concentrated sulphuric acid forming alkyl hydrogen sulphates. These undergo hydrolysis with boiling water or steam and form alcohols (Indirect method of hydration).



$$\underset{\text{Alkene}}{R-\underset{\underset{CH_2}{\|}}{CH}} + H_2SO_4 \rightarrow \underset{\text{Alkyl hydrogen sulphate}}{R-\underset{\underset{CH_3}{|}}{CH}-HSO_4} \xrightarrow[\text{Boil}]{H_2O} \underset{\text{Alcohol}}{R-\underset{\underset{CH_3}{|}}{CHOH}} + H_2SO_4$$

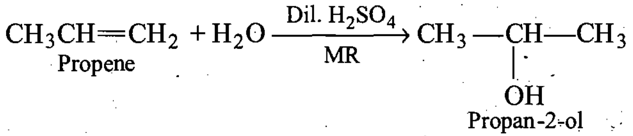


$$\underset{\text{Ethene}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}} + H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{\begin{matrix}CH_3\\ |\\ CH_2HSO_4\end{matrix}} \xrightarrow[\text{Boil}]{H_2O} \underset{\text{Ethyl alcohol}}{\begin{matrix}CH_3\\ |\\ CH_2OH\end{matrix}} + H_2SO_4$$

The overall process is the addition of water to double bond.

This is an **Industrial method** for obtaining alcohols as alkenes are obtained in large amount during the cracking of petroleum. *Except ethyl alcohol, no other primary alcohol can be prepared by this method* as the addition of H_2SO_4 follows Markownikoff's rule (MR). Generally secondary and tertiary alcohols are obtained.

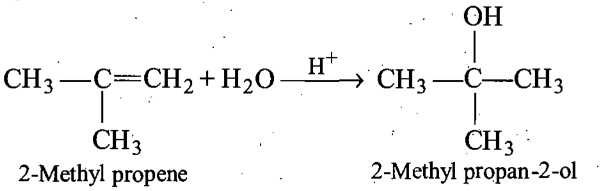
Alkenes may also be catalytically hydrated in presence of dilute acids directly.



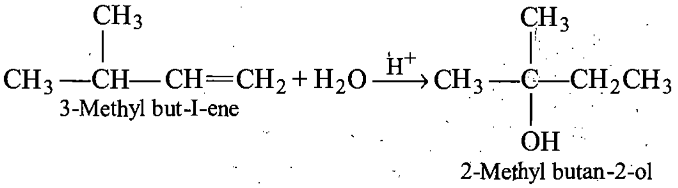
$$\underset{\text{Propene}}{CH_3CH=CH_2} + H_2O \xrightarrow[\text{MR}]{\text{Dil. } H_2SO_4} \underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3}$$

Mechanism : See section. 7.6.

In hydration, H_2SO_4 (and not HBr) is used as a catalyst, because the sulphuric ester which is also formed, can easily be hydrolysed.

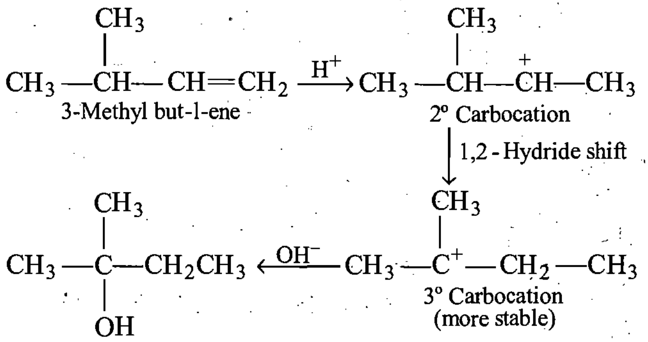


$$\underset{\text{2-Methyl propene}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2} + H_2O \xrightarrow{H^+} \underset{\text{2-Methyl propan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$



$$\underset{\text{3-Methyl but-I-ene}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH=CH_2} + H_2O \xrightarrow{H^+} \underset{\text{2-Methyl butan-2-ol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2CH_3}$$

Intermediate is 2° carbocation that can change to more stable 3° carbocation by 1,2-hydride shift.

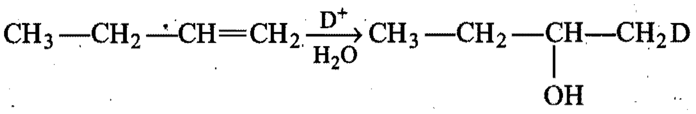


$$\underset{\text{3-Methyl but-l-ene}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH=CH_2} \xrightarrow{H^+} \underset{\text{2° Carbocation}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{+}{C}H-CH_3}$$

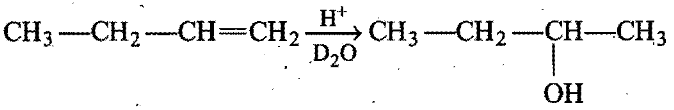
$$\downarrow \text{1,2-Hydride shift}$$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2CH_3 \xleftarrow{OH^-} \underset{\substack{\text{3° Carbocation}\\ \text{(more stable)}}}{CH_3-\overset{\overset{CH_3}{|}}{C^+}-CH_2-CH_3}$$

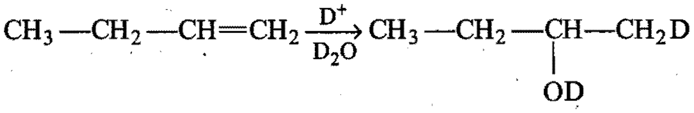
Other examples are:



$$CH_3-CH_2-CH=CH_2 \xrightarrow[H_2O]{D^+} CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2D$$



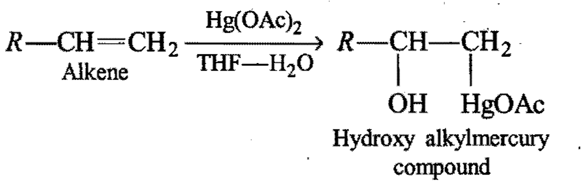
$$CH_3-CH_2-CH=CH_2 \xrightarrow[D_2O]{H^+} CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$



$$CH_3-CH_2-CH=CH_2 \xrightarrow[D_2O]{D^+} CH_3-CH_2-\underset{\displaystyle OD}{\underset{|}{CH}}-CH_2D$$

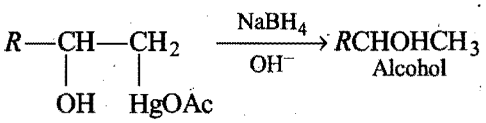
There are two indirect methods for the addition of water to alkenes:

(i) Oxymercuration-demercuration method : Mercuric acetate $(CH_3COO)_2Hg$ or $Hg(OAc)_2$, in presence of water-tetrahydrofuran solution reacts with alkene to form an adduct alkylmercury compound.

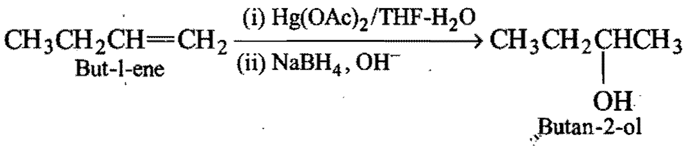


$$\underset{\text{Alkene}}{R-CH=CH_2} \xrightarrow[THF-H_2O]{Hg(OAc)_2} \underset{\text{Hydroxy alkylmercury compound}}{R-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle HgOAc}{\underset{|}{CH_2}}}$$

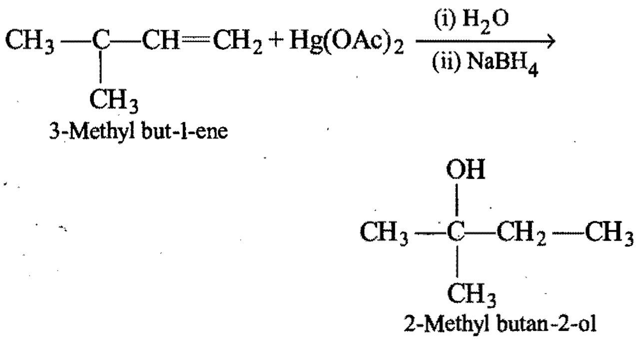
The mercury compound is reduced with $NaBH_4$ in basic medium when alcohol is formed. Addition of water occurs according to Markownikoff's rule.



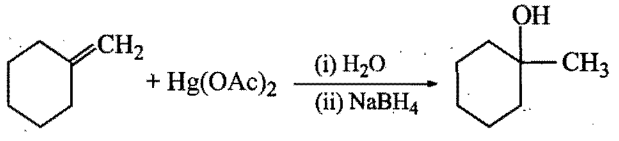
$$R-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle HgOAc}{\underset{|}{CH_2}} \xrightarrow[OH^-]{NaBH_4} \underset{\text{Alcohol}}{RCHOHCH_3}$$



$$\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} \xrightarrow[\text{(ii) } NaBH_4,\, OH^-]{\text{(i) } Hg(OAc)_2/THF\text{-}H_2O} \underset{\text{Butan-2-ol}}{CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3}$$



$$\underset{\text{3-Methyl but-1-ene}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2} + Hg(OAc)_2 \xrightarrow[\text{(ii) } NaBH_4]{\text{(i) } H_2O} \underset{\text{2-Methyl butan-2-ol}}{CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2-CH_3}$$

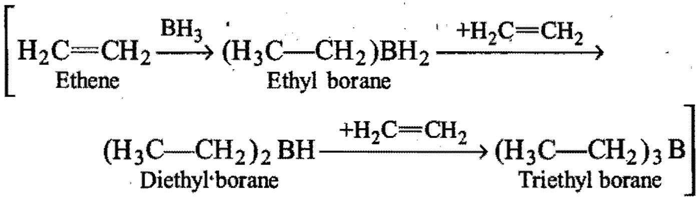


This two step process is called **oxymercuration reduction** or **oxymercuration-demercuration** and forms alcohol.

(ii) Hydroboration-oxidation method : Alkenes undergo addition reaction (called hydroboration) with diborane (B_2H_6). The addition compounds (trialkyl boranes) on subsequent oxidation with alkaline H_2O_2 yield alcohols.

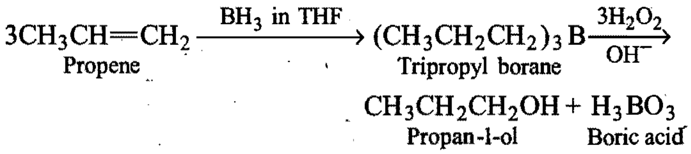
$$(B_2H_6 \longrightarrow 2BH_3)$$

$$6H_2C=CH_2 + B_2H_6 \longrightarrow \underset{\text{Triethyl boron}}{2(CH_3CH_2)_3B}$$



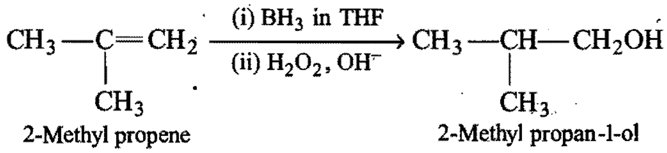
$$\left[\underset{\text{Ethene}}{H_2C=CH_2} \xrightarrow{BH_3} \underset{\text{Ethyl borane}}{(H_3C-CH_2)BH_2} \xrightarrow{+H_2C=CH_2} \underset{\text{Diethyl borane}}{(H_3C-CH_2)_2BH} \xrightarrow{+H_2C=CH_2} \underset{\text{Triethyl borane}}{(H_3C-CH_2)_3B}\right]$$

$$(CH_3CH_2)_3B + 3H_2O_2 \xrightarrow{OH^-} 3CH_3CH_2OH + H_3BO_3$$



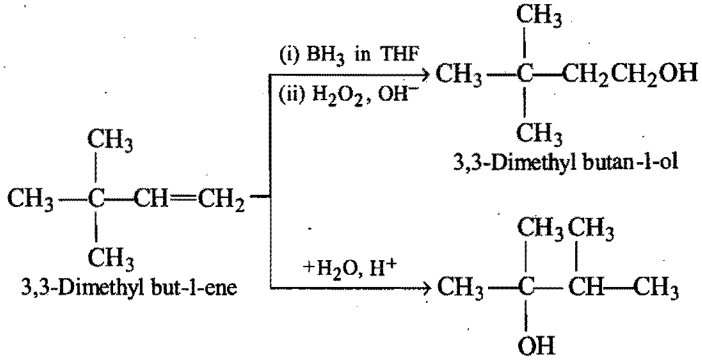
$$\underset{\text{Propene}}{3CH_3CH=CH_2} \xrightarrow{BH_3 \text{ in THF}} \underset{\text{Tripropyl borane}}{(CH_3CH_2CH_2)_3B} \xrightarrow[OH^-]{3H_2O_2} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + \underset{\text{Boric acid}}{H_3BO_3}$$

$$\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} \xrightarrow[\text{(ii) } H_2O_2,\, OH^-]{\text{(i) } BH_3 \text{ in THF}} \underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH}$$



$$\underset{\text{2-Methyl propene}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2} \xrightarrow[\text{(ii) } H_2O_2,\, OH^-]{\text{(i) } BH_3 \text{ in THF}} \underset{\text{2-Methyl propan-1-ol}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH}$$

In Hydroboration-oxidation **(HBO)** process, the carbocations are not the intermediate and hence no rearrangement takes place.



3,3-Dimethyl but-1-ene

3,3-Dimethyl butan-1-ol

2,3-Dimethyl butan-2-ol

The overall (HBO) process occurs with the addition of water by anti-Markownikoff's rule. [Borane is an electron deficient compound and therefore, behaves as an electrophile and attacks at a point of highest electron density. However, the addition of borane follows Markownikoff's rule.]

Hydroboration method has entirely replaced peroxide initiated addition of HBr reaction for anti-Markownikoff's addition.

3. Hydrolysis of ester : Esters on hydrolysis by mineral acids or alkalies form alcohols and carboxylic acids.

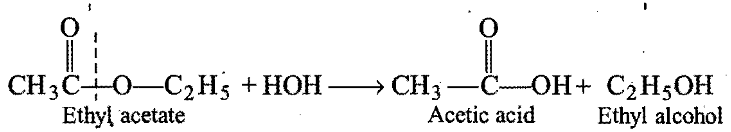
$$\underset{\text{Ester}}{RCOOR'} + H_2O \xrightarrow{H^+ \text{ or } OH^-} \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$$

Alcohols are generally prepared from naturally occurring esters by hydrolysis with aqueous alkalies (saponification).

$$\underset{\text{Ester}}{RCOOR'} + \underset{\text{(aq.)}}{HONa} \longrightarrow \underset{\text{Sod. salt of an acid}}{RCOONa} + \underset{\text{Alcohol}}{R'OH}$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + \underset{\text{Ethanol}}{C_2H_5OH}$$

Alcohols being more volatile than acids can be easily separated by distillation. The hydrolysis of esters takes place by the cleavage of acyl oxygen bond ($R—\overset{O}{\overset{\|}{C}}\vdots OR$) and not by alkyl oxygen bond ($R—\overset{O}{\overset{\|}{C}}—O\vdots R$).



$$\underset{\text{Ethyl acetate}}{CH_3\overset{O}{\overset{\|}{C}}\vdots O—C_2H_5} + HOH \longrightarrow \underset{\text{Acetic acid}}{CH_3—\overset{O}{\overset{\|}{C}}—OH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

This method provides industrial preparation of those alcohols which naturally occur as esters.

Note: Tertiary halides do not give a satisfactory yield of alcohols on hydrolysis. These are first converted into esters and then by doing hydrolysis, tertiary alcohols are obtained in good yields.

$$\underset{\substack{\text{Tertiary}\\\text{halide}}}{R_3CX} + \underset{\text{Silver acetate}}{CH_3COOAg} \longrightarrow \underset{\text{Ester}}{CH_3COOCR_3} + AgX$$

$$CH_3COOCR_3 + H_2O \longrightarrow CH_3COOH + \underset{\text{Tertiary alcohol}}{R_3COH}$$

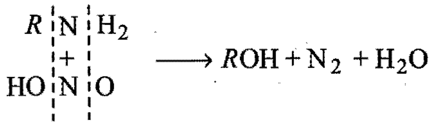
4. Hydrolysis of ethers : Ethers when heated with dilute sulphuric acid under pressure are hydrolysed to the corresponding alcohols.

$$ROR' + HOH \xrightarrow[\Delta]{H_2SO_4\text{(dil.)}} ROH + R'OH$$

$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + HOH \xrightarrow[\Delta]{H_2SO_4\text{(dil.)}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH}$$

$$\underset{\text{Ethyl methyl ether}}{CH_3OC_2H_5} + HOH \xrightarrow[\Delta]{H_2SO_4\text{(dil.)}} \underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

5. Action of nitrous acid on primary amines : Primary alcohols are formed when primary amines are treated with nitrous acid ($NaNO_2$ + HCl dil.).



$$\begin{array}{c} R \vdots N \vdots H_2 \\ \vdots + \vdots \\ HO \vdots N \vdots O \end{array} \longrightarrow ROH + N_2 + H_2O$$

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + HNO_2 \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + N_2 + H_2O$$

$$\underset{1^\circ\text{ Amine}}{RCH_2NH_2} + \underset{\text{Nitrous acid}}{HONO} \longrightarrow \underset{1^\circ\text{ Alcohol}}{R—CH_2OH} + N_2 + H_2O$$

Note: (a) Under similar conditions, methylamine does not yield methyl alcohol only, but the other product formed is methyl nitrite or dimethyl ether in excess of nitrous acid.

$$CH_3NH_2 + 2HNO_2 \longrightarrow \underset{\text{Methyl nitrite}}{CH_3—O—N{=}O} + 2H_2O + N_2$$

or

$$2CH_3NH_2 + 2HNO_2 \longrightarrow CH_3—O—CH_3 + 3H_2O + 2N_2$$

(b) Secondary and tertiary alcohols cannot be obtained by this method.

(c) This method is especially used for the preparation of lower alcohols from the corresponding fatty acids.

$$\underset{\text{Fatty acid}}{RCOOH} \xrightarrow{NH_3} \underset{\substack{\text{Ammonium}\\\text{salt}}}{RCOONH_4} \xrightarrow{\text{Heat}} \underset{\text{Amide}}{RCONH_2} \xrightarrow[KOH]{Br_2} \underset{\substack{\text{Primary}\\\text{amine}}}{RNH_2} \xrightarrow{HNO_2} \underset{\text{Alcohol}}{ROH}$$

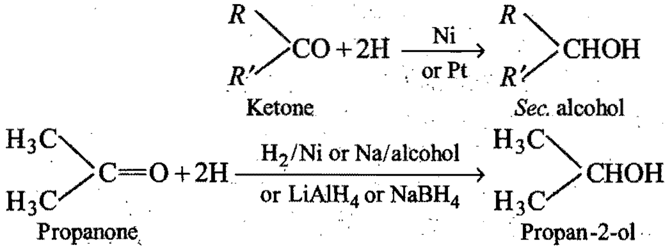
The alcohol obtained consists of one carbon atom less than the fatty acid.

6. Reduction of carbonyl compounds including carboxylic acids and esters : Aldehydes, ketones, acids and acid derivatives on reduction yield alcohols. A number of reducing agents like Zn/HCl, Na/C_2H_5OH, $LiAlH_4$ or $NaBH_4$ can be used for this purpose. Aldehydes and ketones are also reduced to corresponding alcohols by **catalytic hydrogenation** (addition of H_2) with finely divided platinum, palladium, nickel or ruthenium, etc.

(i) Bouveault-Blanc reduction : The reducing agent used is sodium and ethanol. The aldehyde, ketones and esters etc., are reduced by nascent hydrogen into corresponding alcohols.

$$\underset{\text{Aldehyde}}{RCHO} + 2H \xrightarrow[\text{or Pd Catalyst}]{\text{Ni or Pt}} \underset{Pri.\text{ alcohol}}{RCH_2OH}$$

$$\underset{\text{Ethanal}}{CH_3CHO} + 2H \xrightarrow[\text{or } LiAlH_4 \text{ or } NaBH_4]{H_2/\text{Ni or Na/alcohol}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$



$$\underset{\text{Acid}}{RCOOH} + 4H \xrightarrow[\text{or } B_2H_6/\text{ether}]{LiAlH_4} RCH_2OH + H_2O$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + 4H \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} + H_2O$$

$$\underset{\text{Ester}}{RCOOR'} + 4H \xrightarrow[\text{or } LiAlH_4]{Na/C_2H_5OH} RCH_2OH + R'OH$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + 4H \xrightarrow[\text{or } LiAlH_4]{Na/C_2H_5OH} \underset{\text{Ethanol}}{2CH_3CH_2OH}$$

$$\underset{\text{Acid chloride}}{RCOCl} + 4H \longrightarrow RCH_2OH + HCl$$

$$\underset{\text{Ethanoic anhydride}}{(CH_3CO)_2O} + 4H \xrightarrow[\text{ether}]{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} + CH_3COOH$$

(ii) Reduction with lithium aluminium hydride, LAH ($LiAlH_4$) : It is a better reducing agent for the conversion of carbonyl compounds, carboxylic acids and their derivatives into alcohols. $LiAlH_4$ is soluble in ether, THF or dichloromethane, the common solvent and it does not reduce the olefinic linkage if present in the carbonyl compound. The yields of alcohols are very good.

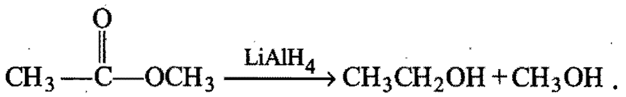
Tertiary alcohols cannot be obtained by reduction of carbonyl compounds.

$NaBH_4$ also does not reduce olefinic linkage.

$$\underset{\text{Unsaturated aldehyde}}{CH_3CH{=}CHCHO} + 4H \xrightarrow[\text{or } LiAlH_4]{NaBH_4} \underset{\text{Unsaturated alcohol}}{CH_3CH{=}CHCH_2OH}$$

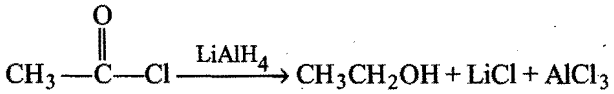
$$R{-}\overset{\overset{\large O}{\|}}{C}{-}OH + 4H \xrightarrow{LiAlH_4} RCH_2OH + H_2O$$

$$CH_3CH{=}CHCOOH + 4H \xrightarrow{LiAlH_4} CH_3CH{=}CHCH_2OH + H_2O$$



$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}OCH_3 \xrightarrow{LiAlH_4} CH_3CH_2OH + CH_3OH\,.$$

$$(CH_3CO)_2O \xrightarrow{LiAlH_4} 2CH_3CH_2OH$$



$$CH_3-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{LiAlH_4} CH_3CH_2OH + LiCl + AlCl_3$$

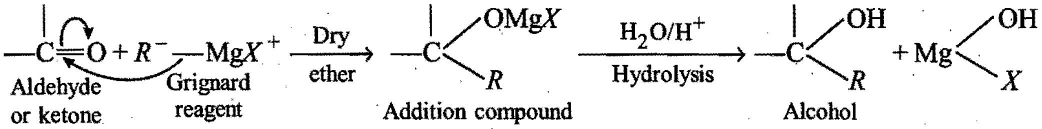
Catalytic hydrogenation reduces carbon-carbon double bond as well as carbonyl group.

$$\underset{\text{Acrolein}}{H_2C{=}CHCHO} + 4H \xrightarrow[\text{Catalyst}]{Ni} \underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH}$$

Reducing agents for carbonyl compounds at a glance :

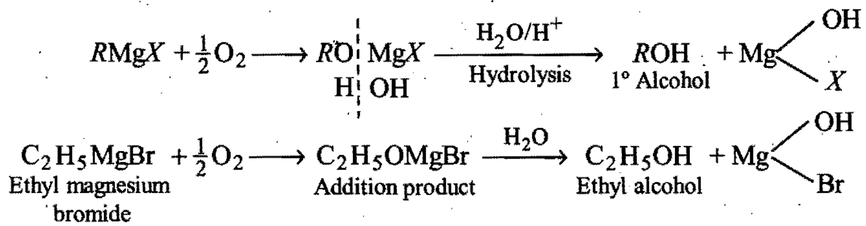
Functional group	Reduction product	Possible reducing agents
—CHO	—CH_2OH	$LiAlH_4$, $NaBH_4$, B_2H_6/THF; Ni/H_2
>C=O	>CH—OH	—do—
—COOH	—CH_2OH	$LiAlH_4$, B_2H_6/THF
—COCl	—CH_2OH	$LiAlH_4$, $NaBH_4$, B_2H_6/THF
$(RCO)_2O$	R—CH_2OH	$LiAlH_4$, B_2H_6/THF, H_2/Ni
>C=C<	—CH_2—CH_2—	H_2/Ni, B_2H_6/THF
—COOR	—CH_2OH	$LiAlH_4$, B_2H_6/THF, H_2/Ni
—CH_2OH	—CH_3	Red P/I_2

7. Addition of Grignard reagents to aldehydes and ketones : All the three types of monohydric alcohols can be prepared by the use of Grignard reagents. Grignard reagents form addition compounds by nucleophile attack with aldehydes and ketones which on hydrolysis with dilute acid yields an alcohol.



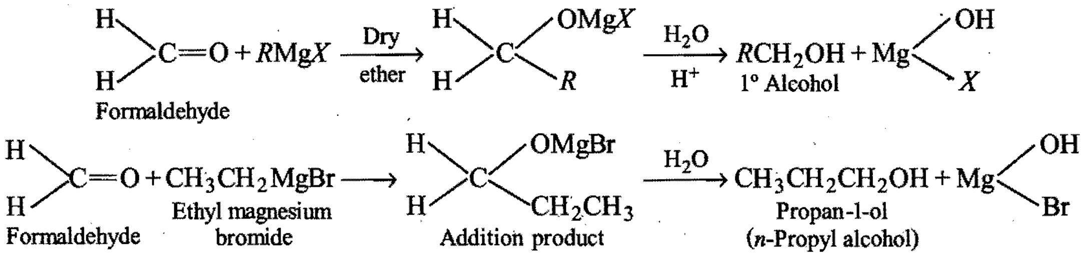
(i) Primary alcohols : Primary alcohols are obtained when Grignard reagent is reacted with oxygen or formaldehyde or ethylene oxide.

(a)



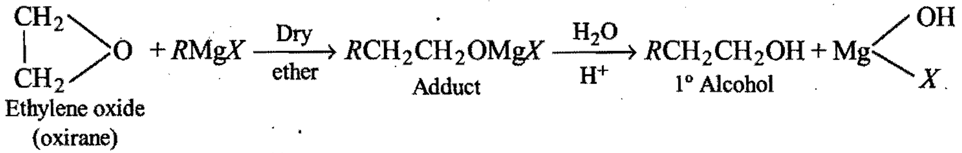
The alcohol has same number of carbon atoms as present in the alkyl group of the Grignard reagent.

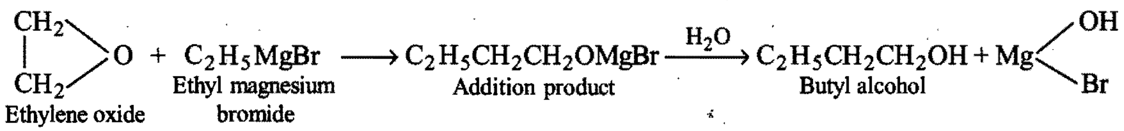
(b)



The alcohol has one carbon atom more than the alkyl group of the Grignard reagent.

(c)

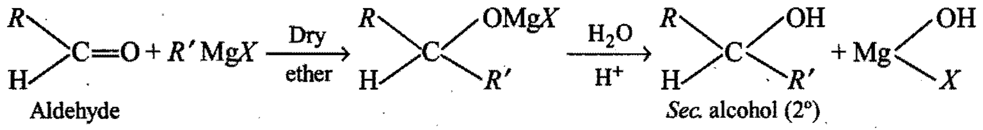


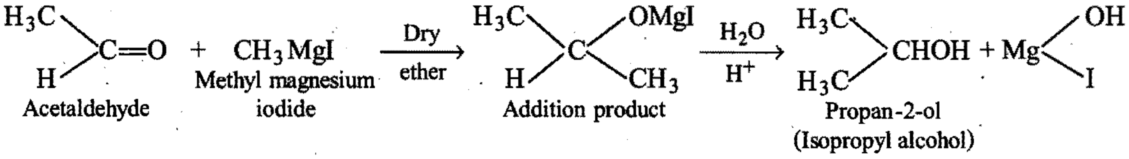


The alcohol has two carbon atoms more than the alkyl group of the Grignard reagent.

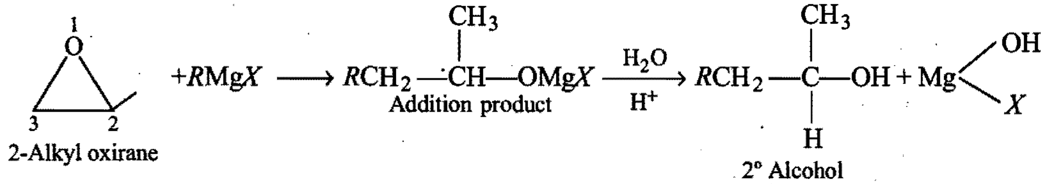
(ii) Secondary alcohols : Secondary alcohols are obtained when Grignard reagent is reacted with an aldehyde other than formaldehyde.

(a)





(b)

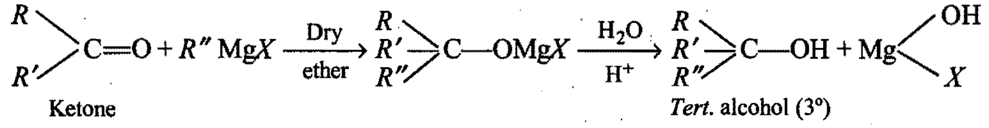


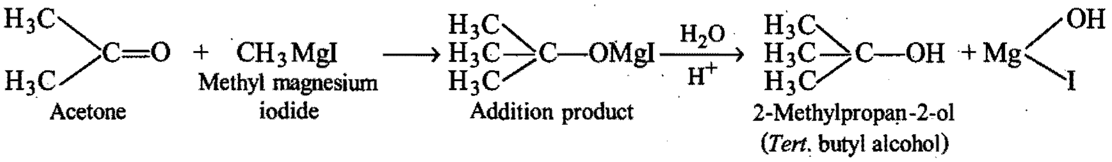
(The ring is opened from least hindered site to form addition product).

The alcohol has three carbon atoms more than the alkyl group of the Grignard reagent.

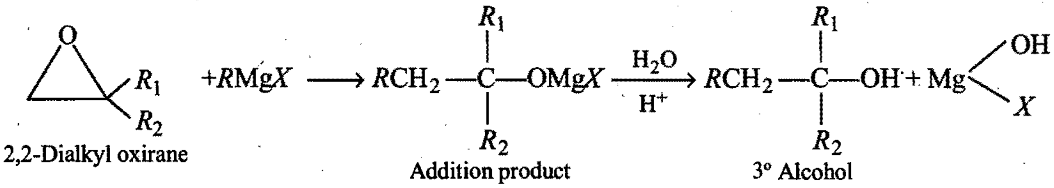
(iii) Tertiary alcohols : Tertiary alcohols are obtained when Grignard reagent is reacted with ketones.

(a)

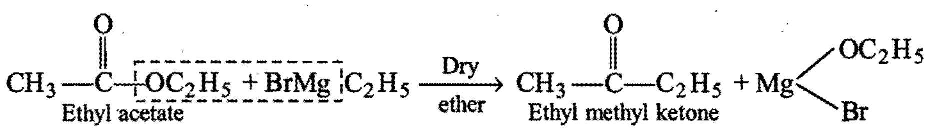




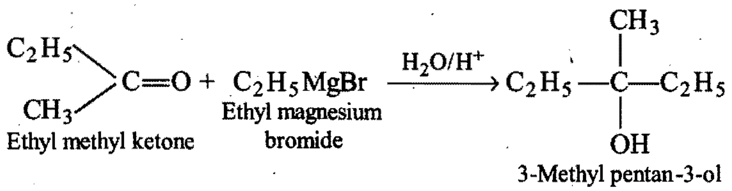
(b)



(c) Esters (*R*COO*R*′) on treatment with Grignard reagent first forms ketone which then reacts with second molecule of Grignard reagent and forms tertiary alcohol.

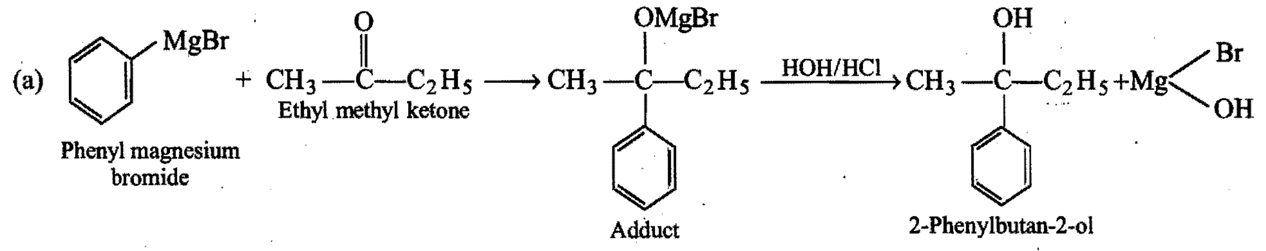


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + BrMgC_2H_5 \xrightarrow[\text{ether}]{\text{Dry}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5 + Mg(OC_2H_5)Br$$

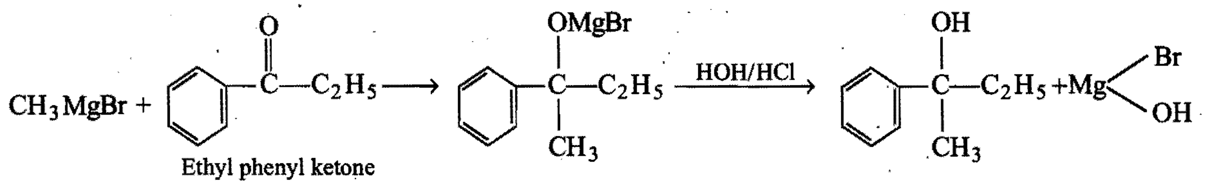


Alternative reactants can be selected for the same product using Grignard reagent:

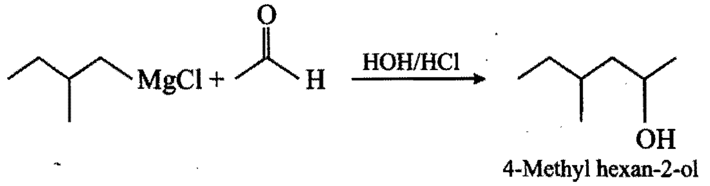
(a)



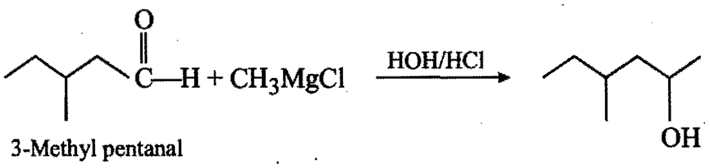
or



(b)

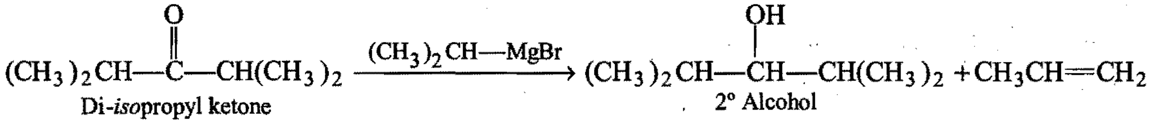


or



Exceptional behaviour of Grignard reagent

Methyl magnesium bromide does not react with di-*tert.* butyl ketone due to steric hindrance. Similarly isopropyl magnesium bromide does not add to di-*tert.* butyl ketone. However, isopropyl magnesium bromide reduces di-isopropyl ketone to secondary alcohol.



$$\underset{\text{Di-}\textit{iso}\text{propyl ketone}}{(CH_3)_2CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH(CH_3)_2} \xrightarrow{(CH_3)_2CH-MgBr} \underset{2^\circ\ \text{Alcohol}}{(CH_3)_2CH-\overset{\overset{\displaystyle OH}{|}}{CH}-CH(CH_3)_2} + CH_3CH{=}CH_2$$

However, isopropyl lithium adds to di-isopropyl ketone despite there is steric hindrance. This is attributed due to high electronegative character of $\bar{R}$ in RLi.

$$\text{ipr—CO—ipr} + \text{ipr}^{-}\text{Li}^{+} \longrightarrow (\text{ipr})_3\text{COLi} \xrightarrow{H_2O} (\text{ipr})_3\text{C—OH}$$

8. Fermentation of carbohydrates : Alcohols can be prepared by the fermentation of carbohydrates under the influence of suitable enzymes. The source of enzymes are yeast and malt extract (germinated barley). The various reactions taking place are:

$$\underset{\substack{\text{Molasses}\\ \text{(Sucrose)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{(in yeast)}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow[\text{(in malt extract)}]{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\substack{\text{Maltose}\\ \text{(Malt sugar)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{(in yeast)}]{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

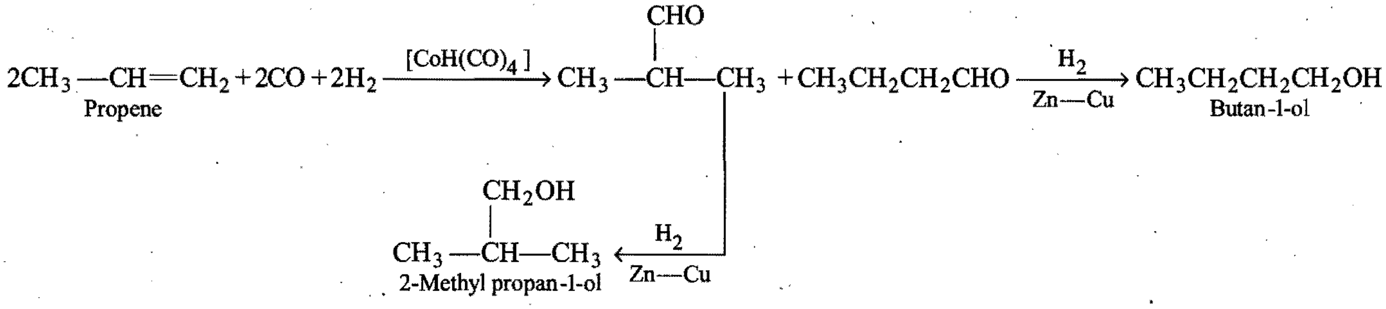
$$\underset{\substack{\text{Glucose}\\ \text{or Fructose}}}{C_6H_{12}O_6} \xrightarrow[\text{(in yeast) }30^\circ\text{C}]{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

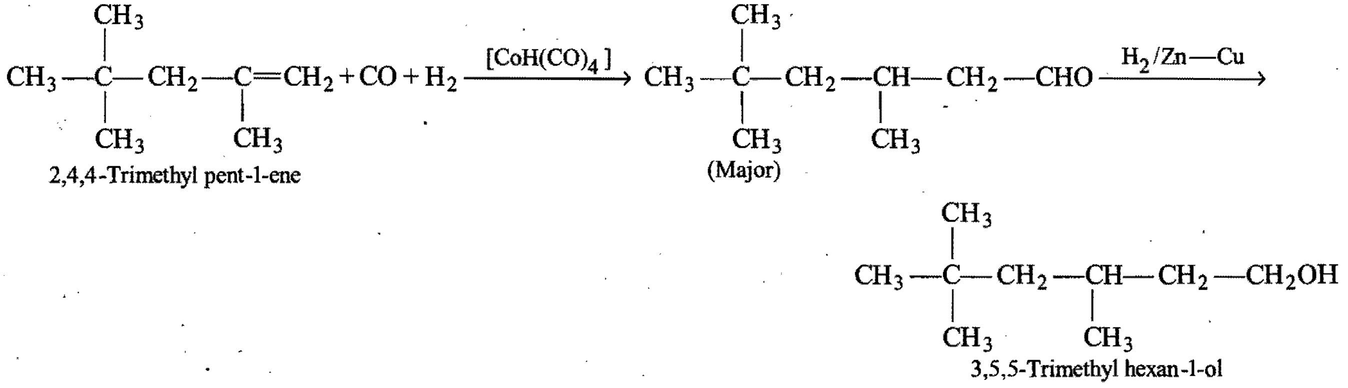
The fermentation of sugar is completed in about three days and the optimum temperature is 27°C. The carbon dioxide is recovered and sold as a byproduct.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \xrightarrow[30\text{–}35^\circ C]{B.\ maceranus} \underset{\text{Acetone (30\%)}}{CH_3COCH_3} + \underset{n\text{-Butyl alcohol (60\%)}}{CH_3CH_2CH_2CH_2OH}$$

9. Oxo-process (Industrial method) : This reaction is also called as **carbonylation** or **hydroformylation.** In this reaction, alkene is converted to alcohol with one carbon atom more. Catalyst used in this process is cobalt carbonyl or cobalt carbonyl hydride $[CoH(CO)_4]$. In this process first of all aldehyde is formed, which is reduced to obtain alcohol, *e.g.*,

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + CO + H_2 \xrightarrow[\text{High temp. and pressure}]{[CoH(CO)_4]} \underset{\text{Propanal}}{CH_3CH_2CHO}$$





9.6 GENERAL CHARACTERISTICS OF ALCOHOLS

Physical properties : (i) The lower members upto C_{11} are colourless mobile liquids. Higher members are wax like solids.

(ii) The lower members have a characteristic smell (alcoholic) and a burning taste while solid members are almost colourless and tasteless.

(iii) Alcohols are toxic substances. Methyl alcohol is highly toxic in nature while ethyl alcohol is less toxic.

(iv) Alcohols are neutral substances. They are lighter than water.

(v) The first three members are highly miscible with water. However, the solubility in water decreases with rise of molecular mass. The solubility in water is due to hydrogen bonding as —OH groups present both in alcohol and water are highly polarised.

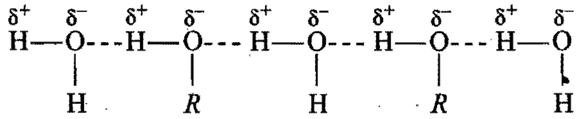


Fig. 9.1 Hydrogen bonding between water and alcohol

The solubility of higher members in water is less. This can be explained in the following manner. The alcohols possess both *hydrophilic* (water loving or water like, —OH group) and *hydrophobic* (water hating, alkane like due to carbon chains) moieties. Thus, with increase in molecular mass the hydrophobic part of the alcohols increases. This reduces their water solubility. Another interesting feature in this connection is that among the isomeric alcohols, the solubility increases with increase in branching. This can be attributed to decrease in relative volume of hydrophobic portion.

(vi) Boiling points of alcohols increase gradually with increase of carbon chain. The difference between boiling points of two consecutive members is about 18–20°C.

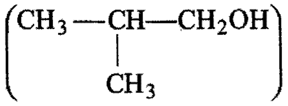
Name	Formula	Boiling point (0°C)
Methanol	CH_3OH	64.5
Ethanol	C_2H_5OH	78.3
Propan-1-ol	C_3H_7OH	97.0
Butan-1-ol	C_4H_9OH	118.0
Pentan-1-ol	$C_5H_{11}OH$	138.0

Among isomeric alcohols, the boiling points are in the following order:

Primary > Secondary > Tertiary

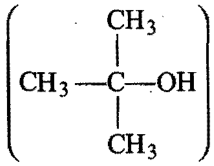
Butan-1-ol > 2-Methyl propan-1-ol

$(CH_3CH_2CH_2CH_2OH)$
b.pt. 118°C


$$\begin{pmatrix} CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2OH \end{pmatrix}$$
b.pt. 108°C

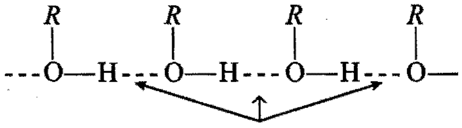
> Butan-2-ol > 2-Methyl propan-2-ol

$[CH_3CH_2CH(OH){\cdot}CH_3]$
b.pt. 99°C


$$\begin{pmatrix} CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-OH \end{pmatrix}$$
b.pt. 83°C

The boiling point decreases with branching.

The boiling points of alcohols are much higher as compared to the corresponding alkanes, ethers and alkyl halides. The reason for the higher boiling points than expected is due to intermolecular association of a large number of molecules due to hydrogen bonding as —OH group is highly polarised.



Hydrogen bonding

No hydrogen bonding is present in alkanes, ethers and alkyl halides.

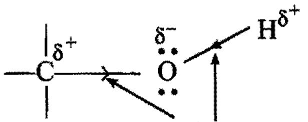
(vii) Lower alcohols form solid derivatives with certain metallic salts.

$CuSO_4{\cdot}2CH_3OH$ $CaCl_2{\cdot}4CH_3OH$ $MgCl_2{\cdot}6CH_3OH$

$CuSO_4{\cdot}2C_2H_5OH$ $CaCl_2{\cdot}4C_2H_5OH$ $MgCl_2{\cdot}6C_2H_5OH$

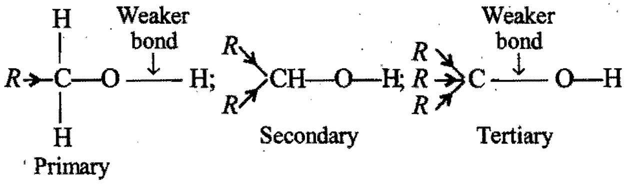
For this reason, alcohols cannot be dried over anhydrous calcium chloride.

Chemical properties : The hydroxyl group present in alcohols is a very reactive group and the characteristic reactions of alcohols are the reactions of the —OH group. The reactions of the hydroxyl group consists of either cleavage (breaking) of C—O bond or the cleavage of O—H bond as both are highly polarised with negative end of both the dipoles at oxygen. Moreover oxygen has two unshared lone pairs of electrons and has partial negative charge so alcohols (or phenols) possess a net dipole moment. Methanol has a dipole moment of 1.71 D. Due to this dipolar nature, alcohols (or phenols) form intermolecular hydrogen bonding.



Polar bonds

C—O bond is weaker in the case of tertiary alcohols due to $+I$ effect of alkyl groups while O—H bond is weaker in primary alcohols as electron density increases between O—H bond and hydrogen tends to separate as a proton.



Thus, primary alcohols are most reactive when there is cleavage of O—H bond while tertiary alcohols are most reactive when there is cleavage of C—O bond.

Hence, in **O—H cleavage, the order of reactivity is,**

Primary > Secondary > Tertiary,

and in **C—O cleavage, the order of reactivity is,**

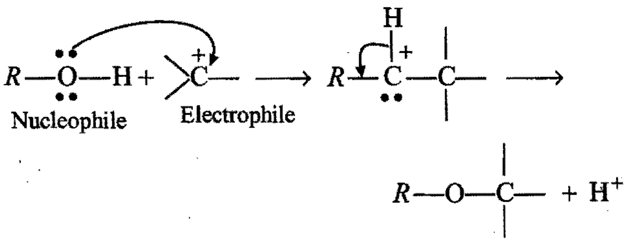
Tertiary > Secondary > Primary.

During O—H cleavage, proton is given out showing that alcohols are acidic in nature. However, alcohols are weaker acids than water. This is because the alkyl groups in alcohols have a $+I$ effect. The negative charge on oxygen makes the release of proton bit difficult. Tertiary alcohols are least acidic due to maximum $+I$ effect of three alkyl groups. Acidic nature increases from tertiary to secondary and from secondary to primary as $+I$ effect decreases. Thus, the following order is followed in the **acidic nature of alcohols.**

CH_3OH > Primary alcohol > *Sec.* alcohol > *Tert.* alcohol

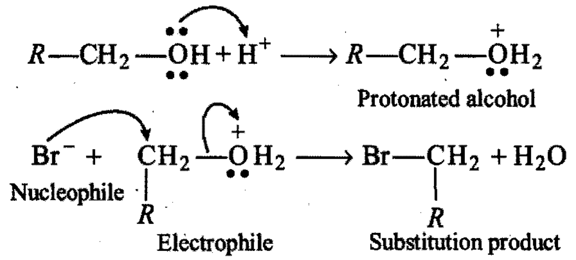
In general, the reactions of alcohols may be divided into the following three categories:

(a) Reactions involving the cleavage of oxygen-hydrogen bond $[C{-}O\,\vdots\,H]$ with substitution or removal of hydrogen as proton (*i.e.*, **alcohols act as nucleophiles).**



(b) Reactions involving the cleavage of carbon-oxygen bond $[C\,\vdots\,OH]$ with substitution or removal of —OH group (*i.e.*, **alcohols act as electrophiles).**

The protonated alcohols react as follows:



Thus, alcohols act both as nucleophiles as well as electrophiles (while phenols usually act as nucleophiles only).

(c) Reactions involving both the cleavage of alkyl and the hydroxyl groups of the alcohol molecules.

Reactions Involving the Cleavage of O—H Bond

The general order of reactivity in this type of reactions is:

$$CH_3 > \text{Primary} > \text{Secondary} > \text{Tertiary}$$

1. Reaction with active metals (Acidic nature) : Alcohols react with active metals like sodium, potassium, calcium, magnesium, aluminium, etc., to liberate hydrogen. The metallic compounds formed are called alkoxides (or alcoholates).

$$\underset{\text{Alcohol}}{2ROH} + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2RONa} + H_2$$

$$\underset{\text{Ethanol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5ONa} + H_2$$

$$2C_2H_5OH + Ca \longrightarrow \underset{\text{Calcium ethoxide}}{(C_2H_5O)_2Ca} + H_2$$

$$\underset{2^\circ\text{ Alcohol}}{3(CH_3)_2CHOH} + Al \xrightarrow{CCl_4} \underset{\text{Aluminium isopropoxide}}{[(CH_3)_2CHO]_3Al} + \tfrac{3}{2}H_2$$

$$\underset{3^\circ\text{ Alcohol}}{3(CH_3)_3C{-}OH} + Al \xrightarrow{CCl_4} \underset{\text{Al. \textit{tert.} butoxide}}{[(CH_3)_3CO]_3Al} + \tfrac{3}{2}H_2$$

Note : Al. isopropoxide is a specific reducing agent for aldehydes and ketones (without affecting $>C{=}C<$, $-C{\equiv}C-$, $-NO_2$ and ether etc).
Al. *tert.* butoxide is used as a catalyst in oppenauer oxidation. It oxidises 1° and 2° alcohols into aldehydes and ketones.

Metal hydride (M^+H^-) or metal amides ($M^+NH_2^-$) are strong bases and on reaction with alcohol also forms alkoxides.

$$R{-}OH + \underset{\text{Sodium hydride}}{Na^+H^-} \longrightarrow \underset{\text{Sodium alkoxide}}{R{-}ONa} + H_2$$

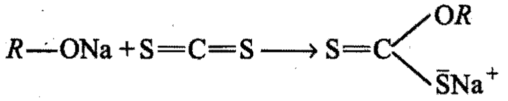
$$CH_3CH_2OH + \underset{\text{Sodamide}}{\overset{+}{Na}\overset{-}{N}H_2} \longrightarrow \underset{\text{Sod. ethoxide}}{CH_3CH_2ONa} + NH_3$$

Alkoxides are extensively employed for the preparation of ethers on treatment with alkyl halide **(Williamson synthesis).**

$$R{-}ONa + \underset{\text{Alkyl halide}}{XR'} \longrightarrow \underset{\text{Ether}}{R{-}O{-}R'} + NaX$$

$$\underset{\text{Sodium ethoxide}}{C_2H_5\bar{O}Na^+} + \underset{\text{Bromo ethane}}{BrC_2H_5} \xrightarrow{\text{Heat}} \underset{\substack{\text{Ethoxyethane}\\ \text{(Diethyl ether)}}}{C_2H_5{-}O{-}C_2H_5} + NaBr$$

Also alkoxides react with CS_2 to form xanthates.



$$R{-}ONa + S{=}C{=}S \longrightarrow S{=}C\begin{matrix}OR\\ \bar{S}Na^+\end{matrix}$$

The alkoxides are electrovalent compounds and are written as RO^-M^+ (M = monovalent, sodium or potassium). These are readily hydrolysed by water.

Note : Alcohols are not acidic enough to react with aqueous NaOH or KOH.

The acidic nature of alcohols is also reflected in their reactivity towards Grignard reagent.

$$R{-}O{-}H + \overset{\delta^-}{R'}\overset{\delta^+}{Mg}X \longrightarrow R'{-}H + R\overset{\delta^-}{O}\overset{\delta^+}{Mg}X$$

$$ROH + \underset{\text{Sod. alkynide}}{\overset{+}{Na}{-}\overset{-}{C}{\equiv}CH} \longrightarrow R{-}ONa + \underset{\text{Ethyne}}{HC{\equiv}CH}$$

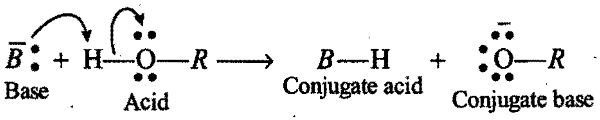
Alcohols are stronger acids than terminal acetylenes and acidic nature is in the order:

$$HOH > ROH > HC{\equiv}CH > NH_3 > RH$$

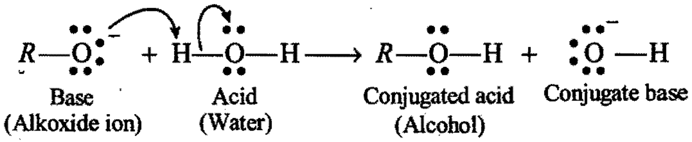
Acidic character of alcohols and water

Water is a better **proton donar** than alcohol, so alcohols are weaker acids than water. Alternatively alkoxide ion is a better proton acceptor than hydroxide ion. In other words, alkoxides are stronger bases than the hydroxide ion. Further electron releasing inductive effect (+*I*) of the alkyl group makes the alcohols weaker acids than water.

In fact, alcohols (and phenols) are **Bronsted acids,** *i.e.*, they can donate a proton to a strong base ($:B^-$).

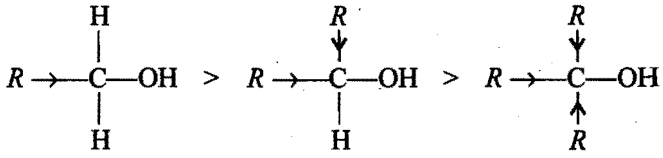


On treating an alkoxide ion with water, the starting alcohol is obtained.



Comparison of acidic character of primary, secondary and tertiary alcohols

The acidic character of alcohols is due to the polar nature of O—H bond. An electron releasing group (*R*) increases electron density on oxygen tending to decrease the polarity of O—H bond. This decreases the acid strength, and so, the acid strength of alcohols decreases in the following order:



1° Alcohol 2° Alcohol 3° Alcohol

The +*I* effect of alkyl group would be maximum in tertiary (3°) alcohol and minimum in primary (1°) alcohol. In other words, primary alcohols are the strongest acids and tertiary the weakest.

2. Reaction with mono carboxylic acids : Alcohols react with organic acids to form esters. The process is known as **esterification.** It is a reversible reaction and hence it is carried out in presence of a dehydrating agent like conc. H_2SO_4 or dry HCl gas which catalysis the forward reaction and also act as a protonating agent.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{HOR'} \xrightarrow[\text{Heat}]{H_2SO_4\text{(conc.)}} \underset{\text{Ester}}{RCOOR'} + H_2O$$

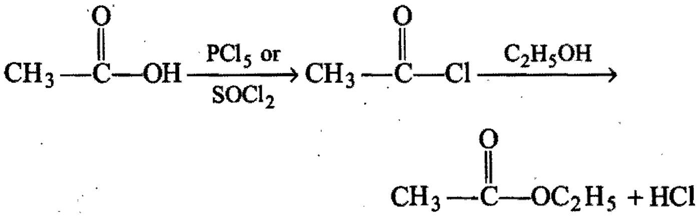
When HCl gas is used as a catalyst, the reaction is usually referred to as **Fischer-Speier esterification.**

Water is removed as soon as it is formed to drive the equilibrium in the forward direction.

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{HOC_2H_5} \xrightarrow[\text{Heat}]{H_2SO_4\text{(conc.)}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

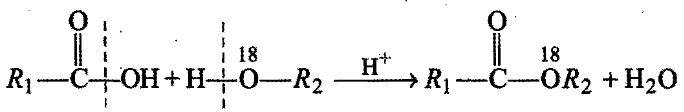
For alcohols ($CH_3OH > 1° > 2° > 3°$)
and the acids are in the order:
$HCOOH > CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCOOH$

Reversible esterification may be achieved by the following scheme of reaction.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[SOCl_2]{PCl_5 \text{ or}} CH_3-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{C_2H_5OH} CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + HCl$$

Mechanism of esterification was confirmed by isotopic labelling.



$$R_1-\overset{\overset{O}{\|}}{C}-OH + H-\overset{18}{O}-R_2 \xrightarrow{H^+} R_1-\overset{\overset{O}{\|}}{C}-\overset{18}{O}R_2 + H_2O$$

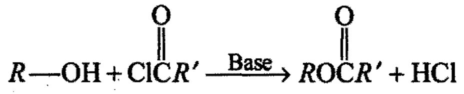
In esterification, it is the —OH group of acid and not that of alcohol that cleaves.

3. Reaction with inorganic acids : Alcohols react with inorganic acids (except halogen acids) to form inorganic esters.

$$C_2H_5OH + \underset{\text{Sulphuric acid}}{HOSO_2OH\text{(conc.)}} \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5OSO_2OH} + H_2O$$

$$C_2H_5OH + \underset{\text{Nitric acid}}{HO-NO_2\text{(conc.)}} \longrightarrow \underset{\text{Ethyl nitrate}}{C_2H_5O-NO_2} + H_2O$$

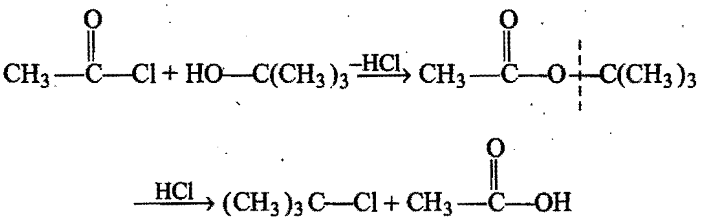
4. Acylation or reaction with acid chlorides and acid anhydrides : When alcohols react with acid chlorides or acid anhydrides in presence of a base catalyst, (such as pyridine or dimethylaniline) the hydrogen of the hydroxyl group is replaced by an acyl group (*R*CO—), resulting in the formation of esters. The process is known as **acylation.** When the hydrogen of —OH group is replaced by CH_3CO— (acetyl) group, the process is termed **acetylation.**



$$R-OH + Cl\overset{\overset{O}{\|}}{C}R' \xrightarrow{\text{Base}} RO\overset{\overset{O}{\|}}{C}R' + HCl$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Acetyl chloride}}{ClOCCH_3} \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl acetate}}{C_2H_5OOCCH_3} + HCl$$

With 3° alcohols, the reaction is usually accompanied by dehydration of alcohols to alkenes or by the formation of 3° alkyl chloride.



$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + HO-C(CH_3)_3 \xrightarrow{-HCl} CH_3-\overset{\overset{O}{\|}}{C}-O-C(CH_3)_3 \xrightarrow{HCl} (CH_3)_3C-Cl + CH_3-\overset{\overset{O}{\|}}{C}-OH$$

$$\underset{\text{Alcohol}}{ROH} + \underset{\text{Acetic anhydride}}{(R'CO)_2O} \xrightarrow{\text{Base}} \underset{\text{Ester}}{ROOCR'} + \underset{\text{Acid}}{R'COOH}$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \xrightarrow[\text{Reflux}]{\text{Pyridine}} \underset{\text{Ethyl acetate}}{C_2H_5OOCCH_3} + \underset{\text{Acetic acid}}{CH_3COOH}$$

The process of acetylation is used to protect the hydroxyl groups in various reactions. The acetyl derivatives of alcohols readily hydrolysed to regenerate the alcohols.

5. Alkylation : When alcohols react with dialkyl sulphates, the hydrogen of the hydroxyl group is replaced by an alkyl group resulting in the formation of ethers.

$$ROH + R'_2SO_4 \longrightarrow ROR' + R'HSO_4$$

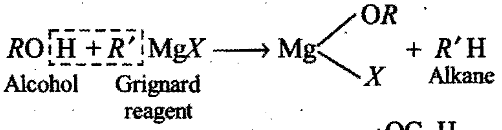
$$C_2H_5OH + \underset{\text{Dimethyl sulphate}}{(CH_3)_2SO_4} \longrightarrow \underset{\text{Ethyl methyl ether}}{C_2H_5OCH_3} + \underset{\text{Methyl hydrogen sulphate}}{CH_3HSO_4}$$

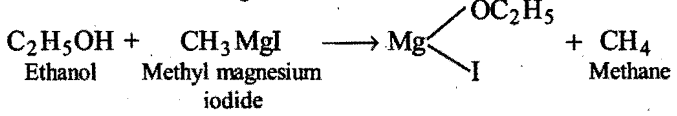
Note : Ethers can also be obtained when alkoxides are heated with alkyl halides.

$$\underset{\text{Sod. ethoxide}}{C_2H_5ONa} + \underset{\text{Ethyl bromide}}{BrC_2H_5} \xrightarrow{\Delta} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + NaBr$$

This reaction is termed Williamson's synthesis.

6. Reaction with Grignard reagents : Hydrogen (acidic) is provided by alcohols which combines with alkyl group of the Grignard reagent to form alkane.





Reactions Involving the Cleavage of C—OH Bond

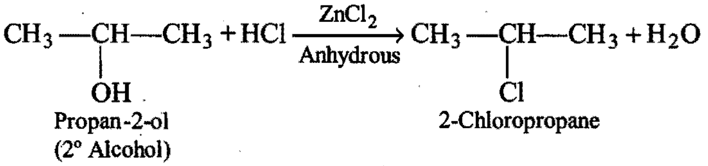
The order of reactivity in this type of reactions is:

Tertiary alcohol > Secondary alcohol > Primary alcohol.

7. Reaction with hydrogen halides : Halogen acids react with alcohols to form alkyl halides. The reactivity of halogen acids is in the order of HI > HBr > HCl > HF and the reactivity of *R*OH is in the order of allyl, benzyl > 3° > 2° > 1°. The reaction follows a nucleophilic substitution mechanism.

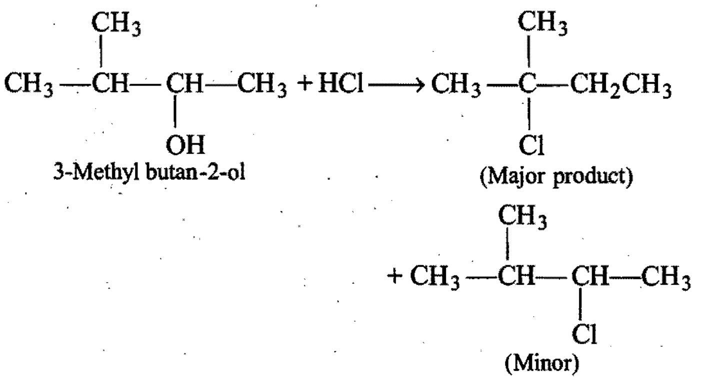
$$ROH + HX \xrightarrow[\text{Anhydrous}]{ZnCl_2} R-X + H_2O$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + HCl \xrightarrow[\text{Anhydrous, heat}]{ZnCl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O$$



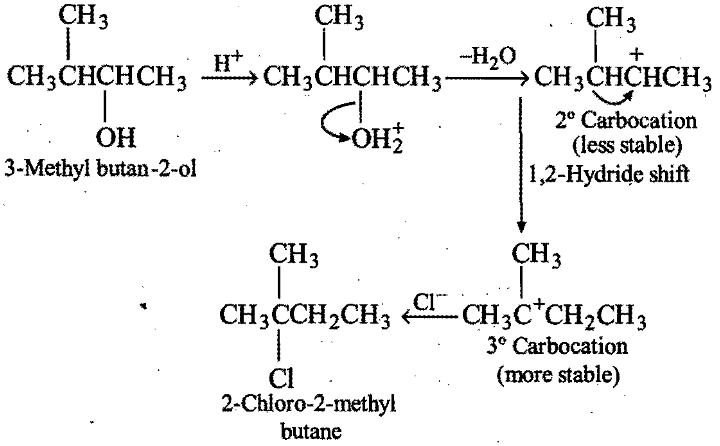
$$\underset{\substack{\text{Propan-2-ol}\\ \text{(2° Alcohol)}}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3} + HCl \xrightarrow[\text{Anhydrous}]{ZnCl_2} \underset{\text{2-Chloropropane}}{CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3} + H_2O$$

In case of higher alcohols, *i.e.*, the intermediate is 2° carbocation that can change to more stable 3° carbocation by 1,2-hydride shift.



$$\underset{\text{3-Methyl butan-2-ol}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3} + HCl \longrightarrow \underset{\text{(Major product)}}{CH_3-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_2CH_3} + \underset{\text{(Minor)}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-CH_3}$$

There can be 1,2 hydride shift to get more stable (3°) carbocation.



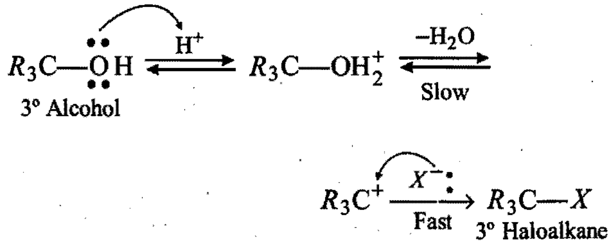
$$\underset{\text{3-Methyl butan-2-ol}}{CH_3\overset{CH_3}{\overset{|}{C}H}\underset{OH}{\underset{|}{C}H}CH_3} \xrightarrow{H^+} CH_3\overset{CH_3}{\overset{|}{C}H}\underset{OH_2^+}{\underset{|}{C}H}CH_3 \xrightarrow{-H_2O} \underset{\substack{\text{2° Carbocation}\\ \text{(less stable)}}}{CH_3\overset{CH_3}{\overset{|}{C}H}\overset{+}{C}HCH_3}$$

$$\xrightarrow{\text{1,2-Hydride shift}} \underset{\substack{\text{3° Carbocation}\\ \text{(more stable)}}}{CH_3\overset{CH_3}{\overset{|}{C^+}}CH_2CH_3} \xrightarrow{Cl^-} \underset{\text{2-Chloro-2-methyl butane}}{CH_3\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}CH_2CH_3}$$

The reaction of 1° and 2° alcohols with HCl gas in presence of anhydrous $ZnCl_2$ is called **Groove's method.**

In 3° (and 2°) alcohols, the S_N1 mechanism operates, however, with tertiary alcohols, no such catalyst is required.

$$\underset{\substack{\text{2-Methyl}\\ \text{propan-2-ol (3°)}}}{(CH_3)_3C-OH} + HCl \xrightarrow{\text{Room temp.}} \underset{\substack{\text{2-Chloro-2-}\\ \text{methyl propane}}}{(CH_3)_3C-Cl} + H_2O$$



$$\underset{\text{3° Alcohol}}{R_3C-\ddot{\underset{\cdot\cdot}{O}}H} \overset{H^+}{\rightleftharpoons} R_3C-OH_2^+ \underset{\text{Slow}}{\overset{-H_2O}{\rightleftharpoons}}$$

$$R_3C^+ \xrightarrow[\text{Fast}]{X^-} \underset{\text{3° Haloalkane}}{R_3C-X}$$

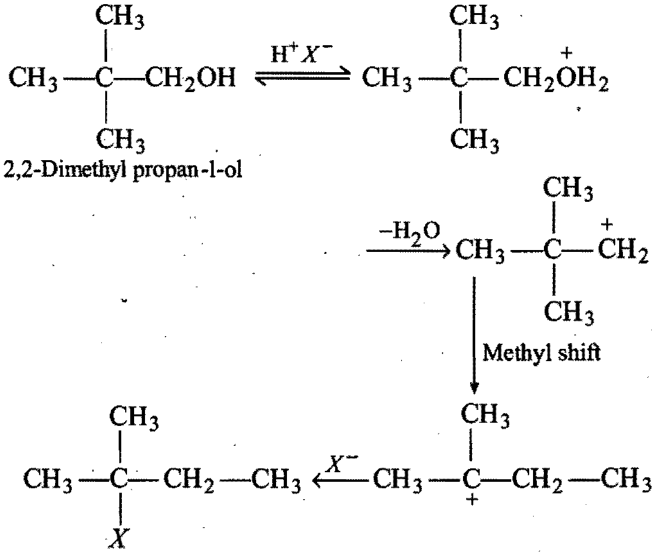
While in primary (1°) alcohols, the rearrangement does not take place as they follow S_N2 mechanism.

$$\underset{\substack{\text{(Protonated}\\ \text{1° alcohol)}}}{R-OH_2^+} + X^- \rightarrow \underset{\text{Transition state}}{[\overset{\delta^-}{X}---R---\overset{\delta^+}{OH_2}]} \rightarrow \underset{\text{1° Alkyl halide}}{R-X} + H_2O$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + HBr \xrightarrow[\text{Heat}]{H_2SO_4(\text{conc.})} \underset{\text{Ethyl bromide}}{C_2H_5Br} + H_2O$$

$$C_2H_5OH + HI \xrightarrow{\text{Heat}} \underset{\text{Ethyl iodide}}{C_2H_5I} + H_2O$$

In case of branched primary alcohol, S_N1 mechanism is involved, *e.g.*,



$$\underset{\text{2,2-Dimethyl propan-1-ol}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2OH} \overset{H^+X^-}{\rightleftharpoons} CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2\overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{+}{C}H_2$$

$$\xrightarrow{\text{Methyl shift}} CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-CH_2-CH_3 \xrightarrow{X^-} CH_3-\overset{CH_3}{\overset{|}{\underset{X}{\underset{|}{C}}}}-CH_2-CH_3$$

Note : If, however, alcohol is heated with conc. HI and red phosphorus it is converted into alkane.

$$C_2H_5OH + 2HI \xrightarrow[\text{Heat}]{\text{Red P}} C_2H_6 + I_2 + H_2O$$

8. Reaction with phosphorus halides : Alcohols react with phosphorus pentahalides (PX_5) and phosphorus trihalides (PX_3) to yield alkyl halides.

$$\underset{\text{Alcohol}}{3ROH} + \underset{\substack{\text{Phosphorus}\\ \text{trihalide}}}{PX_3} \longrightarrow \underset{\substack{\text{Alkyl}\\ \text{halide}}}{3RX} + \underset{\substack{\text{Phosphorus}\\ \text{acid}}}{H_3PO_3}$$

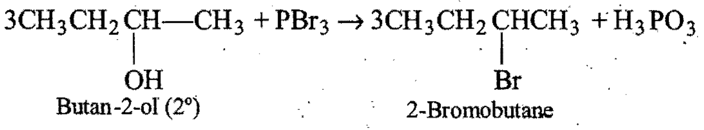
$$ROH + PX_5 \longrightarrow RX + POX_3 + HX$$

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

Generally, in place of PBr_3, red phosphorus and bromine can be used. Similarly in place of PI_3, red phosphorus and iodine can be used. Primary and secondary alcohols react with PX_3 below room temperature by S_N2 mechanism, hence no rearrangement product is formed. Tertiary alcohol gives S_N1 reaction.

$$\underset{\text{Ethanol}}{6C_2H_5OH} + \underbrace{2P + 3Br_2} \longrightarrow \underset{\text{Ethyl bromide}}{6C_2H_5Br} + 2H_3PO_3$$

$$\underset{1^\circ\text{ Alcohol}}{6C_2H_5OH} + \underbrace{2P + 3I_2} \longrightarrow \underset{\text{Ethyl iodide}}{6C_2H_5I} + 2H_3PO_3$$

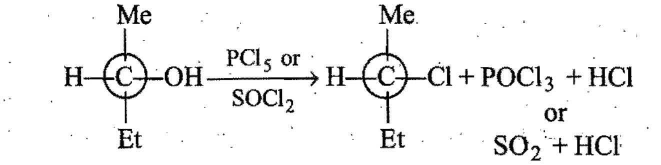


$$\underset{\text{Butan-2-ol (2°)}}{3CH_3CH_2\underset{\underset{OH}{|}}{C}H—CH_3} + PBr_3 \rightarrow \underset{\text{2-Bromobutane}}{3CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3} + H_3PO_3$$

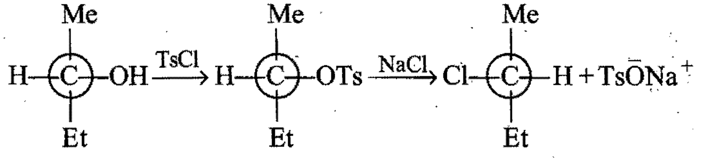
$$\underset{3^\circ\text{ Alcohol}}{3(CH_3)_3C—OH} + PI_3 \rightarrow \underset{\textit{Tert.}\text{ butyl iodide}}{3(CH_3)_3C—I} + H_3PO_3$$

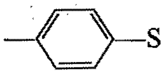
Phosphorus halides form intermediate inorganic esters. The resulting ester group is a very good leaving group that can be displaced by halide ions.

Stereochemistry of the reaction is essential to discuss here:



In this reaction, configuration around chiral carbon does not change.



Here, Ts stands for tosyl group, *i.e.*, CH_3 —  —SO_3^-

In this reaction, inversion of configuration around chiral carbon takes place.

9. Reaction with thionyl chloride : Alkyl chlorides of high purity are formed [because the other products of the reaction (*i.e.*, SO_2 and HCl) are gases] when an alcohol reacts with thionyl chloride in presence of pyridine.

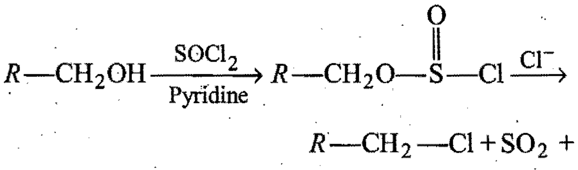
$$ROH + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} RCl + SO_2\uparrow + HCl\uparrow$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + SOCl_2 \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + SO_2 + HCl$$

$$\underset{2^\circ\text{Alcohol}}{R_2CHOH} + SOCl_2 \xrightarrow{\text{Pyridine}} R_2CHCl + SO_2 + HCl$$

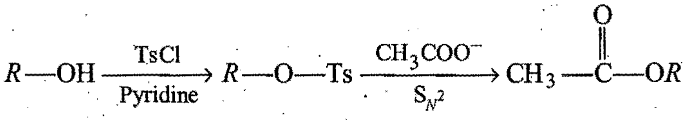
$$\underset{3^\circ\text{Alcohol}}{R_3C—OH} + SOCl_2 \xrightarrow{\text{Pyridine}} R_3C—Cl + SO_2 + HCl$$

Actually thionyl chloride first converts an —OH group into a chloro sulphite group in the presence as well as absence of pyridine as catalyst.



$$R—CH_2OH \xrightarrow[\text{Pyridine}]{SOCl_2} R—CH_2O—\overset{\overset{O}{\|}}{S}—Cl \xrightarrow{Cl^-} R—CH_2—Cl + SO_2 + Cl^-$$

The most important of these leaving groups are those based on sulphonate esters. Primary and secondary alcohols form stable crystalline sulphonate esters with *p*-toluene sulphonyl chloride (TsCl).



$$R—OH \xrightarrow[\text{Pyridine}]{TsCl} R—O—Ts \xrightarrow[S_N2]{CH_3COO^-} CH_3—\overset{\overset{O}{\|}}{C}—OR$$

This tosylate group can be replaced by any nucleophilic group (even weak nucleophile as acetate) and is an example of S_N2 reaction with inversion of configuration.

10. Reaction with ammonia : Alcohols react with alcoholic solution of ammonia when their vapours are passed over heated alumina or thoria catalyst at 360–500°C to form a mixture of primary, secondary and tertiary amines.

$$ROH + \underset{\text{(Alc.)}}{NH_3} \xrightarrow[360°C]{Al_2O_3} \underset{\substack{\text{Primary}\\ \text{amine}}}{RNH_2} \xrightarrow[Al_2O_3]{ROH} \underset{\substack{\text{Secondary}\\ \text{amine}}}{R_2NH} \xrightarrow[Al_2O_3]{ROH} \underset{\substack{\text{Tertiary}\\ \text{amine}}}{R_3N}$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + NH_3 \xrightarrow[360°C]{Al_2O_3} \underset{\text{Ethylamine (1°)}}{CH_3CH_2NH_2} + H_2O$$

$$\underset{1^\circ\text{ Amine}}{CH_3CH_2NH_2} + \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[360°C]{Al_2O_3} \underset{\text{Diethylamine (2°)}}{(CH_3CH_2)_2NH} + H_2O$$

$$\underset{2^\circ\text{ Amine}}{(CH_3CH_2)_2NH} + CH_3CH_2OH \xrightarrow[360°C]{Al_2O_3} \underset{\text{Triethylamine (3°)}}{(CH_3CH_2)_3N} + H_2O$$

Reactions involving both the cleavage of alkyl and hydroxyl groups:

Miscellaneous Reactions

11. Dehydration : The elimination of water from a compound is known as dehydration. The alcohols on dehydration yield alkenes (β-elimination of alcohol). The order of ease of dehydration is:

Tertiary alcohols > Secondary alcohols > Primary alcohols

The process of dehydration is done either by heating the alcohol with concentrated sulphuric or phosphoric acid at higher temperature *viz.*, upto 200°C or by passing the vapours of alcohol over alumina at 350–400°C. Other dehydrating agents used for alcohols may be $KHSO_4/\Delta$, BF_3/Δ, anhyd.

$ZnCl_2/\Delta$, P_2O_5/Δ, dry HCl, boric acid at 443K and *p*-toluene sulphonic acid, etc.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[350°C]{Al_2O_3} \underset{\text{Ethene}}{H_2C{=}CH_2} + H_2O$$

$$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} \xrightarrow[170°C]{H_2SO_4\text{ (conc.)}} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$

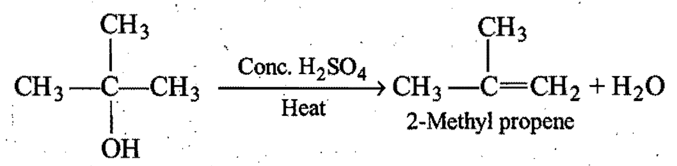
$$\underset{\text{Butan-2-ol}}{CH_3CH_2CH(OH)CH_3} \xrightarrow[250°C]{Al_2O_3} \underset{\text{But-2-ene (Major)}}{CH_3CH{=}CHCH_3}$$

In the case of secondary and tertiary alcohols, **Saytzeff's rule** is followed.

Primary alcohols are dehydrated by conc. H_2SO_4 at 170°C whereas dilute H_2SO_4 is used in the case of secondary and tertiary alcohols.

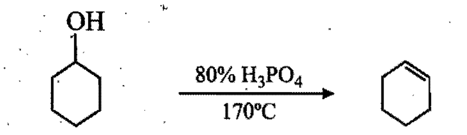
$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[170°C]{H_2SO_4\text{(conc.)}} \underset{\text{Ethene}}{H_2C{=}CH_2} + H_2O$$

$$\underset{\text{Butan-2-ol}}{CH_3CH_2CHOHCH_3} \xrightarrow[\text{Heat}]{H_2SO_4(1:1)} \underset{\text{But-2-ene}}{CH_3CH{=}CHCH_3} + H_2O$$



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\text{Heat}]{\text{Conc. }H_2SO_4} \underset{\text{2-Methyl propene}}{CH_3-\overset{CH_3}{C}{=}CH_2} + H_2O$$

2-Methyl propan-2-ol



Cyclohexanol Cyclohexene

Secondary and tertiary alcohols always give E_1 elimination reaction. Primary alcohols whose β-carbon atom is 3° or 4° also give E_1 reaction.

Primary alcohols whose β-carbon is 1° or 2° give E_2 reaction.

The reaction between ethyl alcohol and conc. sulphuric acid is interesting as different products are obtained at different temperatures. At 110°C ethyl alcohol combines with H_2SO_4 to form ethyl hydrogen sulphate.

$$C_2H_5OH + H_2SO_4 \xrightarrow{110°C} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

(i) When ethyl hydrogen sulphate is heated alone at 170°C, it forms diethyl sulphate.

$$2C_2H_5HSO_4 \xrightarrow{170°C} \underset{\text{Diethyl sulphate}}{(C_2H_5)_2SO_4} + H_2SO_4$$

(ii) When ethyl hydrogen sulphate is heated with excess of conc. H_2SO_4, ethene is formed.

$$C_2H_5HSO_4 \xrightarrow[\text{Conc. }H_2SO_4]{170°C} \underset{\text{Ethene}}{C_2H_4} + H_2SO_4$$

(iii) When ethyl hydrogen sulphate is heated with excess of alcohol at 140°C, ether is formed.

$$C_2H_5HSO_4 + HOC_2H_5 \xrightarrow{140°C} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2SO_4$$

Note: Methanol gives reactions with conc. H_2SO_4 similar to ethanol except the reaction (ii) but methene is not formed

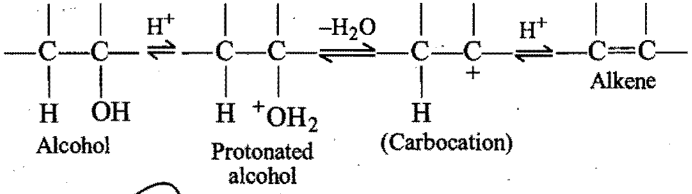
Mechanism : Dehydration involves:

(i) formation of the protonated alcohol, ROH_2^+,

(ii) its slow dissociation into a carbocation, and

(iii) fast expulsion of a hydrogen ion from the carbocation to form an alkene. (See **section 7.5**)

Acid is required to convert the alcohol into the protonated alcohol, which dissociate by loss of weakly basic water molecule much more easily than the alcohol itself.

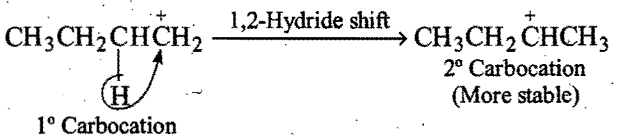


$$\underset{\text{Alcohol}}{-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-} \underset{}{\overset{H^+}{\rightleftharpoons}} \underset{\text{Protonated alcohol}}{-\underset{H}{\overset{|}{C}}-\underset{^+OH_2}{\overset{|}{C}}-} \overset{-H_2O}{\rightleftharpoons} \underset{\text{(Carbocation)}}{-\underset{H}{\overset{|}{C}}-\overset{|}{\underset{+}{C}}-} \overset{H^+}{\rightleftharpoons} \underset{\text{Alkene}}{-\overset{|}{C}{=}\overset{|}{C}-}$$

$$(CH_3CH_2\ddot{\underset{\cdot\cdot}{O}}H \xrightarrow{H^+} CH_3CH_2\overset{+}{\underset{\cdot\cdot}{O}}H_2 \xrightarrow[\text{(Slow)}]{-H_2O} CH_3\overset{+}{C}H_2 \xrightarrow[\text{(Fast)}]{-H} H_2C{=}CH_2)$$

Similarly, propanol gives propene, but butan-1-ol produces but-2-ene as the major product and but-1-ene as the minor product.

$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{H^+} \underset{\text{Protonated alcohol}}{CH_3CH_2CH_2CH_2\overset{+}{O}H_2} \xrightarrow{-H_2O}$$

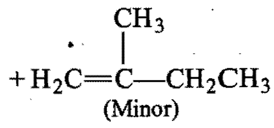


$$\underset{\text{1° Carbocation}}{CH_3CH_2\underset{H}{C}H\overset{+}{C}H_2} \xrightarrow{\text{1,2-Hydride shift}} \underset{\text{2° Carbocation (More stable)}}{CH_3CH_2\overset{+}{C}HCH_3}$$

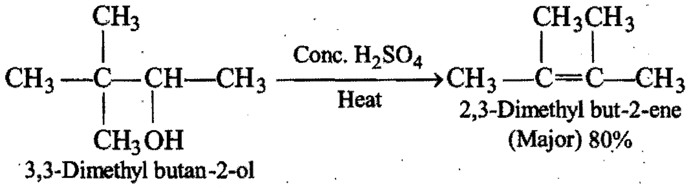
$$\xrightarrow{-H} \underset{\text{(Major)}}{\underset{\text{But-2-ene}}{CH_3CH{=}CHCH_3}} + \underset{\text{(Minor)}}{\underset{\text{But-1-ene}}{CH_3CH_2CH{=}CH_2}}$$

In all cases, intermediate is carbocation and there may be 1,2-hydride or 1,2-methyl shift to form more stable carbocation. *e.g.*,

$$\underset{\text{2,2-Dimethyl propan-1-ol}}{(CH_3)_3CCH_2OH} \xrightarrow[-H_2O]{H^+} \underset{\text{(Major)}}{\underset{\text{2-Methyl but-2-ene}}{(CH_3)_2C{=}CHCH_3}}$$



$$+ \underset{\text{(Minor)}}{H_2C{=}\overset{CH_3}{\overset{|}{C}}-CH_2CH_3}$$



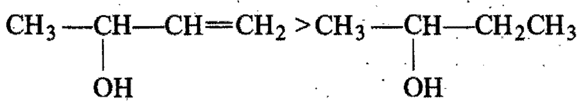
$$\mathrm{CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{Heat}]{\text{Conc. }H_2SO_4} CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3}$$

3,3-Dimethyl butan-2-ol

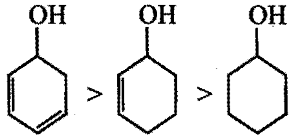
2,3-Dimethyl but-2-ene (Major) 80%

(This is due to 1,2-methyl shift. See problem 10 (c) on page 487).

Further greater the conjugation, greater the stability (due to resonance) and hence easier the dehydration. The dehydration is in the order:



$$\mathrm{CH_3-\underset{OH}{\underset{|}{CH}}-CH=CH_2 > CH_3-\underset{OH}{\underset{|}{CH}}-CH_2CH_3}$$



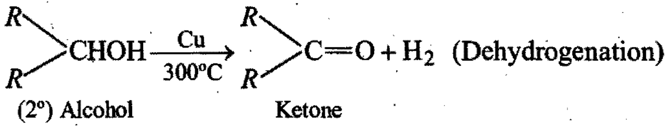
12. Dehydrogenation (Action of hot copper) : Primary, secondary and tertiary alcohols differ in their behaviour when the vapours are passed over hot reduced copper at 300°C.

(i) A primary alcohol loses hydrogen and forms an aldehyde.

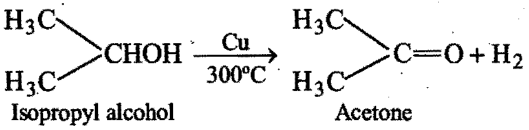
$$\underset{(1^\circ)\text{ Alcohol}}{R\mathrm{CH_2OH}} \xrightarrow[300^\circ\mathrm{C}]{\mathrm{Cu}} \underset{\text{Aldehyde}}{R\mathrm{CHO}} + \mathrm{H_2} \text{ (Dehydrogenation)}$$

$$\underset{\text{Ethyl alcohol}}{\mathrm{CH_3CH_2OH}} \xrightarrow[300^\circ\mathrm{C}]{\mathrm{Cu}} \underset{\text{Acetaldehyde}}{\mathrm{CH_3CHO}} + \mathrm{H_2}$$

(ii) A secondary alcohol loses hydrogen and forms a ketone.

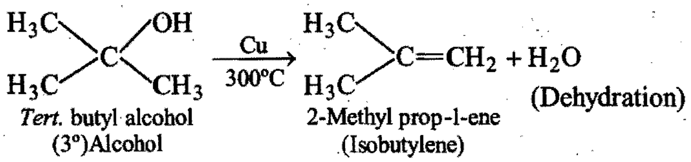


(2°) Alcohol Ketone (Dehydrogenation)



Isopropyl alcohol Acetone

(iii) A tertiary alcohol however, undergoes dehydration to form alkene.



Tert. butyl alcohol (3°)Alcohol

2-Methyl prop-1-ene (Isobutylene) (Dehydration)

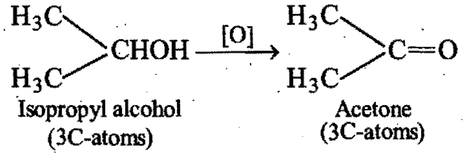
This property is utilized to distinguish between primary, secondary and tertiary alcohols.

13. Oxidation : The nature of the oxidation products depends on whether the alcohol is primary, secondary or tertiary. The oxidising agents usually employed are acidified potassium dichromate ($K_2Cr_2O_7/H_2SO_4$), acidified or alkaline potassium permanganate ($KMnO_4/H^+$ or OH^-) or dilute nitric acid.

(i) A primary alcohol is easily oxidised to an aldehyde and then to an acid both containing the same number of carbon atoms as the original alcohol, *i.e.*, —CH_2OH group is first converted into —CHO (aldehydic group) group, which in turn is converted into —COOH (carboxyl group) group.

$$\underset{\substack{\text{Ethyl alcohol}\\ \text{(2C-atoms)}}}{\mathrm{CH_3CH_2OH}} \xrightarrow{[\mathrm{O}]} \underset{\substack{\text{Acetaldehyde}\\ \text{(2C-atoms)}}}{\mathrm{CH_3CHO}} \xrightarrow{[\mathrm{O}]} \underset{\substack{\text{Acetic acid}\\ \text{(2C-atoms)}}}{\mathrm{CH_3COOH}}$$

(ii) A secondary alcohol when oxidised gives a ketone containing the same number of carbon atoms as the alcohol.



Isopropyl alcohol (3C-atoms)

Acetone (3C-atoms)

Other reagents for oxidation are:

Jones reagent (CrO_3, aqueous H_2SO_4 and acetone as solvent) oxidises alcohol without affecting carbon-carbon multiple bonds, allylic or benzylic C—H bonds and other acid sensitive groups. This reaction is carried out at 0°C.

$$\mathrm{HC{\equiv}C-CH=CH-CH_2OH} \xrightarrow[0^\circ\mathrm{C}]{\mathrm{CrO_3,\ acetone,\ aq.\ H_2SO_4}} \mathrm{HC{\equiv}C-CH=CH-CHO}$$

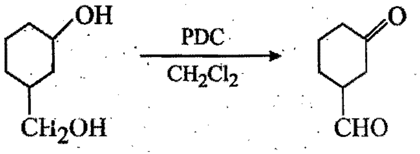
At higher temperature (above 25°C), aldehydes convert into carboxylic acids.

Aluminium tert. butoxide, $[(CH_3)_3CO]_3Al$ in acetone oxidises 1° and 2° alcohols (Particularly) into aldehydes and ketones **(Oppenauer oxidation). N-Bromosuccinimide** (NBS) also oxidises primary and secondary alcohols to aldehydes and ketones.

Pyridinium chlorochromate (PCC) in CH_2Cl_2 **(Sarret reagent)** oxidises primary alcohols to aldehydes, [PCC is an equimolar mixture of CrO_3, HCl and pyridine *i.e.*, $CrO_3 \cdot C_5H_5N{\cdot}HCl$ or $(C_5H_5NH)^+ClCrO_3^-$ or **Corey's reagent].**

Pyridinium dichromate (PDC) is $(C_5H_5NH^+)_2Cr_2O_7^{2-}$ and it oxidises primary alcohols to aldehyde and secondary alcohol to ketone (in excellent yield) without affecting carbon-carbon multiple bonds.

$$\mathrm{C_6H_5CH=CHCH_2OH} \xrightarrow{\mathrm{PDC/CH_2Cl_2}} \mathrm{C_6H_5CH=CHCHO}$$



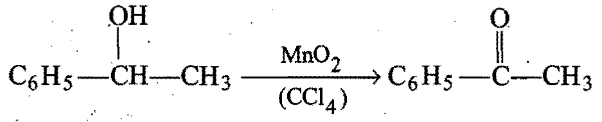
DMSO in $(COCl)_2$ and $(C_2H_5)_3N$ also oxidises primary alcohols to aldehyde without affecting carbon-carbon multiple bonds **(Swern reaction).**

Tosyl derivative of alcohols is also oxidised by DMSO.

$$R-CH_2OH \xrightarrow[\text{(ii) DMSO/NaHCO}_3]{\text{(i) TsCl}} R-CHO$$

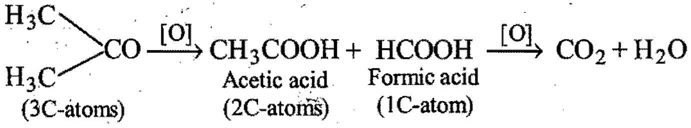
MnO_2 selectively oxidises the —OH group of allylic and benzylic 1° and 2° alcohols to aldehydes and ketones respectively and so is **Collins reagent** (one mole of CrO_3 and 2 moles of pyridine in CH_2Cl_2).

$$H_2C=CH-CH_2OH \xrightarrow[\text{(acetone)}]{MnO_2} H_2C=CH-CHO$$



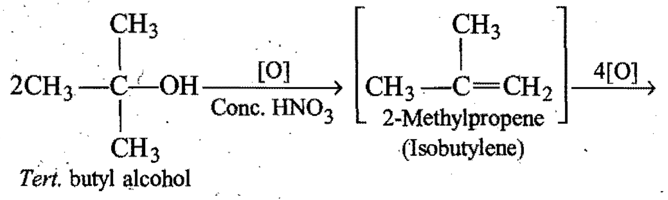
$$C_6H_5-\overset{\substack{OH\\|}}{C}H-CH_3 \xrightarrow[(CCl_4)]{MnO_2} C_6H_5-\overset{\substack{O\\\|}}{C}-CH_3$$

Ketones are difficult to be oxidised further, but on prolonged action of oxidising agents, these are oxidised to carboxylic acid or a mixture of acids each containing lesser number of carbon atoms than the ketone or original alcohol.



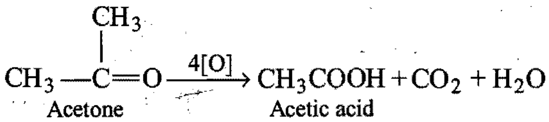
$$\underset{(3C\text{-atoms})}{\begin{matrix}H_3C\\H_3C\end{matrix}\!>CO} \xrightarrow{[O]} \underset{\substack{\text{Acetic acid}\\(2C\text{-atoms})}}{CH_3COOH} + \underset{\substack{\text{Formic acid}\\(1C\text{-atom})}}{HCOOH} \xrightarrow{[O]} CO_2+H_2O$$

(iii) A tertiary alcohol having no oxidisable hydrogen linked to carbon atom bearing hydroxyl group, is stable to oxidation under ordinary conditions. However, under drastic oxidation the carbon chain is ruptured and ketones and acids are formed both having fewer number of carbon atoms than the original alcohols.



$$2CH_3-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}-OH \xrightarrow[\text{Conc. }HNO_3]{[O]} \left[\underset{\substack{\text{2-Methylpropene}\\\text{(Isobutylene)}}}{CH_3-\overset{\substack{CH_3\\|}}{C}=CH_2}\right] \xrightarrow{4[O]}$$

Tert. butyl alcohol



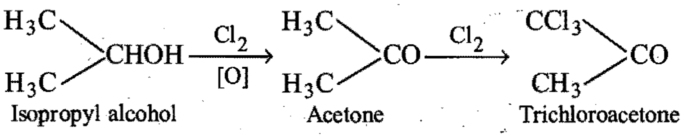
$$\underset{\text{Acetone}}{CH_3-\overset{\substack{CH_3\\|}}{C}=O} \xrightarrow{4[O]} \underset{\text{Acetic acid}}{CH_3COOH}+CO_2+H_2O$$

Some specific oxidising agents are:

	Reagent	Purpose
1.	Chromic acid, H_2CrO_4	1° alcohol to carboxylic acid.
2.	PCC, PDC and DMSO	1° alcohol to aldehyde and 2° alcohol to ketone without affecting double bond.
3.	CrO_3/H_2SO_4	2° alcohol to ketone.
4.	Jones reagent (chromic acid in aqueous acetone.)	1° alcohol to aldehyde and 2° alcohol to ketone, without affecting double bond.
5.	MnO_2	It selectively oxidised allylic and benzylic 1° and 2° alcohols to give aldehyde and ketones respectively.
6.	Ag_2CO_3 in benzene	1° alcohol to aldehyde and 2° alcohol to ketone.
7.	Ceric Ammonium nitrate (CAN)	1° alcohol to aldehyde and aromatic —CH_3 group into —CHO.
8.	Sodium hypochloride ($NaOCl/CH_3COOH$)	2° alcohol to ketone without affecting the 1° alcohol.

14. Reaction with halogens : Halogens, oxidise primary and secondary alcohols to aldehydes and ketones respectively. The oxidation product then undergoes halogenation.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[{[O]}]{Cl_2} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{Cl_2} \underset{\text{Chloral}}{CCl_3CHO}$$



$$\underset{\text{Isopropyl alcohol}}{\begin{matrix}H_3C\\H_3C\end{matrix}\!>CHOH} \xrightarrow[{[O]}]{Cl_2} \underset{\text{Acetone}}{\begin{matrix}H_3C\\H_3C\end{matrix}\!>CO} \xrightarrow{Cl_2} \underset{\text{Trichloroacetone}}{\begin{matrix}CCl_3\\CH_3\end{matrix}\!>CO}$$

15. Reaction with bleaching powder : When the mixture of ethyl alcohol and bleaching powder is heated, chloroform is formed. The conversion occurs in three steps. Bleaching powder brings oxidation in first step, chlorination in second step and hydrolysis in third step respectively.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + \underset{\text{Bleaching powder}}{CaOCl_2} \xrightarrow{\text{Oxidation}} \underset{\text{Acetaldehyde}}{CH_3CHO} + CaCl_2 + H_2O$$

$$2CH_3CHO + 6CaOCl_2 \xrightarrow{\text{Chlorination}} \underset{\text{Chloral}}{2CCl_3CHO} + 3Ca(OH)_2 + 3CaCl_2$$

$$2CCl_3CHO + Ca(OH)_2 \xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium formate}}{(HCOO)_2Ca}$$

16. Haloform reaction : Ethyl alcohol when heated with iodine and sodium hydroxide or aqueous sodium carbonate forms a yellow crystalline solid, **iodoform.**

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + 4I_2 + 6NaOH \xrightarrow{\text{Heat}} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium iodide}}{5NaI} + \underset{\text{Sodium formate}}{HCOONa} + 5H_2O$$

This reaction like the preparation of chloroform also occurs in three steps:

$$CH_3CH_2OH \xrightarrow[(NaOH+I_2)]{\text{Oxidation}} CH_3CHO \xrightarrow[I_2]{\text{Iodination}}$$

$$\underset{\text{Iodal}}{CI_3CHO} \xrightarrow[NaOH]{\text{Hydrolysis}} \underset{\text{Iodoform}}{CHI_3}$$

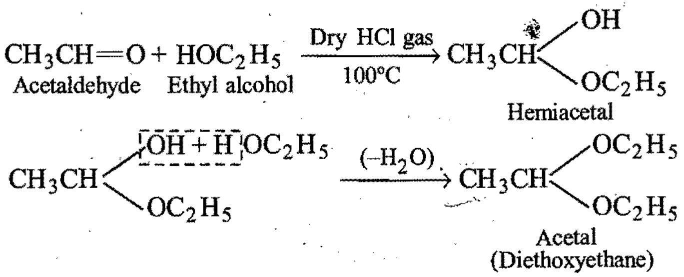
Methyl alcohol does not respond to the iodoform test.

In place of iodine, bromine or chlorine can be taken when the corresponding compounds bromoform or chloroform are to be formed. This reaction in general is known as **haloform reaction.**

$$C_2H_5OH + 4Br_2 + 6NaOH \longrightarrow \underset{\text{Bromoform}}{CHBr_3} + 5NaBr + HCOONa + 5H_2O$$

$$C_2H_5OH + 4Cl_2 + 6NaOH \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + 5NaCl + HCOONa + 5H_2O$$

17. Reaction with acetaldehyde : In presence of dry hydrogen chloride, ethyl alcohol combines with acetaldehyde forming hemiacetal and acetal.



$$\underset{\text{Acetaldehyde}}{CH_3CH{=}O} + \underset{\text{Ethyl alcohol}}{HOC_2H_5} \xrightarrow[100°C]{\text{Dry HCl gas}} \underset{\text{Hemiacetal}}{CH_3CH(OH)(OC_2H_5)}$$

$$CH_3CH(\boxed{OH + H}OC_2H_5)(OC_2H_5) \xrightarrow{(-H_2O)} \underset{\text{(Diethoxyethane)}}{\underset{\text{Acetal}}{CH_3CH(OC_2H_5)(OC_2H_5)}}$$

18. Reaction with P_2S_5 : On heating yields thioalcohol.

$$\underset{\text{Ethanol}}{5C_2H_5OH} + P_2S_5 \xrightarrow{\Delta} \underset{\text{Ethanethiol}}{5C_2H_5SH} + P_2O_5$$

9.7 METHODS OF DISTINGUISHING BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

The following methods are used for distinguishing three types of monohydric alcohols:

1. Lucas test : Alcohols react with an equimolar mixture of concentrated hydrochloric acid and anhydrous zinc chloride at room temperature to form alkyl halides.

$$R{-}OH + \underset{\text{(Conc.)}}{HCl} \xrightarrow[\text{Anhyd.}]{ZnCl_2} \underset{\text{Alkyl halide}}{R{-}Cl} + H_2O$$

The three types of alcohols undergo this reaction at different rates. The rates of reaction with **Lucas reagent** [conc. HCl + $ZnCl_2$ (anhydrous)] follow the following order:

Tertiary alcohol > Secondary alcohol > Primary alcohol

Lucas test is based on this order. An unknown alcohol (monohydric) is mixed with conc. HCl and anhydrous $ZnCl_2$ at room temperature. The alkyl chloride formed is insoluble in the medium, thus the solution becomes cloudy before it separates as a distinct layer. The following observations are made:

(a) If cloudiness (white turbidity) appears immediately, the alcohol is **tertiary.**

(b) If cloudiness appears within 5 minutes, the alcohol is **secondary.**

(c) If the solution remains clear, *i.e.*, no cloudiness is formed, the alcohol is **primary.**

Note: Primary alcohols do not react with Lucas reagent at room temperature. It requires high temperature. The benzyl and allyl alcohol reacts as rapidly as tertiary alcohols with Lucas reagent because their cations are resonance stabilized and stable as 3° cations.

$$H_2C{=}CHCH_2OH \xrightarrow{\text{Lucas reagent}} \text{Turbidity within a minute}$$

$$CH_3CH_2CH_2OH \xrightarrow{\text{Lucas reagent}} \text{Response after a long time}$$

2. Dichromate test (oxidation test) : The test is based on the fact that three types of monohydric alcohols give different oxidation products on oxidation. (For details **see section** 9.6-13).

The unknown alcohol is treated with sodium dichromate in dilute sulphuric acid (orange solution) at room temperature. The oxidation products are identified.

(i) A carboxylic acid with same number of carbon atoms as in the alcohol if formed confirms the primary alcohol. The colour of the solution changes from orange to green.

(ii) A ketone with same number of carbon atoms as in the alcohol if formed confirms the secondary alcohol. The colour of the solution also changes from orange to green.

(iii) In case the colour of the solution does not change, *i.e.*, it remains orange, the unknown alcohol is tertiary as it cannot be oxidised under these conditions.

Primary	**Secondary**	**Tertiary**
RCH_2OH $\downarrow$ [O] $Na_2Cr_2O_7 + H_2SO_4$ $RCHO$ Aldehyde $\downarrow$ [O] $Na_2Cr_2O_7 + H_2SO_4$ $RCOOH$ Acid (Orange solution becomes green)	$(R)(R')CHOH$ $\downarrow$ [O] $Na_2Cr_2O_7 + H_2SO_4$ $(R)(R')CO$ Ketone (Orange solution becomes green)	$(R)(R')(R'')C{-}OH$ $\downarrow$ [O] $Na_2Cr_2O_7 + H_2SO_4$ No reaction (Solution remains orange)

Note: Sodium dichromate in presence of dilute H_2SO_4 acts as an oxidising agent. It is converted into chromic sulphate which is green in colour. The potential equation is:

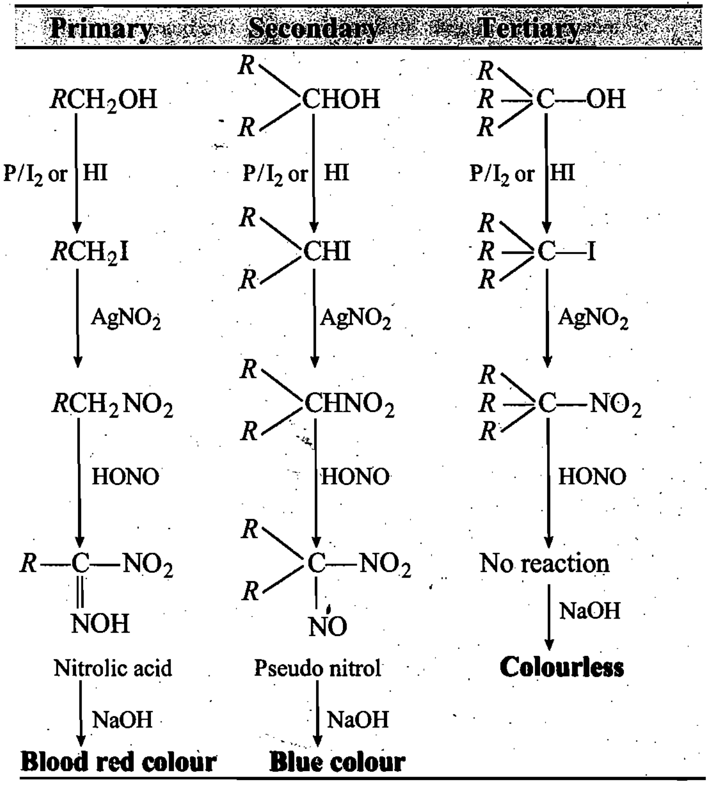
$$\underset{\substack{\text{Sodium dichromate}\\\text{(orange)}}}{Na_2Cr_2O_7} + 4H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\substack{\text{Chromic sulphate}\\\text{(green)}}}{Cr_2(SO_4)_3} + 4H_2O + 3O$$

3. Victor Meyer's test : In this test, the following steps are involved:

(i) Alcohol is reacted with conc. HI or red phosphorus and iodine to form the corresponding alkyl iodide.

(ii) Alkyl iodide is treated with silver nitrite when corresponding nitroalkane is formed.

(iii) Nitroalkane is treated with nitrous acid ($NaNO_2$ + H_2SO_4) and the solution is made alkaline by addition of excess of caustic soda.



4. Catalytic dehydrogenation : It involves the passing of vapours of alcohol over reduced copper at 300°C and the product thus formed is identified.

(i) Primary alcohols give aldehydes (dehydrogenation).

(ii) Secondary alcohols give ketones (dehydrogenation).

(iii) Tertiary alcohols form olefins (alkenes). This is dehydration.

(For details **see section** 9.6–12.)

9.8 ANALYTICAL TESTS FOR ALCOHOLS

The presence of a hydroxyl group in an unknown organic compound may be detected with the help of following tests. If the compound is a solid it is dissolved in an inert solvent, *e.g.*, dry ether or benzene.

1. Alcohols are neutral substances towards litmus : The colour of blue or red litmus does not change when alcohol is added to it.

2. Ceric ammonium nitrate test : The freshly prepared solution of ceric ammonium nitrate (CAN) has yellow colour. When few drops of this reagent are added to the given compound or its solution if colour changes from yellow to red, the compound contains a hydroxyl group.

$$2R—OH + \underset{\text{CAN}}{(NH_4)_2Ce(NO_3)_6} \longrightarrow \underset{\text{Red complex}}{[(ROH)_2Ce(NO_3)_4]} + 2NH_4NO_3$$

3. Acylation test : Acetyl chloride or benzoyl chloride is added to the given compound or its solution, if hydrogen chloride is evolved, it shows that the organic compound is an alcohol.

9.9 SOME COMMERCIALLY IMPORTANT ALCOHOLS

1. Methyl Alcohol or Methanol or Carbinol (CH_3OH)

It is the simplest monohydric alcohol. It is also referred as **wood alcohol** or **wood spirit** or **wood naphtha** as the earliest method for its preparation was by destructive distillation of wood. It occurs in combined state in some essential oils, *e.g.*, oil of winter green (methyl salicylate), oil of cloves (methyl benzoate), oil of orange flowers (methyl anthranilate), etc.

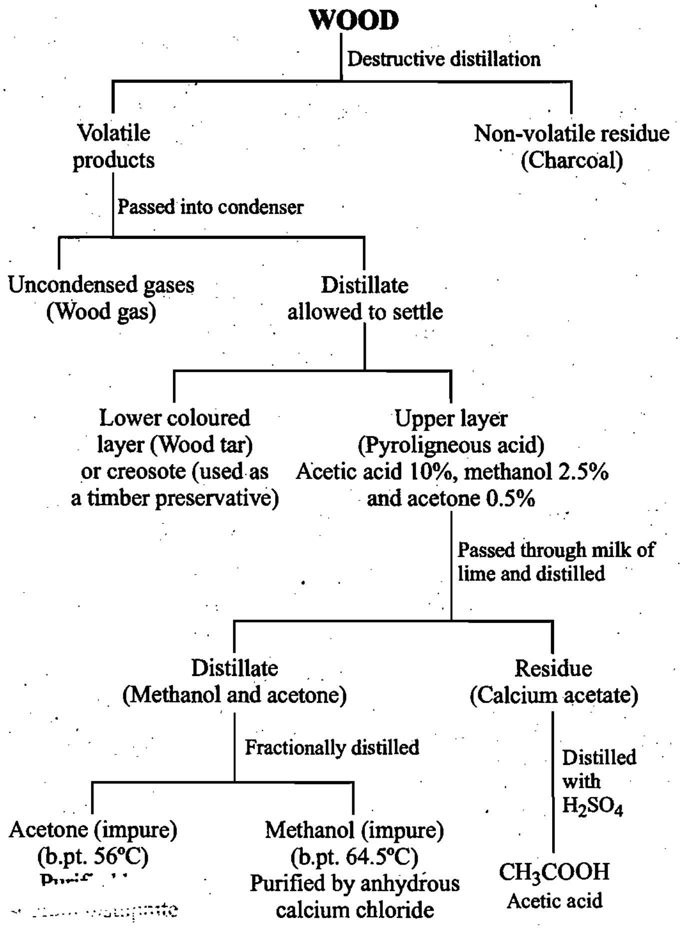
General methods of preparation : Methyl alcohol can be obtained by the general methods of preparation of monohydric alcohols.

Manufacture or Industrial Preparation

1. On a large scale, methyl alcohol is obtained **from wood** by its **destructive distillation method.**

(FLOW-SHEET)

Manufacture of Methyl Alcohol by Destructive Distillation



2. From water gas : Now-a-days methanol is mostly manufactured by this method. Methanol obtained by this method is about 99% pure. The yield is also quantitative.

Water gas is formed by passing steam over coke at 1300°C

$$C + H_2O \xrightarrow{1300^\circ C} \underbrace{CO + H_2}_{\text{Water gas}}$$

Water gas is mixed with half its volume of hydrogen. The mixture is compressed to approximately 200–300 atmosphere. It is then passed over a catalyst ($ZnO + Cr_2O_3$) at 300°C. Methyl alcohol vapours are formed which are condensed.

$$\underset{\text{Compressed gases}}{CO + 2H_2} \xrightarrow[300^\circ C]{ZnO\ +\ Cr_2O_3} \underset{\text{Methyl alcohol}}{CH_3OH}$$

3. From natural gas : A mixture of methane and oxygen (9 : 1 by volume) is passed over copper catalyst at 250°C under pressure (100 atmospheres). Methane is oxidised to methanol.

$$2CH_4 + O_2 \longrightarrow 2CH_3OH$$

Methane required for this purpose is obtained from natural gas.

Physical properties : (i) It is a colourless liquid and boils at 64.5°C.

(ii) It is miscible in water in all proportions. It is soluble in organic solvents also. It is itself a good solvent for fats and oils.

(iii) It is extremely poisonous liquid. When taken internally, it causes blindness, insanity and even death. 30 mL of methyl alcohol can cause death. On account of this property, it can be used for denaturing ethyl alcohol, *i.e.*, to make it unfit for drinking purposes.

(iv) It is inflammable and burns with a faint luminous flame.

(v) It has a pleasant smell and burning taste.

(vi) It cannot be dehydrated with anhydrous calcium chloride as it forms an addition crystalline compound, $CaCl_2{\cdot}4CH_3OH$ with it.

Chemical properties : Chemically, it behaves like a typical monohydric alcohol. It shows many of the general chemical reactions.

Uses : It is used:

(i) as a solvent for oils, fats, paints, varnishes and celluloid.

(ii) for the manufacture of formaldehyde and formalin (40% formaldehyde solution in water) which is widely used as a preservative for biological specimens and in the manufacture of formaldehyde resins such as bakelite, urea-formaldehyde and melamine formaldehyde.

(iii) as a fuel (a petrol substitute). A 20% mixture of methyl alcohol and gasoline is a good motor fuel.

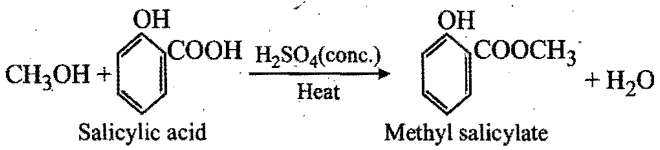
(iv) as an antifreeze for automobile radiators.

(v) to denature ethyl alcohol. The mixture is called methylated spirit.

(vi) in the preparation of dyes, medicines and perfumes. Methyl salicylate and methyl anthranilate are used in perfumery.

Analytical Tests of Methyl Alcohol

1. When warmed with a little salicylic acid in presence of few drops of conc. sulphuric acid, it gives a characteristic fragrant smell of oil of winter green (methyl salicylate).



2. With ceric ammonium nitrate, it gives red colour.

3. Unlike ethyl alcohol, it does not give **iodoform test.**

4. When a red hot copper wire is dipped in methyl alcohol contained in a test tube, a characteristic pungent smell of formaldehyde is observed.

5. A pungent smell of formaldehyde is also observed when methyl alcohol is warmed with potassium dichromate and dilute sulphuric acid.

2. Ethyl Alcohol or Ethanol or Methyl Carbinol, C_2H_5OH

Ethyl alcohol is the most important member of the alcohol series and is commonly known as alcohol. As it is an essential constituent of all wines, it is called a **spirit of wine.** It is also known as **grain alcohol** because it is obtained from starchy grains.

In combined form, it exists as ester in essential oils.

Preparation (general methods) : Ethyl alcohol can be prepared by any of the general methods used for the preparation of monohydric alcohols.

Manufacture or Industrial Preparation

On large scale, ethyl alcohol is manufactured by either, (i) chemical synthesis or (ii) fermentation process.

(i) Chemical synthesis : There are two raw materials; ethylene and acetylene, which are used for chemical synthesis of ethyl alcohol.

(a) From ethylene : Large quantities of ethylene are available from petroleum refineries. This is formed during cracking of petroleum.

Ethylene is passed into concentrated sulphuric acid at 75-80°C under pressure when a mixture of ethyl hydrogen sulphate and diethyl sulphate is formed.

$$C_2H_4 + H_2SO_4 \xrightarrow[\text{Pressure}]{75\text{–}80^\circ C} \underset{\substack{\text{Ethyl hydrogen}\\ \text{sulphate}}}{C_2H_5HSO_4}$$

$$C_2H_5HSO_4 + C_2H_4 \longrightarrow \underset{\text{Diethyl sulphate}}{(C_2H_5)_2SO_4}$$

The reaction mixture is diluted with water and warmed when hydrolysis occurs and ethyl alcohol is obtained together with some ether as a byproduct.

$$C_2H_5HSO_4 + H_2O \xrightarrow{\text{Heat}} C_2H_5OH + H_2SO_4$$

$$(C_2H_5)_2SO_4 + 2H_2O \xrightarrow{\text{Heat}} 2C_2H_5OH + H_2SO_4$$

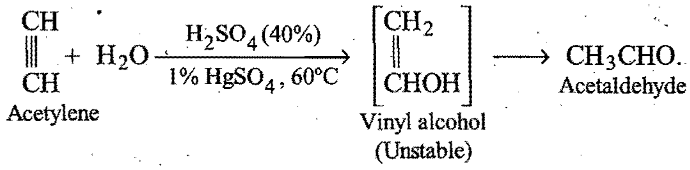
The yield of ethyl alcohol is 90%. The aqueous solution is distilled to separate ethyl alcohol from sulphuric acid.

Alternative method : Ethylene may be converted to ethyl alcohol by direct hydration in presence of phosphoric acid or silica or tungsten oxide as catalyst at 300°C.

$$\underset{\text{Ethylene}}{C_2H_4} + H_2O \xrightarrow[300^\circ C,\ 70\ \text{atm.}]{H_3PO_4} \underset{\text{Ethyl alcohol (95\%)}}{C_2H_5OH}$$

(b) From acetylene : Acetylene is first converted into acetaldehyde which on reduction yields ethyl alcohol.

Acetylene is passed through 40% sulphuric acid containing approximately 1% mercuric sulphate at 60°C. Acetylene is converted into acetaldehyde.



$$\underset{\text{Acetylene}}{\begin{matrix} CH \\ ||| \\ CH \end{matrix}} + H_2O \xrightarrow[1\%\ HgSO_4,\ 60^\circ C]{H_2SO_4\,(40\%)} \underset{\substack{\text{Vinyl alcohol} \\ \text{(Unstable)}}}{\left[\begin{matrix} CH_2 \\ || \\ CHOH \end{matrix}\right]} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO.}$$

Vapours of acetaldehyde are mixed with hydrogen and passed over finely divided nickel at 110–140°C when ethyl alcohol is formed by reduction of acetaldehyde.

$$CH_3CHO + H_2 \xrightarrow[110\text{–}140^\circ C]{Ni} \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(ii) Fermentation process : This is one of the earliest and most important methods for preparing various types of alcoholic preparations. In alcoholic fermentation, cane-sugar or glucose are the fermenting materials. The raw materials for the manufacture of alcohol are:

(a) Substances containing fermentable sugars such as cane juice, beets, dates, molasses and fruit juices.

(b) Substances containing starch such as potatoes, rice, barley and maize.

Molasses is the cheapest source of sucrose and it forms an excellent raw material for making ethyl alcohol. Today hardly 10% ethyl alcohol is produced by this method (90% ethyl alcohol is produced from ethylene, *i.e.*, synthetic method). In India, molasses is still the main source of ethyl alcohol.

The process of fermentation is the slow decomposition of complex organic compounds into simpler substances through the agency of complex nitrogenous compounds called enzymes produced in living organisms.

Fermentation of carbohydrates gives 95% alcohol and the rest 5% being water. This alcohol is called **rectified spirit.**

Preparation of Absolute Alcohol

Absolute alcohol is 100% ethanol. The rectified spirit (95.5% ethanol + 4.5% water) is a **constant boiling mixture (azetropic solution)** and water cannot be removed by simple fractional distillation method.

In the **laboratory,** absolute alcohol is prepared by keeping the rectified spirit in contact with calculated amount of quicklime (CaO) for a few hours and then refluxing and distilling it.

Methylated Spirit or Denatured Alcohol

In order to make the industrial alcohol unfit for drinking purposes, the rectified alcohol is denatured by adding various poisonous compounds like methanol, pyridine, acetone or petroleum naphtha, etc. This **denatured spirit** is 95% ethanol and 5% methanol. The **methylated spirit** is a mixture of 90% ethanol, 9% methanol and 1% other poisonous substances pyridine and acetone or petroleum oil.

Power Alcohol : It has been found that absolute ethyl alcohol mixed with petrol and benzene can be used as a motor fuel. Alcohol thus used for generating power is called **power alcohol.** A mixture of 20% ethanol and 80% gasoline (petrol) is used in internal combustion engines to derive power. Since, alcohol itself, does not mix with petrol, therefore, a third solvent such as benzene, ether or tetralin (tetrahydronaphthalene) is used as a solvent.

Physical properties : (i) Ethyl alcohol is a colourless liquid with a characteristic pleasant smell (alcoholic smell) and burning taste.

(ii) It is inflammable and burns with a blue flame.

(iii) It boils at 78.1°C and has specific gravity 0.789 at 20°C.

(iv) Unlike methyl alcohol, it is not a toxic liquid.

(v) It mixes with water in all proportions. It dissolves in water with evolution of heat and contraction in volume. It forms a constant boiling mixture (95.6% ethyl alcohol + 4.4% water) with water which boils at 78.15°C. It is also miscible with a number of organic solvents.

(vi) Ethyl alcohol is a good solvent for oils, fats, resins, etc. It also dissolves inorganic substances like caustic soda, sulphur, phosphorus, etc.

(vii) Like methyl alcohol, it cannot be dried over anhydrous calcium chloride as it forms an addition product $CaCl_2 \cdot 4C_2H_5OH$.

(viii) When taken internally ethyl alcohol is readily oxidised by the system and is, therefore, an important source of immediate energy. The blood begins to flow faster and dilates the blood vessels.

Chemical properties : Ethyl alcohol shows all the general characteristics of a monohydric (primary) alcohol. It is a neutral substance. It does not affect the pH of the water. It burns with blue flame in air or oxygen forming carbon dioxide and water.

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

Uses : Ethyl alcohol is one of the most extensively used organic compounds. Its main uses are:

(i) in the manufacture of alcoholic beverages.

(ii) as a solvent for pharmaceutical preparations and a constituent of medicines.

(iii) as a solvent for paints, oils, perfumes, dyes, varnishes, gums, etc.
(iv) as a preservative for biological specimens.
(v) in the manufacture of acetaldehyde, acetic acid, ethyl halides, ethyl acetate, chloroform, iodoform, etc.
(vi) as an antifreeze in automobile radiators.
(vii) as a low freezing and mobile liquid in scientific apparatus such as thermometers and spirit levels.
(viii) in hospitals as an antiseptic.
(ix) as a fuel in spirit lamps and stoves.
(x) as a petrol substitute (power alcohol).
(xi) laboratory reagent as a reaction medium, extractant and crystallizing solvent.
(xii) for making solid alcohol fuel. It is prepared by mixing ethyl alcohol with saturated calcium acetate solution. A solid gel is formed which is known as canned heat or solid alcohol. It burns like alcohol.

Analytical Tests of Ethyl Alcohol

1. Iodoform test : When a few drops of ethyl alcohol are warmed with iodine and potassium hydroxide, yellow precipitate of iodoform with characteristic smell is obtained.

2. Ester test : When ethyl alcohol is heated gently with sodium acetate and concentrated sulphuric acid, a characteristic fruity odour of ethyl acetate is formed.

3. Acidified potassium dichromate test : Ethyl alcohol when heated with potassium dichromate and dilute sulphuric acid is oxidised to acetaldehyde which has characteristic pungent smell. If a paper dipped in ammoniacal silver nitrate solution is dipped in this solution a black spot appears on the paper due to reduction of silver nitrate by acetaldehyde.

4. Ceric ammonium nitrate test : With a few drops of alcohol and dilute ceric ammonium nitrate, a red colour indicates alcoholic hydroxy group.

9.10 ALCOHOLIC BEVERAGES AND ALCOHOLOMETRY

Liquors used for drinking purposes containing ethyl alcohol as the principal constituent are called alcoholic beverages. Besides alcohol, these contain large amount of water, colouring and flavouring materials. These are prepared from different starting materials like molasses, barley, grape and other fruit juices by alcoholic fermentation. Alcoholic beverages are of two types:

1. Undistilled beverages : These are prepared from fruit juices and grains. Those prepared from grapes and other fruit juices are known as wines. Wines contain 18–20% of ethyl alcohol and are used as such after fermentation, *i. e.*, without distillation. The natural wines when made stronger by the addition of rectified alcohol are known as fortified wines.

2. Distilled beverages : These are prepared by the fermentation of molasses, barley, maize, etc. The fermented liquor is then distilled. These contain a higher percentage of ethyl alcohol which may be as high as 50%.

The colour, flavour and taste of a particular beverage depend on the materials used, process of fermentation and subsequent treatments. The following list includes some common beverages with their alcoholic content and source from which it is obtained.

Undistilled			**Distilled**		
Name	**Percentage of alcohol**	**Source**	**Name**	**Percentage of alcohol**	**Source**
Beer	3–6	Barley	Whisky	35–40	Malt
Cider	2–6	Apples	Rum	45–55	Molasses
Wine (Champagne)	8–10	Grapes	Gin	40–45	Maize
Claret	7–13	Grape juice	Brandy	40–45	Grape juice
Port and Sherry (Fortified)	14–24	Grape juice	Cognac	40–50	Grape juice

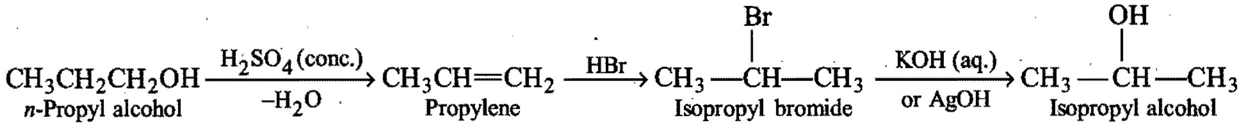
Alcoholic beverages when taken in small quantity act as stimulants but when taken regularly in excess, may decrease the energy of the body, retard the mental powers and damage the liver causing **cirrhosis of liver.**

The process of determining the percentage of alcohol in a given sample is known as alcoholometry. This is done by measuring the specific gravity of the sample with the help of hydrometer and then reading the percentage of alcohol against this value of specific gravity from a standard reference table.

An alcohol water mixture having specific gravity 0.91976 at 15°C and containing 57.1% of ethyl alcohol by volume or 49.3% by weight is called **proof-spirit.** A sample having higher percentage of ethyl alcohol in comparison to proof-spirit is referred to as **over-proof** (O.P.) and the one having lower alcohol content than proof-spirit is known as **under-proof** (U.P.). Thus, 15 U.P. means that 100 mL of the sample contains as much alcohol as 85 mL of proof-spirit. Similarly, 15 O.P. means that 100 mL of the sample contains as much of alcohol as 115 mL of proof-spirit.

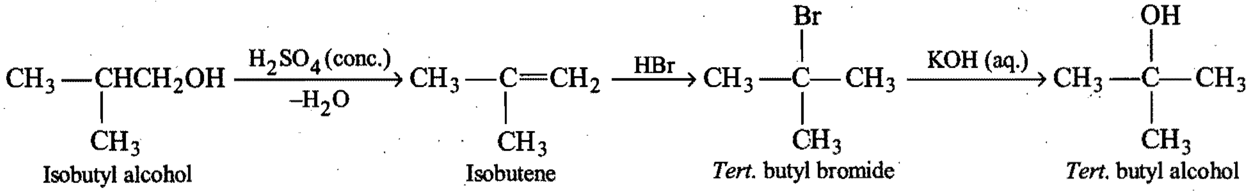
9.11 INTERCONVERSIONS

1. Conversion of primary alcohol into isomeric secondary alcohol, *e.g.*, *n*-propyl alcohol into isopropyl alcohol:



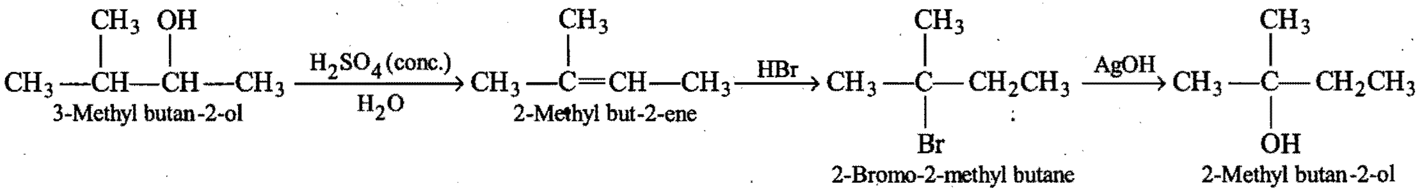
$$\underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow[-H_2O]{H_2SO_4\text{(conc.)}} \underset{\text{Propylene}}{CH_3CH{=}CH_2} \xrightarrow{HBr} \underset{\text{Isopropyl bromide}}{CH_3-\overset{\overset{Br}{|}}{C}H-CH_3} \xrightarrow[\text{or AgOH}]{\text{KOH (aq.)}} \underset{\text{Isopropyl alcohol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3}$$

2. Conversion of primary alcohol into isomeric tertiary alcohol, *e.g.*, isobutyl alcohol into tertiary butyl alcohol or (2-Methyl propan-1-ol into 2-methyl propan-2-ol):



$$\underset{\text{Isobutyl alcohol}}{CH_3-\underset{\underset{CH_3}{|}}{C}HCH_2OH} \xrightarrow[-H_2O]{H_2SO_4\text{(conc.)}} \underset{\text{Isobutene}}{CH_3-\underset{\underset{CH_3}{|}}{C}{=}CH_2} \xrightarrow{HBr} \underset{\textit{Tert.}\text{ butyl bromide}}{CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3} \xrightarrow{\text{KOH (aq.)}} \underset{\textit{Tert.}\text{ butyl alcohol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

3. Conversion of secondary alcohol into isomeric tertiary alcohol, *e.g.*, 3-methyl butan-2-ol into 2-methyl butan-2-ol: Secondary alcohol having —OH group adjacent to tertiary carbon atom can be converted into a tertiary alcohol.



$$\underset{\text{3-Methyl butan-2-ol}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{OH}{|}}{C}H-CH_3} \xrightarrow[H_2O]{H_2SO_4\text{(conc.)}} \underset{\text{2-Methyl but-2-ene}}{CH_3-\overset{\overset{CH_3}{|}}{C}{=}CH-CH_3} \xrightarrow{HBr} \underset{\text{2-Bromo-2-methyl butane}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_2CH_3} \xrightarrow{AgOH} \underset{\text{2-Methyl butan-2-ol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2CH_3}$$

Note: Conversion of tertiary or secondary into isomeric secondary and primary alcohol is not possible. However, higher homologues can be converted into lower homologues.

Ascent of Series

1. Conversion of lower primary alcohol into higher primary alcohol

(a) By cyanide synthesis:

$$RCH_2OH \xrightarrow{P + I_2} RCH_2I \xrightarrow{KCN} RCH_2CN \xrightarrow{4H} RCH_2CH_2NH_2 \xrightarrow{HNO_2} RCH_2CH_2OH$$

(b) By Grignard synthesis:

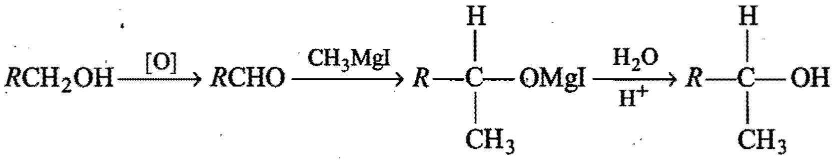
$$RCH_2OH \xrightarrow{P + I_2} RCH_2I \xrightarrow[\text{Ether}]{Mg} RCH_2MgI \xrightarrow{HCHO} RCH_2CH_2OMgI \xrightarrow{H_2O} RCH_2CH_2OH$$

Problem 3. *How will you make the following conversions?*
(i) Methyl alcohol into ethyl alcohol,
(ii) Ethyl alcohol into n-propyl alcohol.

Solution : (i) $$CH_3OH \xrightarrow{P + I_2} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{KCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[4H]{\text{Reduction}} \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

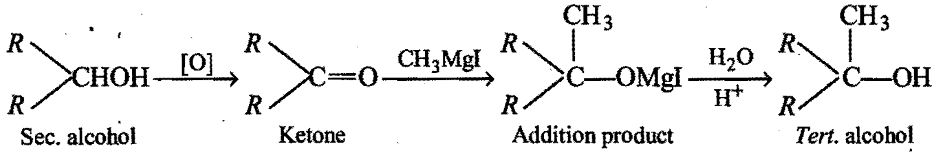
(ii) $$CH_3CH_2OH \xrightarrow{P + I_2} \underset{\text{Ethyl iodide}}{CH_3CH_2I} \xrightarrow[\text{Ether}]{Mg} \underset{\text{Ethyl magnesium iodide}}{CH_3CH_2MgI} \xrightarrow{HCHO} \underset{\text{Addition product}}{CH_3CH_2CH_2OMgI} \xrightarrow[H^+]{H_2O} \underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH}$$

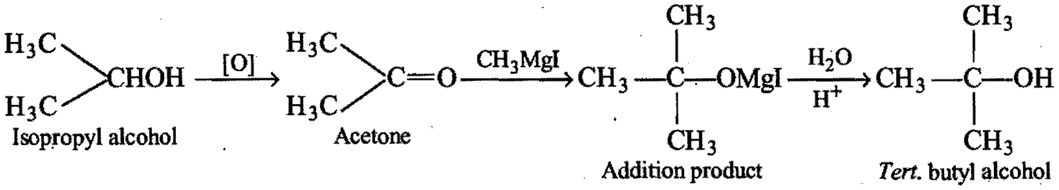
2. Conversion of lower primary alcohol into higher secondary alcohol



$$RCH_2OH \xrightarrow{[O]} RCHO \xrightarrow{CH_3MgI} R-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-OMgI \xrightarrow[H^+]{H_2O} R-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

3. Conversion of secondary alcohol into higher tertiary alcohol :





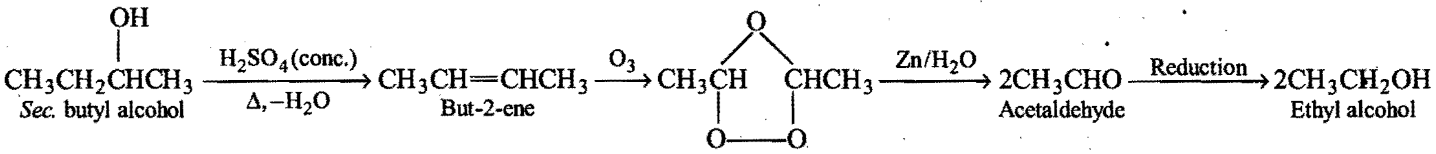
Descent of Series

1. Conversion of higher primary alcohol into a lower primary alcohol :

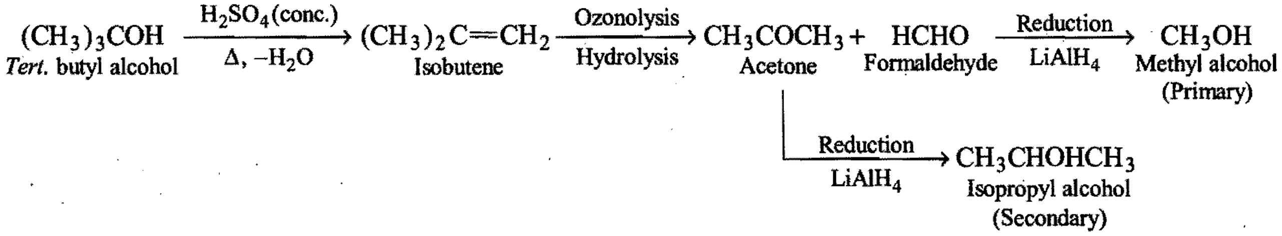
(a) $RCH_2OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH \xrightarrow{NH_3} RCOONH_4 \xrightarrow{Heat} RCONH_2 \xrightarrow[Br_2]{KOH} RNH_2 \xrightarrow{HNO_2} ROH$

(b) $RCH_2OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH \xrightarrow{NaOH} RCOONa \xrightarrow{\text{Soda lime}} RH \xrightarrow[UV]{Cl_2} RCl \xrightarrow{KOH(aq.)} ROH$

2. Conversion of higher secondary alcohol into a lower primary alcohol :



3. Conversion of a tertiary alcohol into a lower secondary and a primary alcohol :



$$\underset{\textit{Tert. butyl alcohol}}{(CH_3)_3COH} \xrightarrow[\Delta,\,-H_2O]{H_2SO_4(conc.)} \underset{\text{Isobutene}}{(CH_3)_2C{=}CH_2} \xrightarrow[\text{Hydrolysis}]{\text{Ozonolysis}} \underset{\text{Acetone}}{CH_3COCH_3} + \underset{\text{Formaldehyde}}{HCHO} \xrightarrow[LiAlH_4]{\text{Reduction}} \underset{\text{Methyl alcohol (Primary)}}{CH_3OH}$$

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow[LiAlH_4]{\text{Reduction}} \underset{\text{Isopropyl alcohol (Secondary)}}{CH_3CHOHCH_3}$$

Problem 4. *How will you distinguish? (i) Methyl alcohol from ethyl alcohol, (ii) Ethyl alcohol from chloroform.*

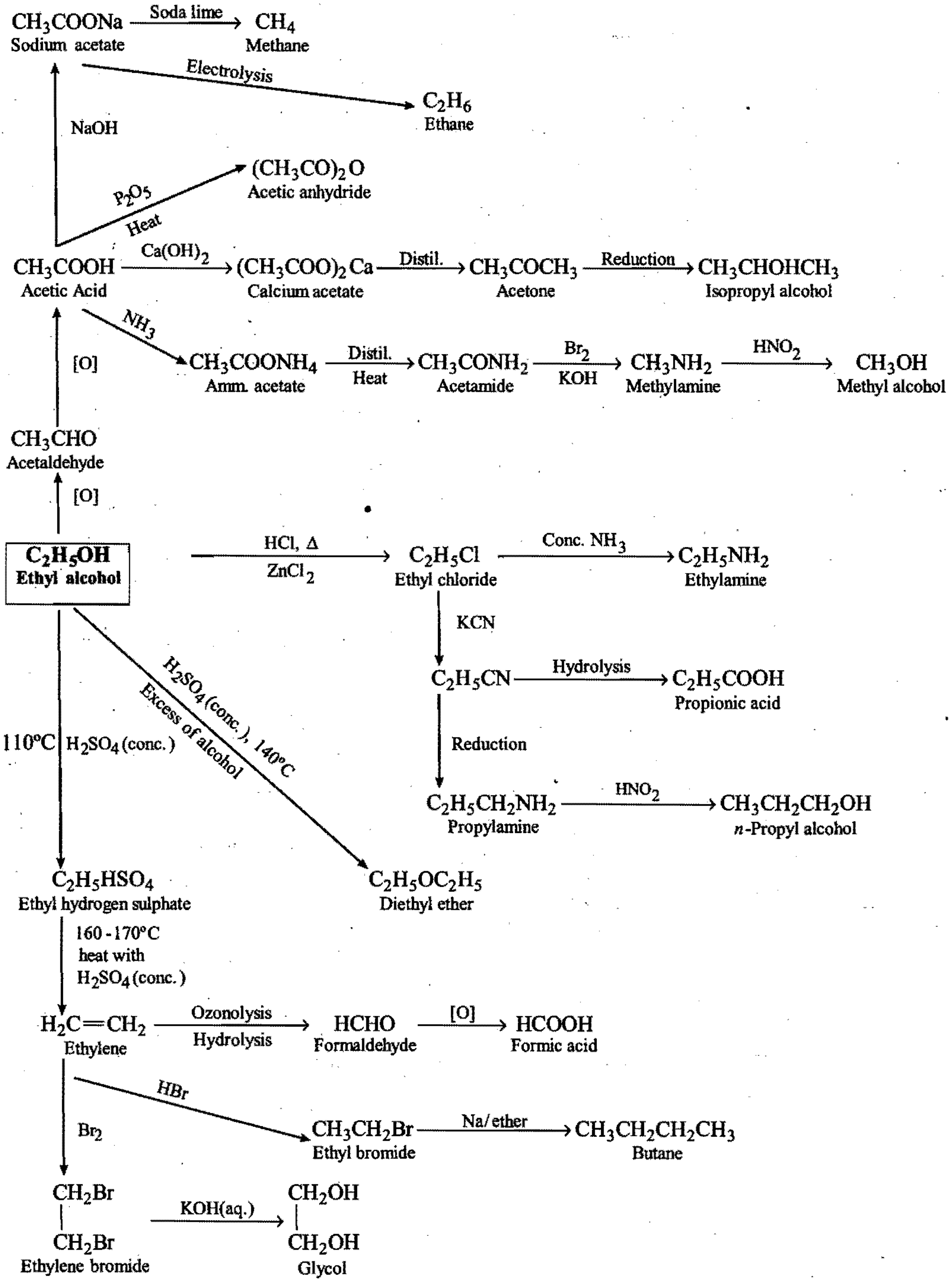
Solution : (i)

Tests	Methyl alcohol	Ethyl alcohol
1. Iodoform test On heating with I_2 and NaOH	No yellow compound is formed.	Yellow compound with characteristic odour is formed.
2. Oil of winter green test On heating with salicylic acid and conc. H_2SO_4	Gives characteristic odour of oil of winter green.	Does not give odour of oil of winter green.
3. Ester test On heating with glacial acetic acid and conc. H_2SO_4	Forms methyl acetate with characteristic odour.	Forms ethyl acetate which has fruity odour.

(ii)

Tests	Ethyl alcohol	Chloroform
1. Iodoform test On heating with I_2 and NaOH	Forms yellow crystals with characteristic odour.	Does not give the test.
2. Isocyanide test On heating with aniline and alcoholic KOH	No reaction.	Forms phenyl isocyanide which has a characteristic bad odour.
3. Solubility test	It is soluble in water.	It is insoluble in water.

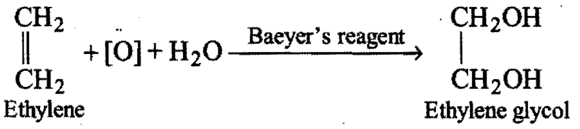
Conversion of Ethyl Alcohol into Various Compounds



9.12 ETHYLENE GLYCOL, $\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}$; (ETHANE-1,2-DIOL)

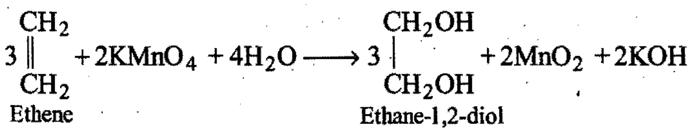
Ethylene glycol is the simplest and most important dihydric alcohol. The following methods can be used for its preparation:

1. From ethylene (Lab method) : (a) Ethylene is passed through cold dilute alkaline solution of potassium permanganate **(Baeyer's reagent)** when it is oxidised to glycol (Hydroxylation of alkenes).



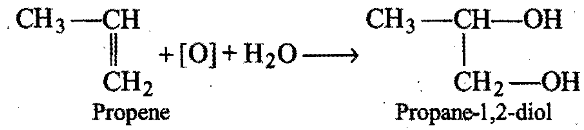
$$\underset{\text{Ethylene}}{\begin{array}{c}CH_2\\\|\\CH_2\end{array}} + [O] + H_2O \xrightarrow{\text{Baeyer's reagent}} \underset{\text{Ethylene glycol}}{\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}}$$

OR

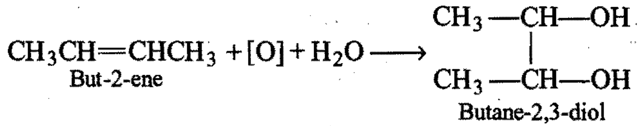


$$3\underset{\text{Ethene}}{\begin{array}{c}CH_2\\\|\\CH_2\end{array}} + 2KMnO_4 + 4H_2O \longrightarrow 3\underset{\text{Ethane-1,2-diol}}{\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}} + 2MnO_2 + 2KOH$$

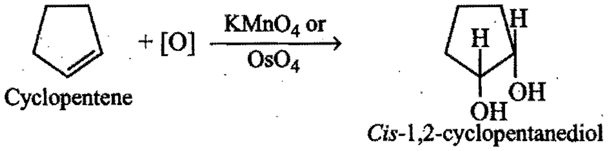
Higher alkenes give *cis*-glycols.



$$\underset{\text{Propene}}{\begin{array}{l}CH_3-CH\\\qquad\;\|\\\qquad CH_2\end{array}} + [O] + H_2O \longrightarrow \underset{\text{Propane-1,2-diol}}{\begin{array}{l}CH_3-CH-OH\\\qquad\;\;|\\\qquad CH_2-OH\end{array}}$$

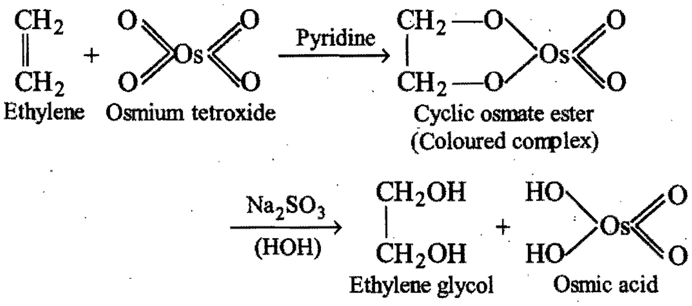


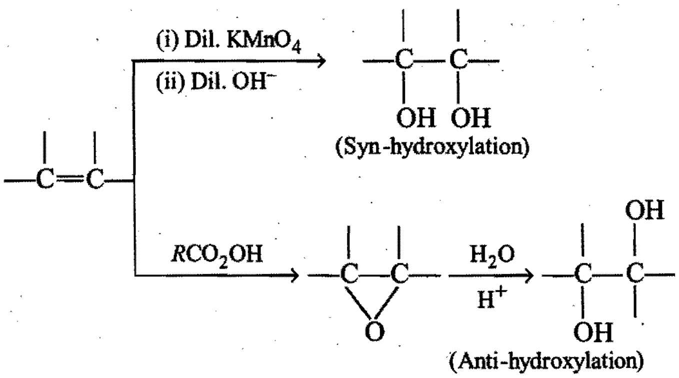
$$\underset{\text{But-2-ene}}{CH_3CH{=}CHCH_3} + [O] + H_2O \longrightarrow \underset{\text{Butane-2,3-diol}}{\begin{array}{l}CH_3-CH-OH\\\qquad\;\;|\\CH_3-CH-OH\end{array}}$$



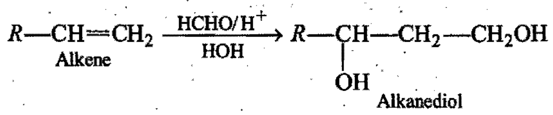
Cis-1,2-cyclopentanediol

Hydroxylation of a double bond can also be done by the action of osmium tetroxide (OsO_4) and the cyclic osmate ester thus, formed on decomposition with ethanolic Na_2SO_3 solution gives glycols in quantitative yield.

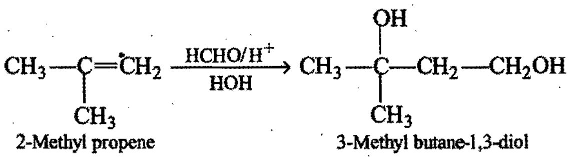




Note : A compound containing both —OH and —CH_2OH groups, can be obtained from alkenes by the addition with formaldehyde in presence of acid as a catalyst. This addition reaction is known as **Prins** reaction.

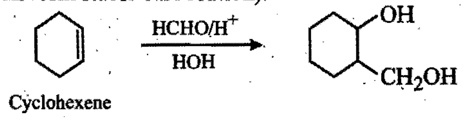


$$\underset{\text{Alkene}}{R-CH{=}CH_2} \xrightarrow[\text{HOH}]{\text{HCHO/H}^+} \underset{\text{Alkanediol}}{\begin{array}{l}R-CH-CH_2-CH_2OH\\\qquad\;|\\\qquad OH\end{array}}$$

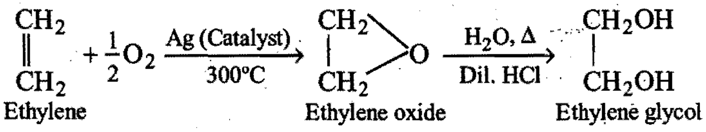


$$\underset{\text{2-Methyl propene}}{\begin{array}{l}CH_3-C{=}CH_2\\\qquad\;|\\\qquad CH_3\end{array}} \xrightarrow[\text{HOH}]{\text{HCHO/H}^+} \underset{\text{3-Methyl butane-1,3-diol}}{\begin{array}{l}\qquad\;OH\\\qquad\;|\\CH_3-C-CH_2-CH_2OH\\\qquad\;|\\\qquad CH_3\end{array}}$$

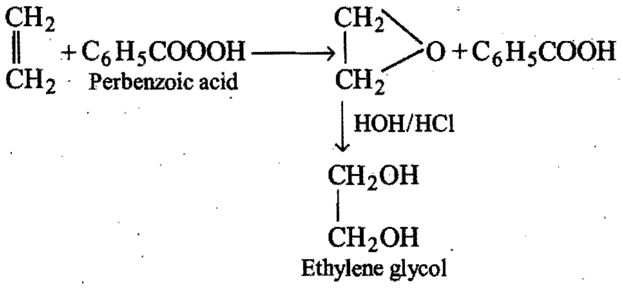
The —OH group always adds on the doubly bonded carbon which has least number of hydrogen (or doubly bonded carbon which can form stable carbocation).



(b) Ethylene is first converted into ethylene oxide by passing a mixture of ethylene and air under pressure over silver catalyst at 200–400°C.

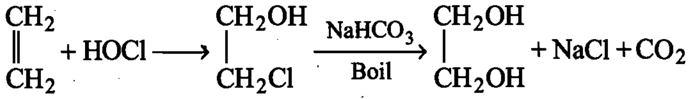


Ethylene oxide can also be obtained by treatment of ethylene with per acid.



Ethylene oxide undergoes hydrolysis when treated with dilute hydrochloric acid to form glycol. This is an **industrial method.**

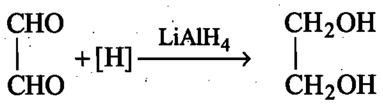
(c) Ethylene is passed through hypochlorous acid when ethylene chlorohydrin is formed. This intermediate is hydrolysed by boiling with sodium bicarbonate to yield glycol. This is also an **industrial method.**



$$\begin{array}{c}CH_2\\ \parallel\\ CH_2\end{array} + HOCl \longrightarrow \begin{array}{c}CH_2OH\\ |\\ CH_2Cl\end{array} \xrightarrow[\text{Boil}]{NaHCO_3} \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array} + NaCl + CO_2$$

Ethylene chlorohydrin Ethylene glycol

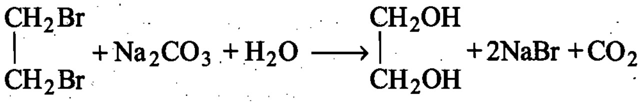
2. By reduction of glyoxal : Glyoxal on reduction with $LiAlH_4$ gives ethylene glycol.



$$\begin{array}{c}CHO\\ |\\ CHO\end{array} + [H] \xrightarrow{LiAlH_4} \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}$$

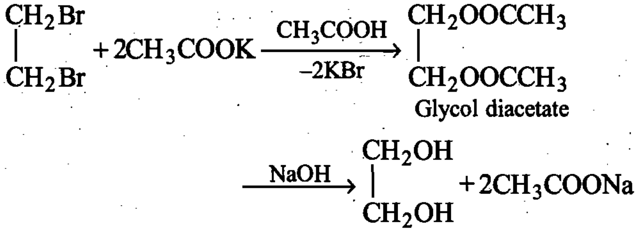
Glyoxal Ethylene glycol

3. From 1,2-dibromoethane : Glycol can be obtained in the laboratory by doing hydrolysis of 1,2-dibromoethane with boiling Na_2CO_3 solution.



$$\begin{array}{c}CH_2Br\\ |\\ CH_2Br\end{array} + Na_2CO_3 + H_2O \longrightarrow \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array} + 2NaBr + CO_2$$

Vinyl bromide is formed as byproduct. Best yield of glycol can be obtained by heating 1,2-dibromoethane with potassium acetate in glacial acetic acid. Glycol diacetate is formed which on hydrolysis with dilute NaOH gives free glycol.



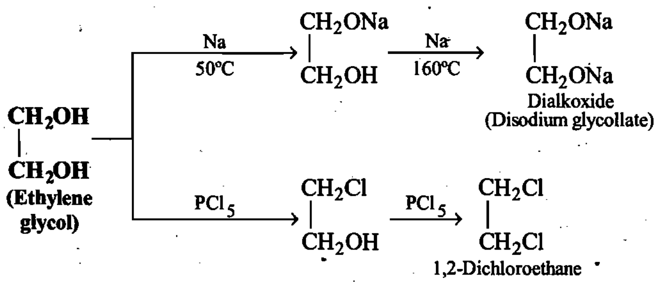
$$\begin{array}{c}CH_2Br\\ |\\ CH_2Br\end{array} + 2CH_3COOK \xrightarrow[-2KBr]{CH_3COOH} \begin{array}{c}CH_2OOCCH_3\\ |\\ CH_2OOCCH_3\end{array}$$

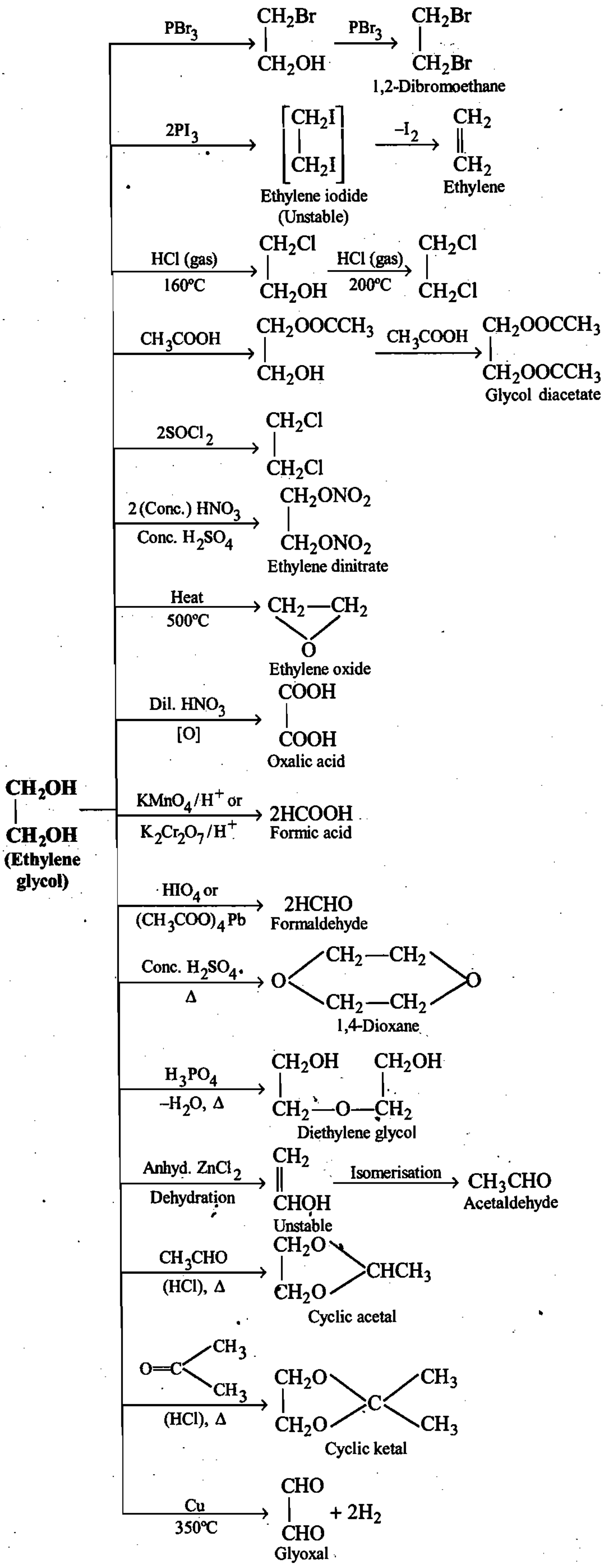
Glycol diacetate

$$\xrightarrow{NaOH} \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array} + 2CH_3COONa$$

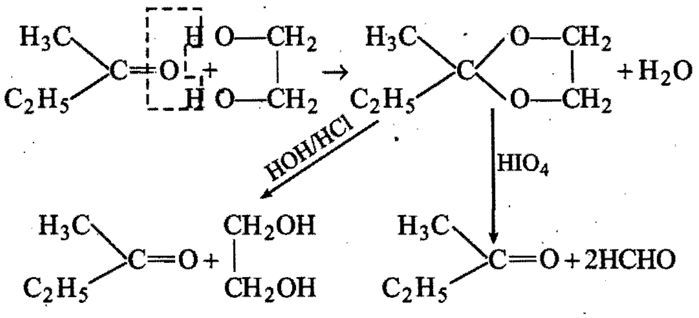
Physical properties : It is a colourless, syrupy liquid and sweet in taste. It is miscible with water and ethanol in all proportions, but insoluble in ether. It boils at 197°C. The high solubility in water and its high boiling point is due to intermolecular hydrogen bonding. It is as toxic as methyl alcohol when taken orally.

Chemical properties : There are two primary alcoholic groups present in glycol molecule. Its reactions are, therefore, those of primary alcohols twice over. The two —OH groups, however, are not equally reactive; one group always completely reacts before the other is attacked.





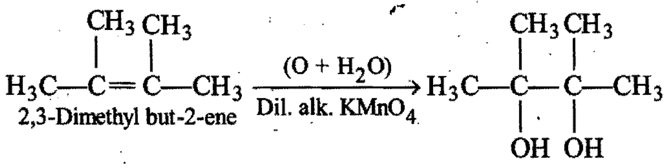
Cyclic ketals or acetal are also called as **dioxolanes.** Formation of dioxolane is a method of protecting carbonyl group for a reaction to be carried out in basic medium. Carbonyl group may be regenerated by either hydrolysis in acid medium or by the addition of periodic acid.



Uses : Ethylene glycol is used:

(i) as an antifreeze under the name **preston** in car radiators.
(ii) in the manufacture of dacron, (terylene), glyptal, dioxan and ethylene oxide.
(iii) as a solvent and as a preservative.
(iv) as a cooling agent in aeroplanes.
(v) as an explosive in the form of dinitrate.

Pinacol; 2,3-Dimethyl butane-2,3-diol

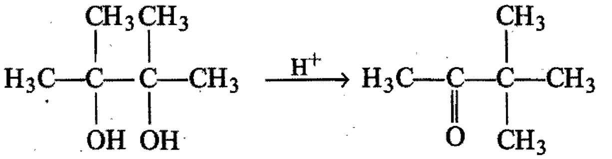


$$H_3C-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3 \xrightarrow[\text{Dil. alk. KMnO}_4]{(O+H_2O)} H_3C-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

2,3-Dimethyl but-2-ene

Pinacol

Pinacol on treatment with mineral acids (HCl) undergoes dehydration and rearrangement to form ketones (Pinacolone).



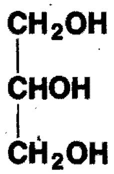
$$H_3C-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow{H^+} H_3C-\underset{O}{\underset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

2,3-Dimethyl butane-2,3-diol (Pinacol)

3,3-Dimethyl butane-2-one (Pinacolone)

This conversion of pinacol into pinacolone is an example of 1,2-alkyl shift and is termed **Pinacol-Pinacolone rearrangement** (or simply pinacol rearrangement).

9.13 GLYCEROL OR GLYCERINE,

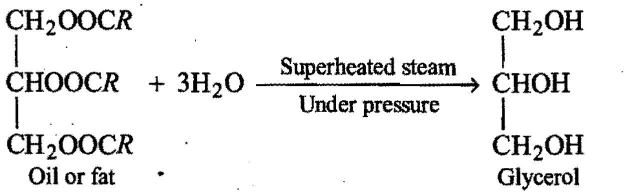


$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}$$

Glycerol is a trihydric alcohol. It may be considered as derivative of propane, obtained by replacement of three hydrogen atoms from different carbon atoms by three hydroxyl groups. Its IUPAC name is **propane-l,2,3-triol** and in industry, it is known as glycerine. It occurs in combined state as esters of higher fatty acids like palmitic ($C_{15}H_{31}COOH$), oleic ($C_{17}H_{33}COOH$) and stearic ($C_{17}H_{35}COOH$) in natural fats and oils. These esters are called glycerides.

Manufacture

1. From fats and oils : On hydrolysis of fats and oils in superheated steam under pressure, glycerol and higher fatty acids are formed.



$$\begin{array}{l}CH_2OOCR\\|\\CHOOCR\\|\\CH_2OOCR\end{array} + 3H_2O \xrightarrow[\text{Under pressure}]{\text{Superheated steam}} \begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + 3RCOOH$$

Oil or fat

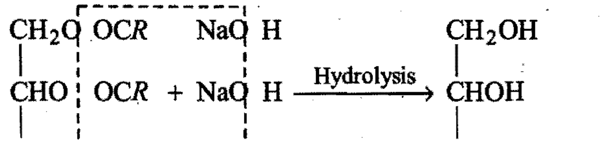
Glycerol

Fatty acid (Waxy solid used in candle manufacture)

Some examples of fatty acids are:

$C_{17}H_{35}COOH$	Stearic acid (formed by hydrolysis of fat)
$C_{15}H_{31}COOH$	Palmitic acid (formed by hydrolysis of fat)
$C_{17}H_{33}COOH$	Oleic acid (formed by hydrolysis of oil)

The hydrolysis is carried out either by alkali solution (Lye) or by superheated steam.



$$\begin{array}{l}CH_2O\;OCR\\|\\CHO\;OCR\\|\\CH_2O\;OCR\end{array} + \begin{array}{l}NaO\;H\\NaO\;H\\NaO\;H\end{array} \xrightarrow{\text{Hydrolysis}} \begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + 3RCOONa$$

Fat or oil

Alkali

Glycerol

Soap (Sodium salt of higher fatty acids)

Since, sodium or potassium salts of higher fatty acids are called **soaps** and this alkaline hydrolysis of oils and fats is called **'saponification'.**

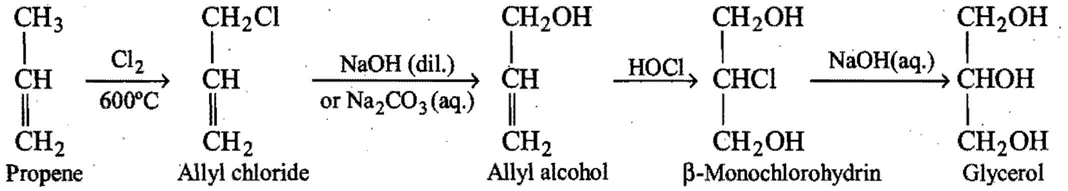
In the manufacture of soap (sodium salt of higher fatty acids) and fatty acids (required in candle industry), glycerol is obtained as byproduct.

2. By fermentation of sugars : During alcoholic fermentation of sugar about 3% glycerol is formed. However, if the fermentation is done in presence of sodium sulphite, the yield can be increased to 25%.

$$C_6H_{12}O_6 \xrightarrow[Na_2SO_3]{\text{Yeast}} C_3H_8O_3 + CH_3CHO + CO_2$$

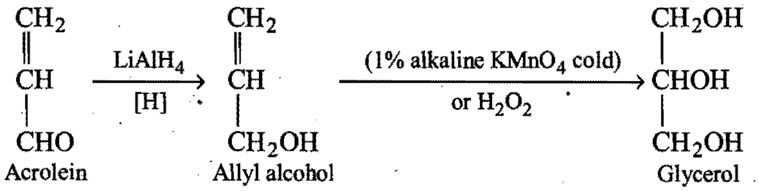
Glucose (Aq. solution) Glycerol Acetaldehyde

3. Synthesis (from propene) : Today much of glycerol is obtained from propene (a product of catalytic cracking of petroleum).



$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[600^\circ C]{Cl_2} \underset{\text{Allyl chloride}}{CH_2Cl-CH=CH_2} \xrightarrow[\text{or } Na_2CO_3(aq.)]{NaOH\text{ (dil.)}} \underset{\text{Allyl alcohol}}{CH_2OH-CH=CH_2} \xrightarrow{HOCl} \underset{\beta\text{-Monochlorohydrin}}{CH_2OH-CHCl-CH_2OH} \xrightarrow{NaOH(aq.)} \underset{\text{Glycerol}}{CH_2OH-CHOH-CH_2OH}$$

4. From acrolein : Acrolein on reduction with $LiAlH_4$ gives allyl alcohol, which on treatment with Baeyer's reagent gives glycerol.



$$\underset{\text{Acrolein}}{CH_2=CH-CHO} \xrightarrow[[H]]{LiAlH_4} \underset{\text{Allyl alcohol}}{CH_2=CH-CH_2OH} \xrightarrow[\text{or } H_2O_2]{(1\%\text{ alkaline } KMnO_4 \text{ cold})} \underset{\text{Glycerol}}{CH_2OH-CHOH-CH_2OH}$$

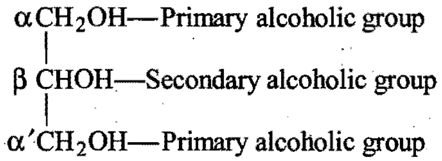
Physical properties : (i) It is a colourless, odourless, viscous and hygroscopic liquid.

(ii) The liquid is sweet in taste and non-toxic in nature and steam volatile.

(iii) It is soluble in water and ethyl alcohol but insoluble in ether.

(iv) It has high boiling point, *i.e.*, 290°C. The high viscosity and high boiling point of glycerol are due to association through extensive intermolecular hydrogen bonding.

Chemical properties : The molecule of glycerol contains two primary —OH groups and one secondary —OH group. Thus, it shows characteristics of both primary and secondary alcohols. The carbon atoms in glycerol are indicated as α, β and α'.



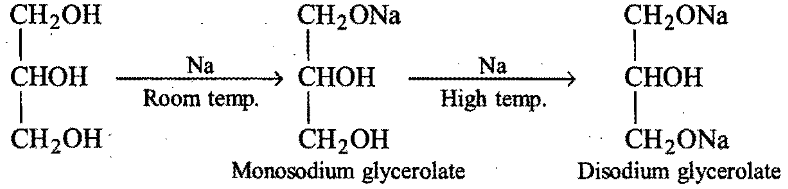
$\alpha\, CH_2OH$—Primary alcoholic group

$\beta\, CHOH$—Secondary alcoholic group

$\alpha'\, CH_2OH$—Primary alcoholic group

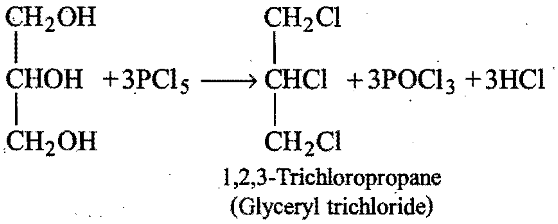
In general, primary —OH groups are more reactive than secondary —OH group.

(i) Reaction with sodium : Only primary alcoholic groups are attacked one by one and secondary alcoholic group is not attacked. Sodium forms monosodium glycerolate at room temperature and disodium glycerolate at higher temperature.

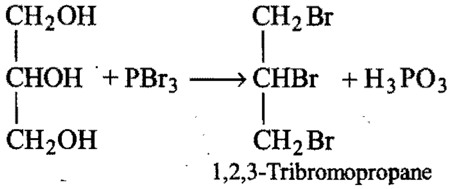


$$CH_2OH-CHOH-CH_2OH \xrightarrow[\text{Room temp.}]{Na} \underset{\text{Monosodium glycerolate}}{CH_2ONa-CHOH-CH_2OH} \xrightarrow[\text{High temp.}]{Na} \underset{\text{Disodium glycerolate}}{CH_2ONa-CHOH-CH_2ONa}$$

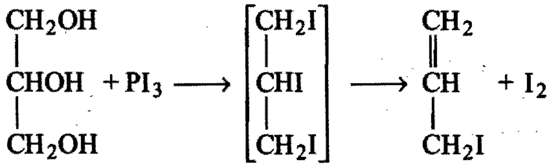
(ii) Reaction with PCl_5, PBr_3 and PI_3 : All three —OH groups are replaced by halogen atoms.



$$CH_2OH-CHOH-CH_2OH + 3PCl_5 \longrightarrow \underset{\substack{\text{1,2,3-Trichloropropane}\\ \text{(Glyceryl trichloride)}}}{CH_2Cl-CHCl-CH_2Cl} + 3POCl_3 + 3HCl$$



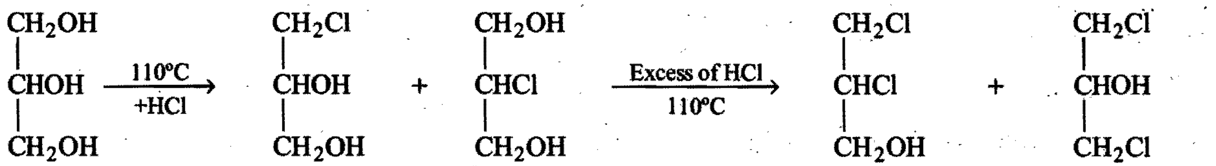
$$CH_2OH-CHOH-CH_2OH + PBr_3 \longrightarrow \underset{\text{1,2,3-Tribromopropane}}{CH_2Br-CHBr-CH_2Br} + H_3PO_3$$



$$CH_2OH-CHOH-CH_2OH + PI_3 \longrightarrow [CH_2I-CHI-CH_2I] \longrightarrow CH_2{=}CH-CH_2I + I_2$$

(Unstable) Allyl iodide

(iii) Reaction with HCl or HBr : When HCl (gas) is passed into glycerol at 110°C, both α or β-glycerol monochlorohydrins are formed. If the HCl gas is passed for sufficient time, glycerol α, α′-dichlorohydrin and glycerol α, β-dichlorohydrin are formed.



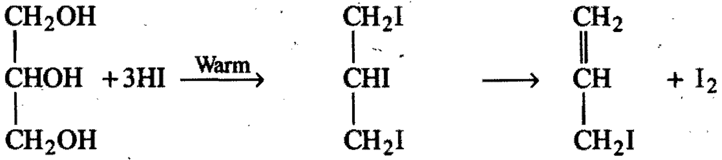
$$CH_2OH-CHOH-CH_2OH \xrightarrow[+HCl]{110^\circ C} CH_2Cl-CHOH-CH_2OH + CH_2OH-CHCl-CH_2OH \xrightarrow[110^\circ C]{\text{Excess of HCl}} CH_2Cl-CHCl-CH_2OH + CH_2Cl-CHOH-CH_2Cl$$

Glycerol; α-Glycerol monochlorohydrin (66%); β-Glycerol monochlorohydrin (34%); Glycerol α,β-dichlorohydrin; Glycerol α,α′-dichlorohydrin (56%)

Same reactions occur with HBr.

(iv) Reaction with HI : Glycerol reacts with HI in two ways:

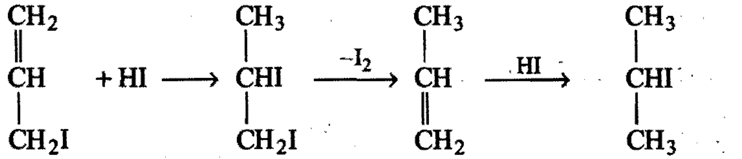
(a) When glycerol is warmed with a small amount of hydrogen iodide, allyl iodide is formed.



$$CH_2OH-CHOH-CH_2OH + 3HI \xrightarrow{\text{Warm}} CH_2I-CHI-CH_2I \longrightarrow CH_2{=}CH-CH_2I + I_2$$

Glycerol; 1,2,3-Tri-iodopropane (Unstable); Allyl iodide

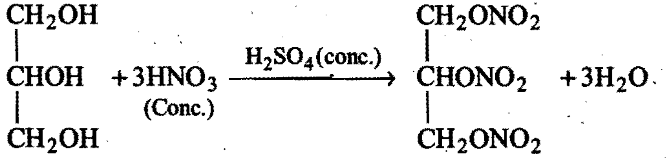
(b) When glycerol is heated with a large amount of HI, the allyl iodide first formed is reduced to propene, which in presence of excess of HI forms isopropyl iodide.



$$CH_2{=}CH-CH_2I + HI \longrightarrow CH_3-CHI-CH_2I \xrightarrow{-I_2} CH_3-CH{=}CH_2 \xrightarrow{HI} CH_3-CHI-CH_3$$

Allyl iodide; Unstable; Propene; Isopropyl iodide

(v) Reaction with (conc.) nitric acid : When one part of glycerol in a thin stream is added to three times concentrated nitric acid and five parts of concentrated sulphuric acid, nitroglycerine (glyceryl trinitrate) or Nobel's oil is formed.



$$CH_2OH-CHOH-CH_2OH + \underset{(Conc.)}{3HNO_3} \xrightarrow{H_2SO_4(conc.)} CH_2ONO_2-CHONO_2-CH_2ONO_2 + 3H_2O$$

Glycerol; Glyceryl trinitrate (T.N.G.)

Glyceryl trinitrate is an yellow oily liquid. It is poisonous and causes headache. It explodes violently when heated rapidly or subjected to sudden shock. Nitroglycerine is not only an explosive but it is also a medicine for heart patients as vasodilator.It releases large volume of gases and occupy 10,900 times the volume of nitroglycerine.

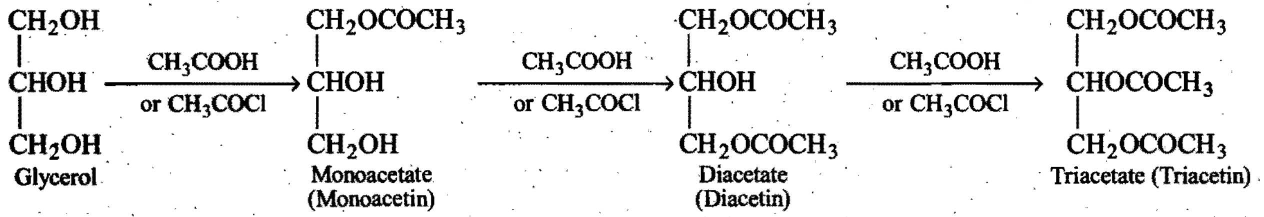
$$4C_3H_5(ONO_2)_3 \longrightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

It becomes a safer explosive when absorbed on kieselguhr. In this form, it is known as **dynamite.** Dynamite was discovered by Alfred Nobel in 1867. The other important explosives prepared from glyceryl trinitrate are:

(a) Blasting gelatin—A mixture of glyceryl trinitrate and cellulose nitrate (gun cotton).

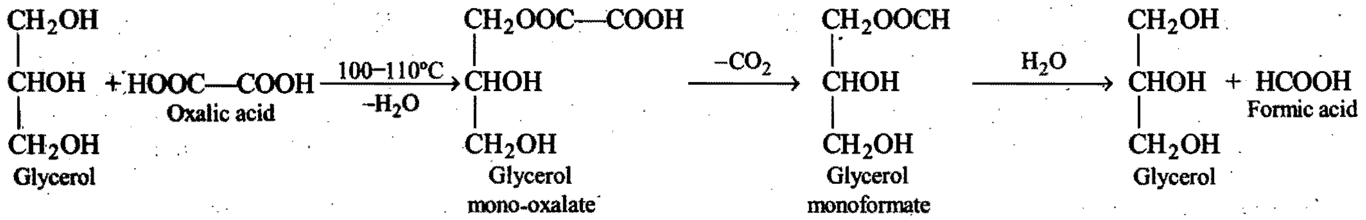
(b) Cordite—It is obtained by mixing glyceryl trinitrate with gun cotton and vaseline. It is smokeless explosive.

(vi) Reaction with CH_3COOH, acetic anhydride or acetyl chloride : Mono-, di- and tri-esters are formed.

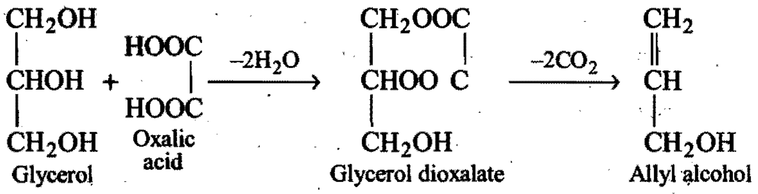


(vii) Reaction with oxalic acid : Different products are formed under different conditions.

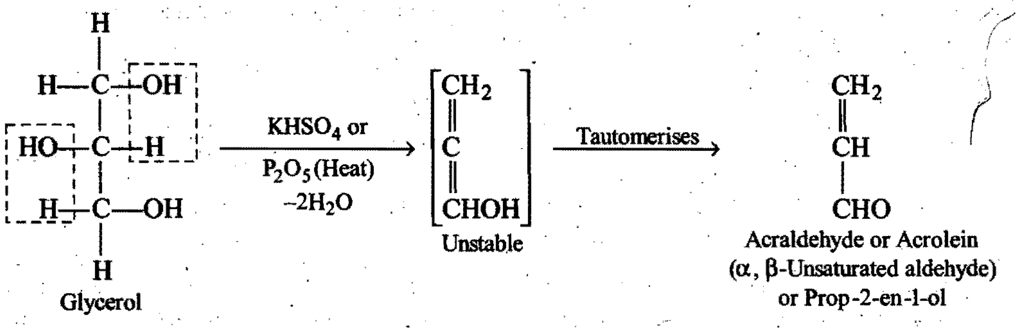
(a) At 110°C and with excess of oxalic acid, formic acid is formed.



(b) At 260°C, allyl alcohol is formed.

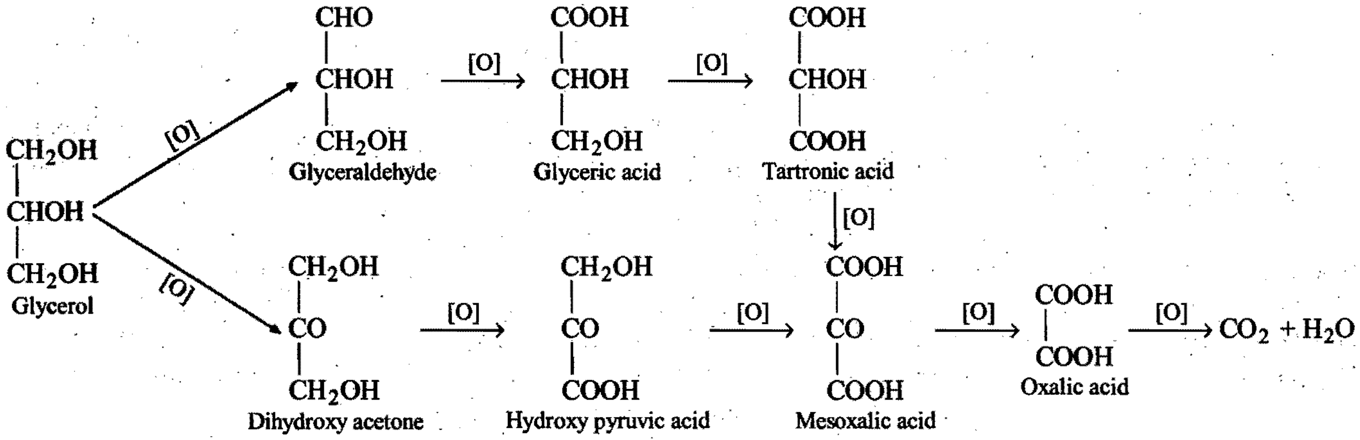


(viii) Dehydration : Glycerol when heated alone or with dehydrating agents such as potassium hydrogen sulphate or phosphorus pentoxide or concentrated sulphuric acid, acrolein or acraldehyde is formed which has a characteristic bad smell.



This reaction can be used as a test of glycerol.

(ix) Oxidation : Glycerol gives different oxidation products depending on the nature of oxidising agent. The following products may be visualised during oxidation of glycerol.



(a) Conc. HNO_3 gives mainly glyceric acid.

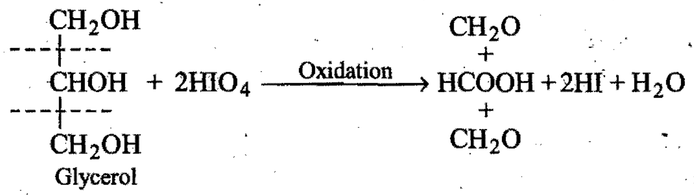
(b) Dilute HNO_3 oxidises glycerol into glyceric acid and tartronic acid.

(c) Bismuth nitrate, $Bi(NO_3)_3$ or $NaNO_3$ gives mainly mesoxalic acid.

(d) Fenton's reagent ($H_2O_2 + FeSO_4$) or NaOBr or Br_2 water in presence of Na_2CO_3 oxidises glycerol into a mixture of glyceraldehyde and dihydroxy acetone (or glycerose) which on addition of dil. NaOH gives **dl-fructose.**

(e) With solid $KMnO_4$, glycerol is oxidised to oxalic acid and carbon dioxide. The reaction is violent and explosion occurs, hence, used in **time-bombs.**

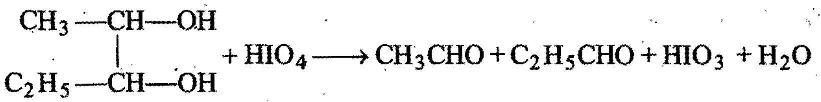
Glycerol undergoes oxidative cleavage by HIO_4 (periodic acid) giving formaldehyde and formic acid.



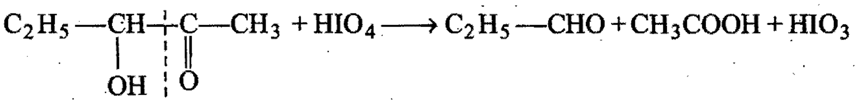
$$\underset{\text{Glycerol}}{\begin{array}{c}CH_2OH\\ \text{---}|\text{---}\\ CHOH\\ \text{---}|\text{---}\\ CH_2OH\end{array}} + 2HIO_4 \xrightarrow{\text{Oxidation}} \begin{array}{c}CH_2O\\ +\\ HCOOH + 2HI + H_2O\\ +\\ CH_2O\end{array}$$

HIO_4 is specific reagent for cleavage of C—C bond if two —OH groups or —OH and carbonyl group or only carbonyl $\left(\overset{O}{\overset{\|}{-C-}}\right)$ group are present at adjacent carbons.

e.g.,

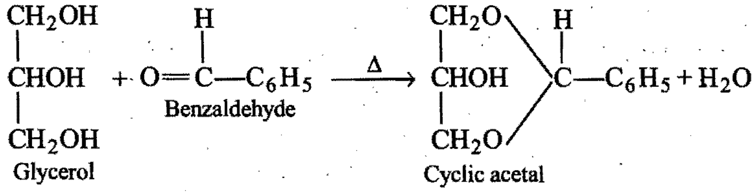


$$\begin{array}{l}CH_3-CH-OH\\ \qquad\quad\;\; |\\ C_2H_5-CH-OH\end{array} + HIO_4 \longrightarrow CH_3CHO + C_2H_5CHO + HIO_3 + H_2O$$



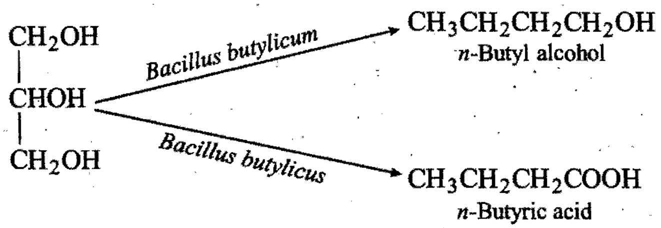
$$C_2H_5-\underset{OH}{\underset{|}{CH}}\,\vdots\,\underset{O}{\underset{\|}{C}}-CH_3 + HIO_4 \longrightarrow C_2H_5-CHO + CH_3COOH + HIO_3$$

(x) **Formation of cyclic acetal :** Glycerol gives acetal when mixture of glycerol and benzaldehyde is heated or treated with HCl in cold.



Glycerol Benzaldehyde Cyclic acetal

(xi) **Fermentation:**



(xii) **Reaction with phthalic anhydride :** Glycerol (or glycol) on treatment with phthalic acid (or anhydride) gives polyester called **glyptals.**

Uses : Glycerol is used:

(i) as a sweetening agent in confectionery, beverages and medicines being non-toxic in nature.
(ii) in the manufacture of explosives like dynamite and cordite.
(iii) in the manufacture of plastics and synthetic fibres and alkyd resins.
(iv) as antifreeze in automobile radiators.
(v) in the preparation of good quality of transparent soap, hand lotions, vanishing creams, shaving creams and tooth pastes.
(vi) in the manufacture of various organic compounds like formic acid, allyl alcohol, acrolein, etc.
(vii) as a lubricant in watches and clocks.
(viii) in the preparation of non-drying inks, printing inks and stamp pad inks.
(ix) as a preservative.

Analytical Tests of Glycerol

(i) **Acrolein test :** When glycerol is heated with potassium hydrogen sulphate, a very offensive odour is produced due to formation of acrolein. Its aqueous solution restores the colour of Schiff's reagent and reduces Fehling's solution and Tollens' reagent.

(ii) **Dunstan's test :** A drop of phenolphthalein is added to approximately 5 mL of borax solution. The pink colour appears. On adding 2-3 drops of glycerol, the pink colour disappears. The pink colour reappears on heating and disappears on cooling again.

(iii) To an equimolar mixture of phenol and glycerol, few drops of conc. H_2SO_4 are added and heated to 130°C. It is then cooled by adding water. Addition of ammonium hydroxide to this solution produces red colour.

9.14 ESTIMATION OF THE NUMBER OF HYDROXYL GROUPS IN A POLYHYDRIC ALCOHOL

A known mass (Wg) of the acetyl derivative of the polyhydric alcohol is taken. It is mixed with V mL (excess) of a standard alkali solution (KOH). Both are refluxed. Alkali is used in the hydrolysis of acetyl derivative. The unused alkali is measured by doing titration with a standard acid solution. Let the used alkali be w g. Let the alcohol's formula be $A(OH)_n$, *i. e.*, one molecule consists nOH groups. Let the molecular mass of the alcohol be M.

$$A(OH)_n \xrightarrow{CH_3COCl} A(OCOCH_3)_n \xrightarrow[56n\text{ g}]{n\text{KOH}} A(OH)_n + nCH_3COOK$$

Mol. mass M $\qquad (M - n + 43n) = M + 42n$

W g of the acetyl derivative utilises w g of KOH

$$(M + 42n)\text{ g of acetyl derivative will require} = \frac{w}{W} \times (M + 42n)\text{g of KOH}$$

It should be equal to 56n. $\qquad \frac{w}{W}(M + 42n) = 56n$

From this equation, n can be determined.

Problem 5. 0.436 *g of acetyl derivative of a polyhydric alcohol (molecular mass* = 92*) require* 0.336 g KOH *for hydrolysis. Calculate the number of hydroxy groups in the alcohol.*

Solution : We know that, $\qquad \frac{w}{W}(M + 42n) = 56n$

where w is the amount of alkali, W amount of acetyl derivative, M is the molecular mass of alcohol and n number of hydroxyl groups.

$$\frac{0.336}{0.436}(92 + 42n) = 56n$$

or $$92 + 42n = \frac{0.436}{0.336} \times 56n = \frac{218}{3}n$$

or $$276 + 126n = 218n \quad \text{or} \quad n = 3$$

(The alcohol is trihydric.)

9.15 UNSATURATED ALCOHOLS

Vinyl alcohol, $H_2C{=}CHOH$, is still unknown. Whenever an attempt is made to prepare vinyl alcohol, acetaldehyde is formed in its place.

$$\underset{\text{Vinyl bromide}}{H_2C{=}CHBr} + AgOH \longrightarrow [H_2C{=}CHOH] \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}$$

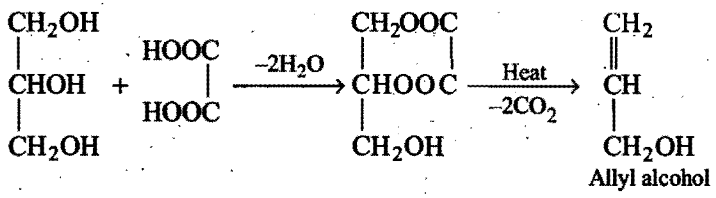
However, **allyl alcohol**, $CH_2{=}CHCH_2OH$, is known.

It is prepared by the application of following methods:

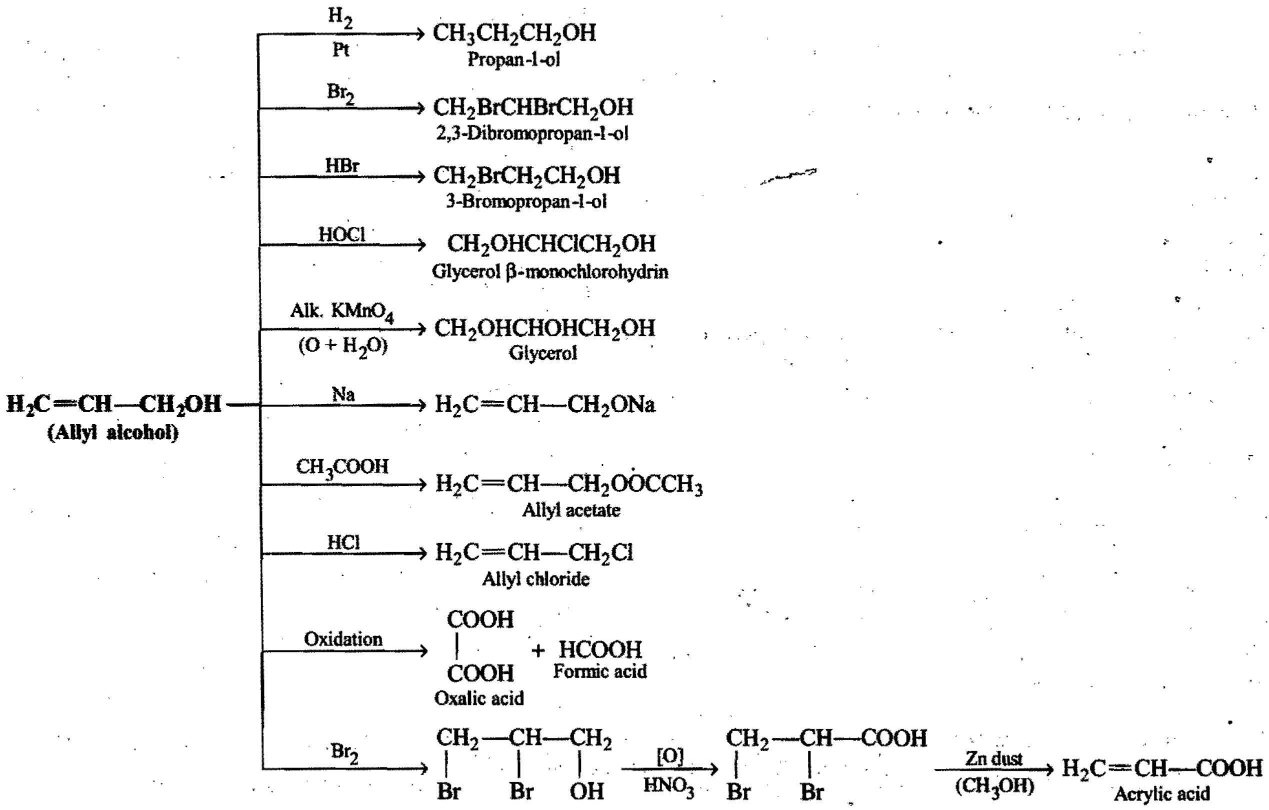
(1) **From allyl halide :** Allyl chloride or allyl bromide undergoes hydrolysis when boiled with water. The formation of allyl alcohol occurs.

$$H_2C{=}CH{-}CH_2Br + H_2O \longrightarrow \underset{\text{Allyl alcohol}}{H_2C{=}CH{-}CH_2OH} + HBr$$

(2) By heating glycerol with oxalic acid at 260°C.



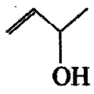
Properties : It is a colourless pungent smelling liquid. It is soluble in water, alcohol and ether in all proportions. It shows the properties of an unsaturated compound and a primary alcohol.



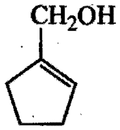
ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Give the IUPAC names of the following:

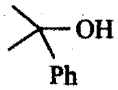
(a)



(b)



(c)



[Ans : (a) But-3-en-2-ol, (b) 1-Cyclopentenyl methanol, (c) 2-Phenylpropan-2-ol]

2. A compound soluble in conc. H_2SO_4. It does not decolourise bromine in CCl_4 but oxidised by chromic anhydride in aqueous H_2SO_4 within two seconds, turning orange solution to blue, green and then opaque. The original compound is :
   - (a) an alkene
   - (b) a primary alcohol
   - (c) a tertiary alcohol
   - (d) an ether

   [Ans (b)]

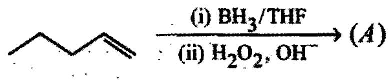
3. Lucas reagent is :
   - (a) anhydrous $CaCl_2$ and conc. HCl
   - (b) anhydrous $ZnCl_2$ and conc. HCl
   - (c) anhydrous $AlCl_3$ and conc. HCl
   - (d) anhydrous $PdCl_2$ and conc. HCl

   [Ans (b)]

4. Glucose on fermentation in presence of sodium sulphite gives mainly:
   - (a) ethylene glycol and acetaldehyde
   - (b) glycerol and propionaldehyde
   - (c) glycerol and acetaldehyde
   - (d) ethyl alcohol and propionaldehyde

   [Ans (c)]

5. What is the product (*A*) in the following reaction?



   - (a) Pentan-1-ol
   - (b) 2-Methyl butan-1-ol
   - (c) 2-Methyl butan-2-ol
   - (d) 3-Methyl butan-1-ol

   [Ans (a)]

6. Acrolein on complete reduction gives:
   - (a) propanal

(b) allyl alcohol
(c) propane
(d) propan-l-ol
[Ans : (d)]

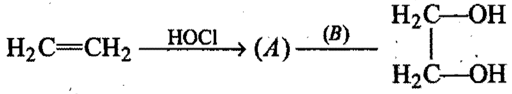
[Hint : $H_2C{=}CHCHO + 4H \xrightarrow[\text{Catalyst}]{\text{Ni}} CH_3CH_2CH_2OH$]

7. Ethyl alcohol can be prepared from Grignard reagent by the reaction of :
(a) HCHO
(b) CH_3CHO
(c) RCN
(d) $RCOCl$
[Ans : (a)]

8. Propene on reaction with carbon monoxide and hydrogen at high temperature under pressure in presence of cobalt carbonyl catalyst gives:
(a) butan-1-ol
(b) 2-methyl propan-l-ol
(c) 2-methyl propan-2-ol
(d) a mixture of butan-1-ol and 2-methyl propan-1-ol
[Ans : (d)]

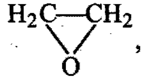
9. During the dehydration of alcohols to alkenes by heating with conc. H_2SO_4, the initiating step is:
(a) elimination of water
(b) protonation of an alcohol molecule
(c) formation of an ester
(d) formation of carbocation
[Ans : (b)]

10. In this reaction,



$H_2C{=}CH_2 \xrightarrow{\text{HOCl}} (A) \xrightarrow{(B)}$

the molecule (*A*) and the reagent (*B*) are :

(a)  , hot water
(b) CH_3CH_2OH, H_2SO_4
(c) $ClCH_2{-}CH_2OH, NaHCO_3$
(d) $CH_3CH_2Cl, NaOH$
[Ans : (c)]

11. The conversion,
$CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCH_2OH$, can be affected with :
(a) H_2/Ni (b) Zn/HCl
(c) $NaBH_4$ (d) none of these
[Ans : (c)]

12. The enzyme which can catalyse the conversion of sucrose to ethanol is (are) :
(a) invertase (b) zymase
(c) maltase (d) diastase
[Ans : (a,b)]

SOME SOLVED PROBLEMS

Problem 6. *Explain:*

(*a*) *Alcohols have higher boiling points than alkanes, ethers and alkyl halides of comparable molecular mass.*
(*b*) ROH *with three or fewer carbon atoms are water soluble but those with five or more carbon atoms are insoluble.*
(*c*) *When volumes of ethanol and water are mixed, the total volume is less than the sum of the two individual volumes.*
(*d*) *Ethanol cannot be used as a solvent with Grignard reagent or* $LiAlH_4$.
(*e*) *The relative acidity of alcohols is in the order of* $3° < 2° < 1° < CH_3OH$.
(*f*) *Sodium metal cannot be used to remove last traces of water from ethanol.*

Solution : (a) O—H bond of alcohols is highly polarized. This gives rise to intrahydrogen bonding, *i.e.*, molecules are brought nearer to each other and held together by attractive forces. No such hydrogen bonding exists in alkanes, ethers and alkyl halides. This is the reason why the boiling points of alcohols are higher than alkanes, ethers and alkyl halides of comparable mass.

(b) The water solubility of alcohols is attributed to hydrogen bonding with water. However, with increase of carbon atoms, the hydrophobic part increases which predominates the hydrophilic part, *i.e.*, OH part of alcohols and thus, the solubility decreases.

(c) Hydrogen bonding between ethanol and water permits the two unlike molecules to move closer in the solution than can ethanol to ethanol and water to water molecules and thus, the total volume decreases.

(d) Ethanol being acidic readily reacts with strongly basic *R* of Grignard reagent.

$$CH_3CH_2OH + RMgX \longrightarrow \underset{\text{Alkane}}{R{-}H} + CH_3CH_2OMgX$$

$LiAlH_4$ reacts with alcohol to form hydrogen.

$$4CH_3CH_2OH + LiAlH_4 \longrightarrow LiAl(OCH_2CH_3)_4 + 4H_2\uparrow$$

(e) The order of decrease of acidity from CH_3OH to 3° alcohol is attributed due to $+I$ effect of alkyl group which intensify the charge on the base RO^- and the removal of proton becomes difficult.

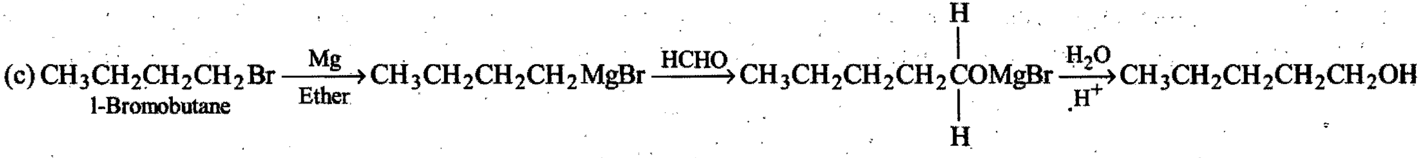
(f) Ethanol being acidic reacts with sodium metal, although not as vigorously as water, and form sodium ethoxide with evolution of hydrogen.

$$2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2$$

Problem 7. *Prepare pentan-1-ol from (a) Pent-1-ene, (b) 1-Bromopentane, (c) 1-Bromobutane and (d) 1-Bromopropane.*

Solution : (a) $\underset{\text{Pent-1-ene}}{CH_3CH_2CH_2CH{=}CH_2} \xrightarrow[THF]{B_2H_6} (CH_3CH_2CH_2CH_2CH_2)_3B \xrightarrow[OH^-]{H_2O_2} \underset{\text{Pentan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH}$

(b) $\underset{\text{1-Bromopentane}}{CH_3CH_2CH_2CH_2CH_2Br} \xrightarrow{OH^-/H_2O} \underset{\text{Pentan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH} + HBr$



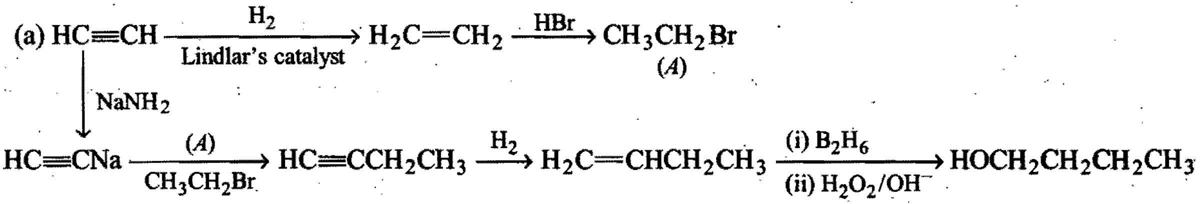
(c) $\underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow[Ether]{Mg} CH_3CH_2CH_2CH_2MgBr \xrightarrow{HCHO} CH_3CH_2CH_2CH_2\overset{H}{\underset{H}{C}}OMgBr \xrightarrow[H^+]{H_2O} CH_3CH_2CH_2CH_2CH_2OH$

(d) $\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[Ether]{Mg} CH_3CH_2CH_2MgBr \xrightarrow{\text{Ethylene oxide}} CH_3CH_2CH_2CH_2CH_2OMgBr \xrightarrow{H^+} CH_3CH_2CH_2CH_2CH_2OH$

Problem 8. *How will you synthesise?*

(a) n-Butyl alcohol from acetylene, (b) Allyl alcohol from propane, (c) Glycerol from acetylene.

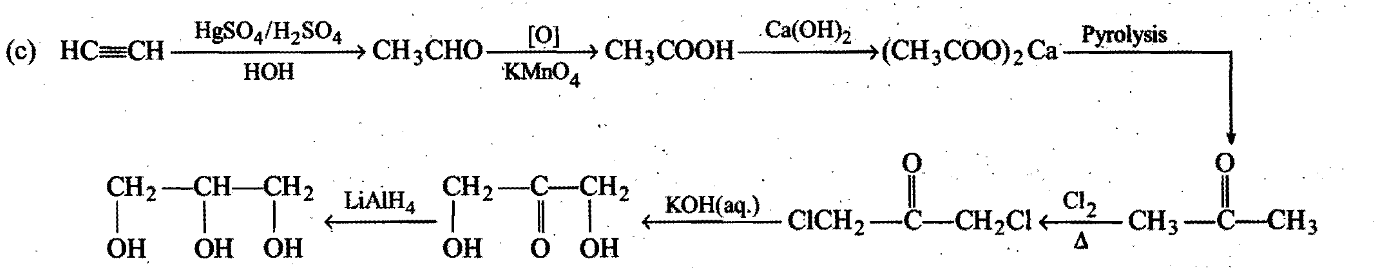
Solution :



(a) $HC{\equiv}CH \xrightarrow[\text{Lindlar's catalyst}]{H_2} H_2C{=}CH_2 \xrightarrow{HBr} \underset{(A)}{CH_3CH_2Br}$

$HC{\equiv}CH \xrightarrow{NaNH_2} HC{\equiv}CNa \xrightarrow[CH_3CH_2Br]{(A)} HC{\equiv}CCH_2CH_3 \xrightarrow{H_2} H_2C{=}CHCH_2CH_3 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} HOCH_2CH_2CH_2CH_3$

(b) $CH_3CH_2CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CHClCH_3 \xrightarrow{\text{Alc. KOH}} H_2C{=}CH{-}CH_3 \xrightarrow[500°C]{Cl_2} H_2C{=}CH{-}CH_2Cl \xrightarrow{AgOH(aq.)} H_2C{=}CH{-}CH_2OH$



(c) $HC{\equiv}CH \xrightarrow[HOH]{HgSO_4/H_2SO_4} CH_3CHO \xrightarrow[KMnO_4]{[O]} CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{\text{Pyrolysis}} CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

$CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xrightarrow[\Delta]{Cl_2} ClCH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_2Cl \xrightarrow{KOH(aq.)} \underset{OH}{CH_2}{-}\underset{O}{\overset{\|}{C}}{-}\underset{OH}{CH_2} \xrightarrow{LiAlH_4} \underset{OH}{CH_2}{-}\underset{OH}{CH}{-}\underset{OH}{CH_2}$

Glycerol

Problem 9. *Give one chemical test to distinguish the following:*

(a) Methanol and ethanol.

(b) Tert. butyl alcohol and n-butyl alcohol.

(c) Hexane and ethanol.

Solution : (a) Ethanol gives iodoform test while methanol does not.

(b) *Tert.* butyl alcohol gives Lucas test, *i.e.*, cloudiness immediately with HCl/$ZnCl_2$ but *n*-butyl alcohol does not.

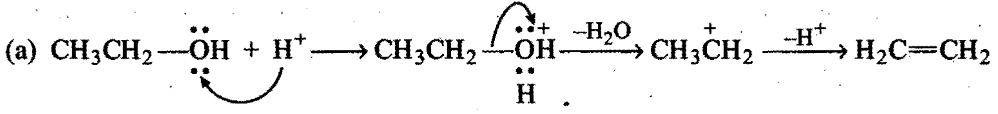
(c) Ethanol reacts with sodium and evolves hydrogen but hexane does not.

Problem 10. *(a) Give the mechanism of acid catalysed dehydration of ethyl alcohol if the reaction is carried at 170°C when ethene is formed.*

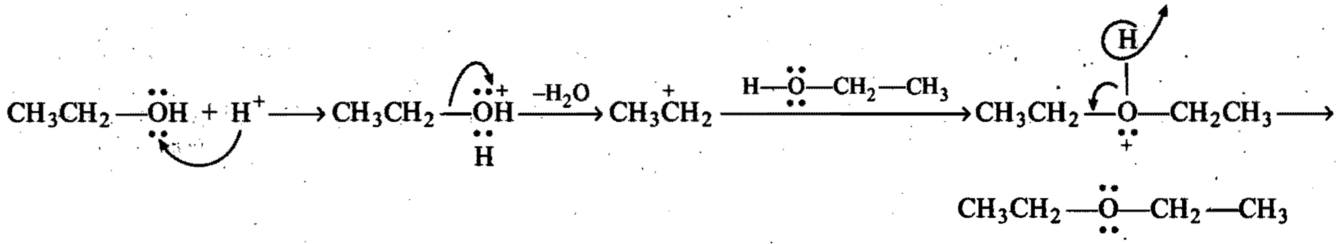
(b) Give the mechanism of acid catalysed dehydration of ethyl alcohol if the reaction is carried at 140°C when ether is formed.

(c) 3,3-Dimethyl butan-2-ol loses a molecule of water in the presence of conc. H_2SO_4 *to give tetramethyl ethylene as a major product. Suggest a suitable mechanism.*

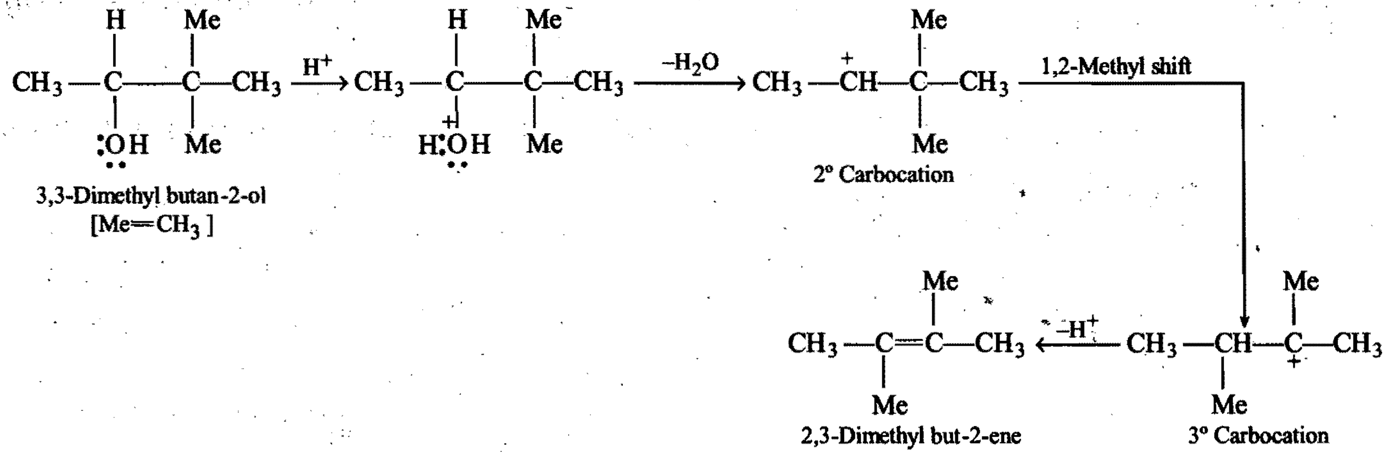
Solution :



(a) $CH_3CH_2{-}\ddot{O}H + H^+ \longrightarrow CH_3CH_2{-}\underset{H}{\overset{+}{\ddot{O}}}H \xrightarrow{-H_2O} CH_3\overset{+}{C}H_2 \xrightarrow{-H^+} H_2C{=}CH_2$

(b)


(c) The hydroxyl group in 3,3-dimethyl butan-2-ol undergoes protonation followed by dehydration to form a secondary carbocation which undergoes a methyl shift to form a more stable *tert.* carbocation and the removal of H^+ gives a double bond.

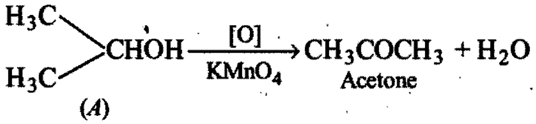


Problem 11. *An alcohol (A) when heated with concentrated* H_2SO_4 *gives an alkene (B). When (B) is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound (C) is obtained. The compound (C) gives (D) when treated with dilute* H_2SO_4 *in presence of* $HgSO_4$. *(D) can also be obtained either by oxidising (A) with* $KMnO_4$ *or from acetic acid through its calcium salt. Identify (A), (B), (C) and (D).*

Solution : (*D*) is obtained by heating calcium acetate. It should be acetone.

$$(CH_3COO)_2Ca \longrightarrow \underset{\text{Acetone}}{\underset{(D)}{CH_3COCH_3}} + CaCO_3$$

(*D*) can also be obtained by oxidation of (*A*). Thus, (*A*) is secondary alcohol, *i.e.*, propan-2-ol.



(*A*) with conc. H_2SO_4 gives an alkene (propene).

$$CH_3CHOHCH_3 \xrightarrow[\text{Heat}]{\text{Conc. } H_2SO_4} \underset{\text{Propene}}{\underset{(B)}{CH_3-CH=CH_2}}$$

(*B*) reacts with bromine to form 1,2-dibromopropane which on dehydrohalogenation yields propyne.

$$CH_3-CH=CH_2 + Br_2 \longrightarrow CH_3CHBrCH_2Br \xrightarrow{NaNH_2} \underset{\text{Propyne } (C)}{CH_3C\equiv CH} \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{Acetone } (D)}{CH_3COCH_3}$$

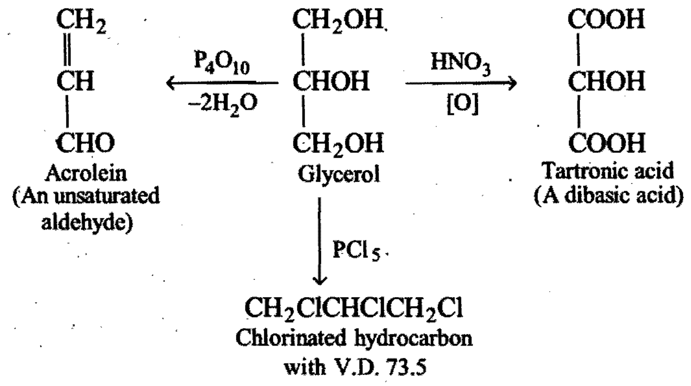
Problem 12. *An organic compound of the formula,* $C_3H_8O_3$, *gave the following reactions:*

(*a*) *On oxidation with nitric acid, it gave a dibasic acid.*

(*b*) *With* P_4O_{10}, *it gave an unsaturated aldehyde.*

(*c*) *With* PCl_5, *it gave a chlorinated hydrocarbon, with vapour density, 73.5. What structural formula would you assign to the compound?*

Solution : The expected compound is glycerol.



Problem 13. *Compound 'X' (molecular formula* C_5H_8O*) does not react appreciably with Lucas reagent at room temperature but gives a white precipitate with ammoniacal silver nitrate solution. With excess of* MeMgBr, 0.42 *g of 'X' gives* 224 *mL of* CH_4 *at STP. Treatment of 'X' with* H_2 *in presence of* Pt *catalyst followed by boiling with HI, gives n-pentane. Suggest the structure for 'X' and write the equations involved.*

Solution : Since, the compound does not react appreciably with Lucas reagent, it is a primary alcohol, *i.e.*, consists —CH_2OH. The compound gives a precipitate with $AgNO_3$, hence it consists —C≡CH group at the extreme. Thus, the compound may be:

$$\overset{5}{HC}\equiv\overset{4}{C}-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2OH$$

4-Pentyn-1-ol

$$\text{Molecular mass of 'X'} = 84\text{ g}$$

$$0.42\text{ g of compound} = \frac{0.42}{84} = 0.005\text{ mol}$$

$$224\text{ mL of }CH_4 = \frac{224}{22400} = 0.01\text{ mol}$$

0.005 mol of the compound '*X*' produces 0.01 mol of CH_4 with excess of MeMgBr, it shows that the compound consists two active hydrogen atoms, one due to hydroxyl group and other due to HC≡C— group. The equations of the reactions involved are:

(i) $HC\equiv C-CH_2-CH_2-CH_2OH \xrightarrow{AgNO_3} Ag-C\equiv C-CH_2-CH_2-CH_2OH$

(ii) $HC\equiv C-CH_2-CH_2-CH_2OH \xrightarrow{MeMgBr} BrMg-C\equiv C-CH_2-CH_2CH_2OMgBr + 2CH_4$

(iii) $HC\equiv C-CH_2-CH_2-CH_2OH \xrightarrow[Pt]{H_2} H_3C-CH_2-CH_2-CH_2-CH_2OH \xrightarrow[Boil]{HI} H_3C-CH_2-CH_2-CH_2-CH_3$

Problem 14. *An organic compound of formula* $C_3H_8O_3$ *yields on acetylation with acetic anhydride a derivative of the formula* $C_9H_{14}O_6$*. How many hydroxyl groups are present in the compound?*

Solution : $R-OH \xrightarrow{(CH_3CO)_2O} ROCOCH_3$

In this reaction for every —OH group, C_2H_2O is increased on acetylation.

$$\text{Total increase} = C_9H_{14}O_6 - C_3H_8O_3 = C_6H_6O_3$$

Thus, the increase is equivalent to the presence of 3—OH groups in the alcohol.

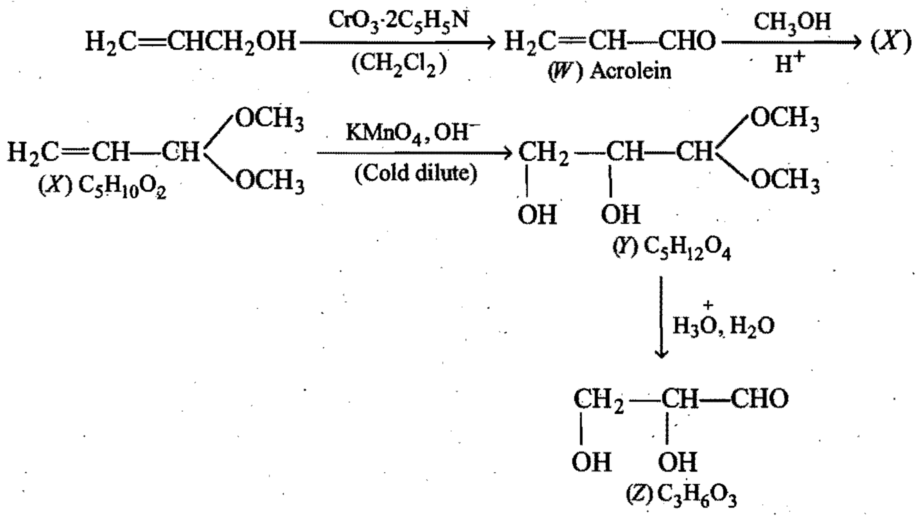
Problem 15. *Give the structures of (W), (X), (Y) and (Z) in the following reactions:*

$$H_2C=CH-CH_2OH \xrightarrow[(CH_2Cl_2)]{CrO_3\cdot 2C_5H_5N} (W) \xrightarrow[H^+]{CH_3OH} (X)$$

$$(X)C_5H_{10}O_2 \xrightarrow[\text{(Cold dilute)}]{KMnO_4,\ OH^-} (Y)C_5H_{12}O_4 \xrightarrow[H_2O]{H_3O^+} (Z)C_3H_6O_3$$

[Roorkee 2000]

Solution :



$$H_2C{=}CHCH_2OH \xrightarrow[(CH_2Cl_2)]{CrO_3\cdot 2C_5H_5N} \underset{(W)\ \text{Acrolein}}{H_2C{=}CH{-}CHO} \xrightarrow[H^+]{CH_3OH} (X)$$

$$\underset{(X)\ C_5H_{10}O_2}{H_2C{=}CH{-}CH\langle{}^{OCH_3}_{OCH_3}} \xrightarrow[\text{(Cold dilute)}]{KMnO_4,\ OH^-} \underset{(Y)\ C_5H_{12}O_4}{\underset{OH}{CH_2}-\underset{OH}{CH}-CH\langle{}^{OCH_3}_{OCH_3}}$$

$$\xrightarrow{\overset{+}{H_3O},\ H_2O} \underset{(Z)\ C_3H_6O_3}{\underset{OH}{CH_2}-\underset{OH}{CH}-CHO}$$

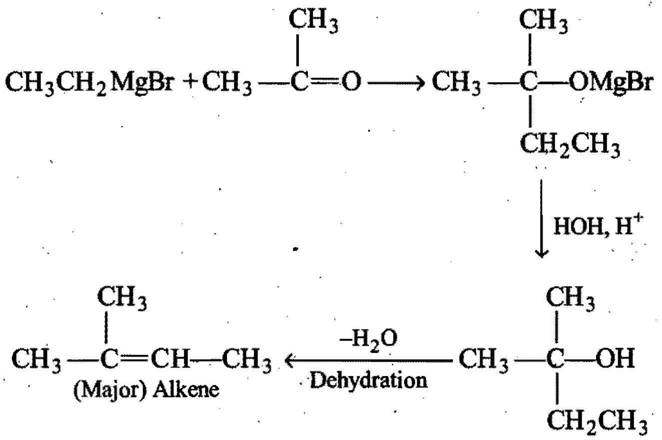
Problem 16. $(A) \xrightarrow[250°C]{Al_2O_3} (B) \xrightarrow[(ii)\ AgOH]{(i)\ HI} (C) \xrightarrow[150°C]{Al_2O_3} (B) \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6} (A)$

In the above reactions scheme (A) and (C) are isomers. (B) has a formula of C_5H_{10}*, which can also be obtained from the product of the reactions of* CH_3CH_2MgBr *and* $(CH_3)_2CO$*. Give structures of (A), (B) and (C).* **[Roorkee 2000]**

Solution :

$$\underset{(A)}{\text{An alcohol}} \xrightarrow[250°C]{Al_2O_3} \underset{(B)\ C_5H_{10}}{\text{Alkene}} \xrightarrow[(ii)\ AgOH]{(i)\ HI} (C)$$

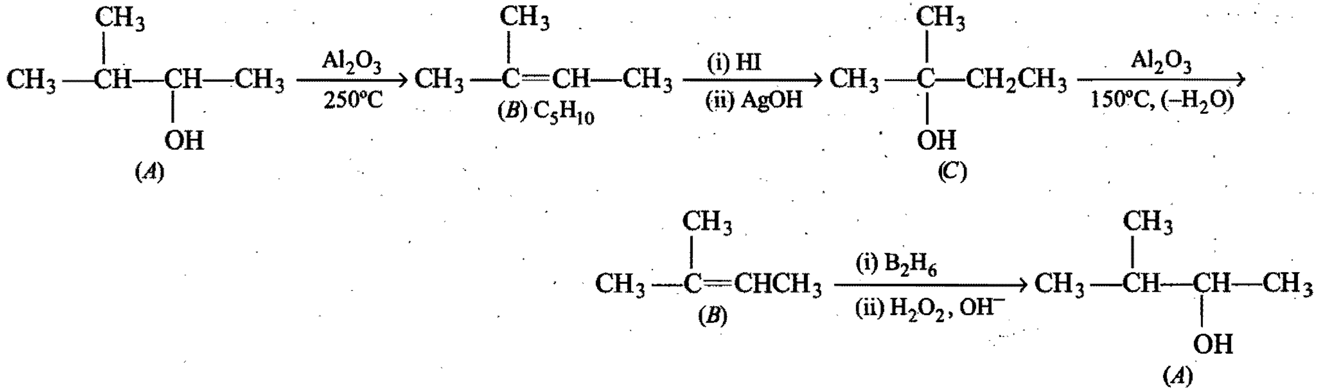
$$\underset{(C)}{\text{Alcohol}} \xrightarrow[150°C]{Al_2O_3} \underset{(B)}{\text{Alkene}} \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6} \underset{(A)}{\text{Alcohol}}$$



$$CH_3CH_2MgBr + CH_3-\overset{CH_3}{C}{=}O \longrightarrow CH_3-\overset{CH_3}{\underset{CH_2CH_3}{C}}-OMgBr$$

$$\xrightarrow{HOH,\ H^+} CH_3-\overset{CH_3}{\underset{CH_2CH_3}{C}}-OH \xrightarrow[\text{Dehydration}]{-H_2O} \underset{\text{(Major) Alkene}}{CH_3-\overset{CH_3}{C}{=}CH-CH_3}$$

So,

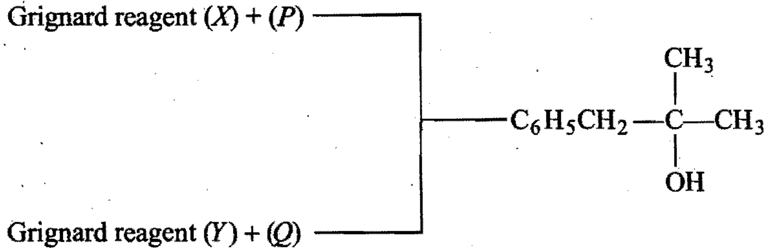


$$\underset{(A)}{CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}-CH_3} \xrightarrow[250°C]{Al_2O_3} \underset{(B)\ C_5H_{10}}{CH_3-\overset{CH_3}{C}{=}CH-CH_3} \xrightarrow[(ii)\ AgOH]{(i)\ HI} \underset{(C)}{CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2CH_3} \xrightarrow[150°C,\ (-H_2O)]{Al_2O_3}$$

$$\underset{(B)}{CH_3-\overset{CH_3}{C}{=}CHCH_3} \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6} \underset{(A)}{CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}-CH_3}$$

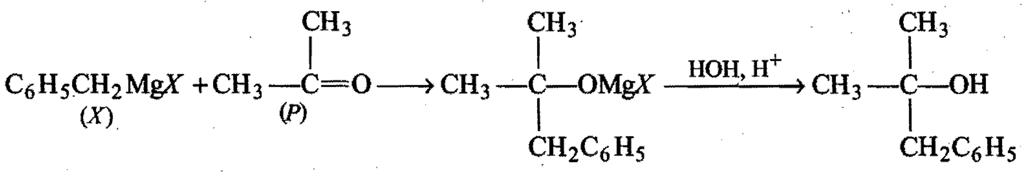
Problem 17. *Two different Grignard reagents (X) and (Y) produce* $C_6H_5CH_2C(CH_3)_2OH$ *on reaction with (P) and (Q) respectively. Give the structures of (X), (Y), (P) and (Q).* **[Roorkee 2000]**

Solution :

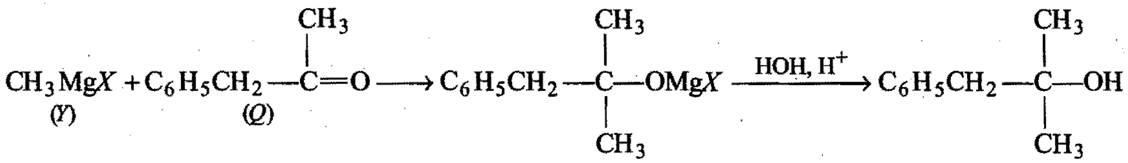


$$\left.\begin{array}{l}\text{Grignard reagent } (X) + (P) \\ \\ \text{Grignard reagent } (Y) + (Q)\end{array}\right] \longrightarrow C_6H_5CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OH}{|}}{C}}-CH_3$$

So,



$$\underset{(X)}{C_6H_5CH_2MgX} + \underset{(P)}{CH_3-\overset{\overset{\large CH_3}{|}}{C}=O} \longrightarrow CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_2C_6H_5}{|}}{C}}-OMgX \xrightarrow{HOH,\ H^+} CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_2C_6H_5}{|}}{C}}-OH$$



$$\underset{(Y)}{CH_3MgX} + \underset{(Q)}{C_6H_5CH_2-\overset{\overset{\large CH_3}{|}}{C}=O} \longrightarrow C_6H_5CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-OMgX \xrightarrow{HOH,\ H^+} C_6H_5CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-OH$$

IMPORTANT POINTS TO REMEMBER (SUMMARY)

☐ Alcohols are hydroxy derivatives of alkanes and also considered as alkyl derivatives of water.

☐ Alcohols are classified as monohydric, dihydric, trihydric and polyhydric depending upon the number of one, two, three and more —OH groups respectively in a molecule on different carbon atoms.

☐ **Monohydric alcohols** (R—OH) are represented by a general molecular formula $C_nH_{2n+1}OH$ ($C_nH_{2n+2}O$). They are further divided into primary (1°), secondary (2°) and tertiary (3°) alcohols as $-CH_2OH$, $>$CHOH and $-\overset{|}{\underset{|}{C}}-OH$ respectively.

☐ Monohydric saturated alcohols show **chain** isomerism, **position** isomerism, **functional** isomerism and **optical** isomerism.

Methods of preparation for monohydric alcohols

☐ **From alkyl halides :** By the hydrolysis with aqueous alkali or moist silver oxide. 1°—RX gives good yield of alcohols, 2°—RX gives a mixture of alcohol and alkene, while 3°—RX mainly gives alkene due to dehydrohalogenation.

Hydrolysis of 1° halides proceeds by S_N2 mechanism while those of 3° halide by S_N1 mechanism. The hydrolysis of 2° alkyl halides may proceed by S_N1 or S_N2 method.

☐ **From alkenes** (by hydration method) :

Alkenes are absorbed in cold conc. H_2SO_4 forming alkyl hydrogen sulphates which on hydrolysis with boiling water form alcohols. Only ethene gives 1° alcohol while all other alkenes give 2° or 3° alcohols.

Alkenes may be directly hydrated to alcohols in presence of dilute acids (H^+).

☐ **Oxymercuration demercuration method :** Mercuric acetate $(CH_3COO)_2Hg$, in presence of water-THF solution reacts with alkene to form an adduct alkyl mercury compound which on reduction with $NaBH_4$ in basic medium forms alcohol.

☐ **Hydroboration Oxidation (HBO) method :** Alkenes undergo addition reaction with diborane $(BH_3)_2$ followed by hydrolysis with H_2O_2/OH^- yield alcohols. The overall addition of water proceeds by anti-MarkowniKoff's rule.

☐ **From esters :** By hydrolysis with mineral acids or alkalies form alcohols.

☐ **From ethers :** On heating with dil. H_2SO_4 under pressure give alcohols.

☐ **From p-amines :** By the action of HNO_2 ($NaNO_2$ + dil. HCl) on p-amines only form corresponding alcohols.

☐ **From aldehydes, ketones, carboxylic acids and acid derivatives :** By reduction with Zn/HCl, Na/C_2H_5OH, $LiAlH_4$ or $NaBH_4$, etc.

☐ **Bouveault-Blanc reduction :** The reducing agent is **Na/alcohol.** The aldehydes, ketones, acids and acid derivatives are reduced by nascent hydrogen into corresponding alcohols.

☐ **Reduction with $LiAlH_4$:** It reduces aldehydes, ketones, carboxylic acids and their derivatives into alcohols (even without affecting the $>C=C<$).

☐ **Reduction with $NaBH_4$:** It also reduces $>C=O$ compounds to alcohols without attacking $>C=C<$

☐ **Addition of Grignard reagents to aldehydes and ketones** followed by hydrolysis.

☐ **Primary alcohols** are obtained when GR is treated with oxygen or formaldehyde or ethylene oxide.

☐ **Secondary alcohols** are obtained when GR is treated with an aldehyde other than formaldehyde.

☐ **Tertiary alcohols** are obtained when GR (1 mole) is treated with ketones. GR (2 moles) on reacting with esters ($RCOOR'$) also form tertiary alcohols.

☐ **Fermentation of carbohydrates :** Alcohols can be prepared by the fermentation of carbohydrates under the influence of certain enzymes.

Diastase converts starch into maltose.

Invertase converts molasses (sucrose) into a mixture of glucose and fructose.

Maltase converts maltose into glucose.

Zymase converts glucose or fructose into ethyl alcohol.

☐ **Oxo process :** A mixture of alkene, carbon monoxide and hydrogen reacts together at high temperature under pressure in presence of catalyst cobalt carbonyl or cobalt carbonyl hydride to form an aldehyde which is reduced (by Zn—Cu) to obtain alcohol. It is also called **carbonylation** or **hydroformylation.**

☐ **From alkanes :** A mixture of methane and oxygen (9 : 1 by volume) is passed over copper catalyst at 250°C under pressure, oxidises to methanol.

☐ Alkanes having 3° H atoms are oxidised by $KMnO_4$ or CrO_3 to 3° alcohol.

Physical properties :

☐ Lower alcohols are volatile liquids having characteristic smell (alcoholic) and burning taste. Alcohols are neutral and highly toxic substances. The lower alcohols are completely soluble in water and solubility decreases as the molecular weight increases. The solubility in water is due to intermolecular H-bonding between water and alcohol molecules due to their polar character. Isomeric alcohols have solubility in the order : $1° > 2° > 3°$.

The b.pts of alcohols are much higher as compared to the corresponding alkanes, ethers and alkyl halides, it is due to intermolecular association of their molecules through H-bonding. Among isomeric alcohols, the b.pts are in the order : $1° > 2° > 3°$.

Chemical properties : R—OH

☐ Primary alcohols are most reactive when there is a cleavage of O—H bond while tertiary alcohols are most reactive when there is a cleavage of C—O bond.

☐ **Reactions involving the cleavage of O—H bond :** The reactivity order is : $CH_3 > 1° > 2° > 3°$.

☐ **Action of alkali metals :** Formation of alkoxides or alcoholates (R—ONa).

☐ **Action of monocarboxylic acids :** Formation of esters (R—COOR').

☐ **Action of inorganic acids (H_2SO_4 or HNO_3) :** Formation of inorganic esters (alkyl hydrogen sulphate or alkyl nitrate).

☐ **Action of acid halides, acid amides and acid anhydrides:** Formation of esters ($RCOOR'$) in presence of pyridine (base catalyst).

☐ **Alkylation (action of dialkyl sulphates) :** Formation of ethers (R—O—R').

☐ **Action of Grignard reagent :** Formation of alkanes corresponding to the alkyl (R-) group of GR.

☐ **Reaction with HX :** Alcohols react with HX to form corresponding R—X. The order of reactivity of HX is : HI > HBr > HCl > HF. Hence, HCl reacts only in presence of a catalyst (anhyd. $ZnCl_2$ or $AlCl_3$). The increasing order of reactivity of alcohols towards HX is: CH_3OH < 1° alcohol < 2° alcohol < 3° alcohol < benzylic and allylic alcohols.

☐ Reaction with conc. HCl in presence of anhyd. $ZnCl_2$ (1: 1) is **Lucas reaction.**

☐ **Reaction with PCl_5 and PBr_3 :** Alcohols react with PCl_5 or PBr_3 (Br_2 and red P) or PI_3 (I_2 and red P) to yield alkyl halides.

☐ **Reaction with thionyl chloride ($SOCl_2$) :** Alkyl chlorides (pure) are formed when an alcohol reacts with $SOCl_2$ in presence of pyridine base.

☐ **Reaction with NH_3 (alc.) :** Alcohols react with alc. solution of NH_3 when their vapours are passed over heated Al_2O_3 at 400-500°C to form a mixture of 1°, 2° and 3° amine.

Reactions involving both the cleavage of R— and —OH groups:

☐ **Dehydration of alcohols :** Alcohols on dehydration yield alkenes. The order of ease of dehydration is : $3° > 2° > 1°$. Dehydrating agents for alcohols are : conc. H_2SO_4/Δ, H_3PO_4/Δ, anhyd. Al_2O_3/Δ, $KHSO_4/\Delta$, anhyd. $ZnCl_2/\Delta$ and P_2O_5/Δ etc.

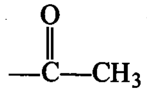
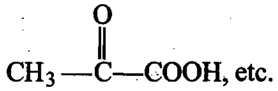
☐ 2° and 3° alcohols always give E_1 reaction. More substituted alkene is more stable.

☐ The less stable carbocation undergoes 1,2-hydride or 1,2-methyl or 1,2-phenyl shift to form more stable carbocation.

☐ 1° alcohols whose β-carbon atom is 1° or 2° gives E_2 reaction.

☐ Dehydration of alcohols depends upon the temperature of the reaction. With conc. H_2SO_4 at 170°C or Al_2O_3 at

350-400°C, alcohols give alkene, while conc. H_2SO_4 at 140°C or with Al_2O_3 at 250°C, ether is formed.

- **Dehydrogenation with copper catalyst at 300°C :** 1° alcohol loses hydrogen and forms an aldehyde. 2° alcohol loses hydrogen and forms a ketone. A 3° alcohol undergoes dehydration rather than dehydrogenation to give an alkene. This property is used to distinguish between 1°, 2° and 3° alcohols.
- **Oxidation :** The compound that is formed by oxidation depends upon the nature of alcohol (1° or 2° or 3°). The oxidising agents used are $K_2Cr_2O_7/H_2SO_4$, acidic or alkaline $KMnO_4$, dil. HNO_3, etc.
- Primary **(1°)** alcohols are oxidised to aldehydes, which are, in turn easily oxidised to carboxylic acids both containing the same number of carbon atoms as the original alcohol.
- Secondary **(2°)** alcohols are oxidised to ketones containing same number of C-atoms. Ketones on oxidation under drastic condition forms mixture of acids each having lesser number of C-atoms than the ketone or original alcohol.
- Tertiary **(3°)** alcohols do not easily undergo oxidation. But on vigorous oxidation gives several products, *i.e.*, an alkene, a ketone (containing less number of C-atoms) and then carboxylic acids (containing even more less number of C-atoms).
- **Reaction with halogens :** Halogens first oxidise primary and secondary alcohols to aldehydes and ketones respectively. The oxidation product then undergoes halogenation. SO_2Cl_2 also acts both as an oxidising agent and halogenating agent.
- **Reaction with bleaching powder :** When a mixture of ethyl alcohol and bleaching powder is heated, $CHCl_3$ is formed.
- **Haloform reaction :** Ethyl alcohol when heated with I_2 and NaOH or aq. Na_2CO_3 forms a yellow crystalline solid, iodoform. The iodoform test is given by C_2H_5OH, CH_3CHO, CH_3COCH_3,  $—\overset{\overset{O}{\|}}{C}—CH_3$ group, $CH_3CH(OH)—$ group, 2-ols, $CH_3CH(OH)COOH$ and  $CH_3—\overset{\overset{O}{\|}}{C}—COOH$, etc.
- **Reaction with acetaldehyde :** Ethyl alcohol combines with acetaldehyde in presence of dry HCl gas to form hemiacetal and acetal.

Distinction between 1°, 2° and 3° alcohols

- The following methods are used for distinguishing *pri.*, *sec.* and *tert.* alcohols.
- **By catalytic dehydrogenation :** Heating with copper catalyst at 300°C.
- **By oxidation method (Dichromate test) :** Using strong oxidising agent like acidified $K_2Cr_2O_7$.
- **Lucas test :** An equimolar mixture of conc. HCl and anhyd. $ZnCl_2$ **(Lucas reagent)** is added to an alcohol to form alkyl halides.
  If cloudiness or turbidity or thick oily layer appears immediately it will be 3° alcohol.
  If cloudiness appears within 5-10 minutes, the alcohol is 2°.
  If the solution remains clear, *i.e.*, no cloudiness is formed at room temperature, the alcohol is 1°.
- **Victor Meyer's test :** This test is based on the fact that 1°, 2°, 3° nitroalkanes behave differently towards HNO_2 and alkali. The three alcohols react with P/I_2, $AgNO_2$, $NaNO_2/H_2SO_4$ or HNO_2 and made alkaline with NaOH or KOH.
- 1° alcohol gives blood red colour, 2° alcohol blue colour, while no colour with 3° alcohol.

Dihydric alcohols

Two —OH groups on adjacent (vicinal) carbon atoms are called glycols. Their common name is alkylene glycol and IUPAC name is **alkanediol.**

Methods of preparation

- **From alkenes :** By hydroxylation with cold, dil. alkaline $KMnO_4$ (Baeyer's reagent) or by oxidation with OsO_4/ethanolic Na_2SO_3.
- By passing a mixture of ethylene and air under pressure over silver catalyst at 300°C to form ethylene oxide which on hydrolysis in presence of dil. HCl gives ethylene glycol.
- By passing ethylene through hypochlorous acid followed by hydrolysis with $NaHCO_3$ yields glycol.
- **From glyoxal :** By reduction with $LiAlH_4$.
- **From 1, 2- dibromoethane :** By hydrolysis with boiling Na_2CO_3 solution.

Properties

- Glycol is colourless, syrupy hygroscopic liquid, b.pt. 197°C, highly soluble in water (due to H-bonding).
- There are two primary alcoholic groups present in glycol molecule. Its reactions are therefore, those of primary alcohols ($—CH_2OH$) twice over.
- **Action of alkali metal (Na or K) :** Formation of mono and disodium glycollate at 160°C.
- **Action of PCl_5 or PBr_3 :** Formation of 1,2-dihalo (chloro or bromo) ethane.
- **Action of PI_3 :** Formation of ethylene iodide (unstable) and finally ethylene.
- **Action of HCl gas at 200°C :** Formation of 1,2-dichloroethane.
- **Action of CH_3COOH or $SOCl_2$:** Formation of glycol diacetate.
- **Action of conc. HNO_3/conc. H_2SO_4 :** Formation of ethylene dinitrate (used as an explosive).
- **Action of heat at 500°C :** Formation of ethylene oxide.
- **Oxidation with dil. HNO_3 :** Formation of oxalic acid.

- **Oxidation with $K_2Cr_2O_7/H^+$ or $KMnO_4/H^+$:** Formation of formic acid (2 moles).
- **Oxidation with HIO_4 or $(CH_3COO)_4Pb$:** Formation of formaldehyde (2 moles).
- **Action of heat with conc. H_2SO_4 (Dehydration) :** Formation of dioxane (diethylene dioxide).
- **Action of heat with H_3PO_4 (Dehydration) :** Formation of diethylene glycol.
- **Action of heat with $ZnCl_2$ (Dehydration) :** Formation of acetaldehyde.
- **Action with CH_3CHO on heating :** Formation of cyclic acetal.
- **Action with CH_3COCH_3 on heating :** Formation of cyclic ketal.

  Cyclic acetals and ketals are also called as dioxolans.
- **Action of heat with Cu catalyst at 350°C :** Formation of glyoxal.

Trihydric alcohols, Glycerol or Propane-1, 2, 3-triol

- It occurs in fats and oils in the form of esters (glycerides) of higher fatty acids like palmitic acid ($C_{15}H_{31}COOH$), stearic acid ($C_{17}H_{35}COOH$) and oleic acid ($C_{17}H_{33}COOH$).

Preparation of glycerol [$HOCH_2—CH(OH)—CH_2OH$]

- **From oils and fats :** By hydrolysis with alkali.

  Glycerol and sod. or pot. salts of higher fatty acids (**Soaps**) are obtained, and this alkaline hydrolysis of oils and fats is called **saponification.**
- **By the fermentation of sugars :** Glucose (aq. solution) on fermentation in presence of Na_2SO_3 forms glycerol alongwith CH_3CHO and CO_2.
- **Synthesis from propene :** By allylic chlorination at 600°C to form allyl chloride which reacts with aq. Na_2CO_3 followed by addition of HOCl and hydrolysis with aq. NaOH yields glycerol.
- **From acrolein :** By reduction with $LiAlH_4$ and then treating with Baeyer's reagent (hydroxylation) gives glycerol.

Properties

- It is a colourless, odourless, sweet, viscous and hygroscopic liquid, b.pt. is 290°C. It is highly miscible with water (due to H-bonding).
- Glycerol contains two primary and one secondary alcoholic groups. Generally *pri.* alcoholic (1°) groups are more reactive than *sec.* alcoholic (2°) group.
- **Reaction with Na or K on heating :** Formation of disodium glycerolate.
- **Reaction with PCl_5 or PBr_3 :** Formation of 1,2,3-tri halo (chloro or bromo) propane.
- **Reaction with PI_3 :** Formation of allyl iodide.
- **Reaction with HCl gas (in excess) :** Formation of α, α'- and α-β-dichlorohydrin.
- **Reaction with HI (in excess) :** Formation of isopropyl iodide as the final product.
- **Reaction with conc. HNO_3/conc. H_2SO_4 :** Formation of glyceryl trinitrate or trinitroglycerine (TNG) which is used as an explosive (dynamite).
- **Reaction with CH_3COOH, CH_3COCl or $(CH_3CO)_2O$ (in excess) :** Formation of glyceryl triacetate (ester).
- **Reaction with oxalic acid :** At 110°C and with excess of oxalic acid, formic acid is formed. At 260°C, allyl alcohol is finally formed.
- **Dehydration with $KHSO_4$ or P_2O_5 or conc. H_2SO_4 :** Formation of acrolein (foul smelling).
- **Oxidation by using different oxidising agents :** Glycerol gives number of products like glyceraldehyde, glyceric acid, tartronic acid, meso-oxalic acid, dihydroxy acetone and oxalic acid, etc.
- **With conc. HNO_3 :** It gives mainly glyceric acid.
- **With dil. HNO_3 :** It gives glyceric acid and tartronic acid.
- **With $Bi(NO_3)_2$ or $NaNO_3$:** It gives meso-oxalic acid.
- **With Fenton's reagent ($FeSO_4$ + H_2O_2) or NaOBr or Br_2 water :** It gives a mixture of glyceraldehyde and dihydroxy acetone (Glycerose).
- **With solid $KMnO_4$:** It gives oxalic acid or $CO_2 + H_2O$. This reaction is violent and explosion occurs, hence, used in time-bombs.
- **With periodic acid (HIO_4) :** Glycerol undergoes oxidative cleavage to give HCHO (2 moles) and HCOOH.
- **Condensation with benzaldehyde :** Formation of cyclic acetal.
- **Fermentation :** With Bacillus butylicum, glycerol forms *n*-butyl alcohol. With Bacillus butylicus, glycerol forms *n*-butyric acid.
- **Reaction with phthalic anhydride :** Glycerol gives **polyester** called **glyptals.**

QUESTIONS

Very Short Answer Type

1. Fill in the blanks:
   - (a) An...........diol has two hydroxyl groups on........... carbon atoms.
   - (b) CO combines with hydrogen when heated to 300°C in presence of a catalyst ($ZnO + Cr_2O_3$) to give...........
   - (c) $CH_3CHO \xrightarrow{CH_3MgBr} \ldots\ldots\ldots \xrightarrow{\ldots\ldots} CH_3CHOHCH_3$.
   - (d) The enzyme that converts glucose to ethyl alcohol is ....
   - (e) Hydrolysis of sucrose into a mixture of glucose and fructose is possible in presence of enzyme...........
   - (f) On oxidation of secondary alcohol...........is formed.
   - (g) The interaction of element S with Grignard reagent gives...........
   - (h) The IUPAC name of methyl carbinol is...........
   - (i) 100% ethyl alcohol is called...........
   - (j) The glycerol has...........primary alcoholic groups and one...........alcoholic group.
   - (k) Glycerol has...........taste and forms explosive with ....
   - (l) Solubility of alcohol in water...........with increase of carbon chain.
   - (m) Acrolein is formed by...........of glycerol.
   - (n) Tertiary alcohols are formed by reaction of Grignard reagents with...........
   - (o) Rum is a/an...........alcoholic beverage.
   - (p) Wine is a/an...........alcoholic beverage.
   - (q) Propan-2-ol on oxidation with $K_2Cr_2O_7/H_2SO_4$ yields ....
   - (r) Ethyl alcohol vapours are passed over hot copper to form...........
   - (s) Rectified spirit is the mixture of...........and...........
   - (t) Tertiary alcohols can...........oxidised easily.
   - (u) Boiling points of alcohols are...........than those of corresponding alkanes.
   - (v) When an organic acid reacts with..........., an ester is formed. The process is known as ....
   - (w) The intermediate compound in the preparation of ethylene from ethyl alcohol and conc. H_2SO_4 is ....
   - (x) The mixture of ethyl alcohol, methyl alcohol and water is...........for drinking.
   - (y) Dynamite, an explosive, consists mainly...........
   - (z) The ease of dehydration of alcohols is in the order .... > secondary > ....
2. State whether the following statements are **True or False:**
   - (a) The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol.
   - (b) Ethyl alcohol reacts with aqueous sodium hydroxide to form sodium ethoxide.
   - (c) The favourable temperature for alcoholic fermentation of glucose to ethyl alcohol is 30-35°C.
   - (d) Methyl alcohol gives iodoform test.
   - (e) Pyroligneous acid contains ethyl alcohol, acetone and acetaldehyde.
   - (f) Glycerine explodes with solid potassium permanganate.
   - (g) Ethylene can be used for the synthesis of ethyl alcohol.
   - (h) Methyl alcohol is more toxic than ethyl alcohol.
   - (i) Primary alcohols are dehydrated easily than secondary and tertiary alcohols.
   - (j) A tertiary alcohol gives colourless solution in Victor Meyer's test.
   - (k) Proof-spirit contains 57.1% ethyl alcohol by volume.
   - (l) Ethanol on treatment with excess of chlorine forms chloroform.
   - (m) Tertiary butyl alcohol gives turbidity fastest with $HCl/ZnCl_2$ than other isomeric alcohols.
   - (n) All alcohols undergo acetylation.
   - (o) Alcohols are stronger acids than water.
   - (p) Both glycerol and glycols are used as antifreeze in car radiators.
   - (q) Lucas reagent is equimolar mixture of zinc chloride and HCl.
   - (r) Tertiary alcohol is more acidic than primary alcohol.
   - (s) C_2H_5OH can accept a proton to give protonated, $C_2H_5\overset{+}{O}H_2$, *i.e.*, it can act as an acid.
   - (t) Ethylene glycol is an example of secondary alcohol.
   - (u) All alcohols are equally miscible with water.
   - (v) Power alcohol is a mixture of petrol and alcohol.
   - (w) Glycerol when heated with $KHSO_4$ forms allyl alcohol.
   - (x) Glycerol contains all primary alcoholic groups.
   - (y) Ethylene glycol on treatment with PI_3 yields ethylene.
   - (z) $FeSO_4 + H_2O_2$ is called Fenton's reagent.
3. Match the following:

(i)

(A) Fermentation	1. Secondary alcohol
(B) Dynamite	2. Methyl alcohol
(C) Absolute alcohol	3. $ZnCl_2 + HCl$
(D) Glycerine	4. Dihydric alcohol
(E) Wood spirit	5. Nitroglycerine
(F) Lucas reagent	6. Propane-1,2,3-triol
(G) Propan-2-ol	7. 100% ethyl alcohol
(H) Glycol	8. Invertase

(ii)

(A) Methylated spirit	1. Elimination reaction
(B) Enzyme	2. Bouveault Blanc reduction
(C) C_2H_5OH + Conc. H_2SO_4	3. Antifreeze
(D) Lucas test	4. Esterification
(E) Glycerol	5. Fenton's reagent
(F) $RCHO \xrightarrow{Na/C_2H_5OH}$	6. Zymase

(G) $FeSO_4 + H_2O_2$	7. Denatured alcohol
(H) $C_2H_5OH + CH_3COOH$ in presence of H_2SO_4	8. Tertiary alcohol

4. Complete the following equations:

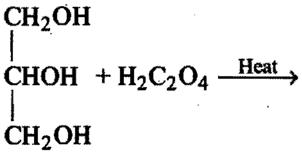
(i) Glucose + Zymase $\longrightarrow$

(ii) Starch + Malt extract $\longrightarrow$

(iii) $CO + H_2 \xrightarrow[\text{Catalyst}]{300^\circ C,\ 200\ \text{atm.}}$

(iv) Sucrose $\xrightarrow{\text{Invertase}}$

(v) $C_2H_5OH + I_2 + NaOH \longrightarrow$

(vi) 

$CH_2OH{-}CHOH{-}CH_2OH + H_2C_2O_4 \xrightarrow{\text{Heat}}$

(vii) $CH_3CH_2CH_2OH \xrightarrow[350^\circ C]{Al_2O_3} (A) \xrightarrow{HBr} (B) \xrightarrow{KOH(aq.)} (C)$

(viii) $C_2H_5OH \xrightarrow{PCl_5} (A) \xrightarrow{KCN} (B) \xrightarrow{H_3O^+} (C) \xrightarrow{NH_3} (D) \xrightarrow{\text{Heat}} (E)$

(ix) $CH_3CH_2CH_2OH \xrightarrow{PBr_5} (A) \xrightarrow{(\text{Alc.})\,KOH} (B) \xrightarrow{HBr} (C) \xrightarrow{NH_3} (D)$

(x) $CH_3CH_2OH \xrightarrow{P/I_2} (A) \xrightarrow{Mg} (B) \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) HCHO}} (C)$

(xi) $C_6H_{12}O(A) \xrightarrow[\text{Heat}]{H_2SO_4} C_6H_{10}(B) \xrightarrow[\text{Heat}]{HNO_3} C_6H_{10}O_4(C)$

$(A) \xrightarrow[\text{Heat}]{HNO_3} (C)$

(xii) $C_6H_6 + H_2C{=}CHCH_2Cl \xrightarrow{AlCl_3} (A) \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } BH_3/THF} (B) \xrightarrow[\text{Heat}]{HF} C_9H_{10}(C)$

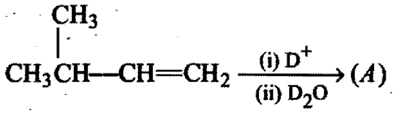
(xiii) $RCH{=}CH_2 \xrightarrow[\text{THF},\ -H_2O]{Hg(OAc)_2} (A) \xrightarrow{NaBH_4} (B)$

(xiv) $CH_3CH_2CH{=}CH_2 \xrightarrow{H_2SO_4} (A) \xrightarrow{HOH} (B)$

(xv) $CH_3CH{=}CH_2 \xrightarrow{B_2H_6} (A) \xrightarrow{H_2O_2} (B)$

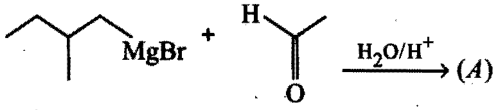
(xvi) $CH_3CH{=}CH_2 \xrightarrow[\text{(ii) } D_2O]{\text{(i) } H^+} (A)$

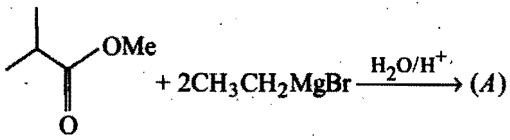
(xvii) $CH_3CH{=}CH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } D^+} (A)$

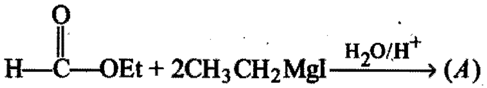
(xviii) 

$CH_3CH(CH_3){-}CH{=}CH_2 \xrightarrow[\text{(ii) } D_2O]{\text{(i) } D^+} (A)$

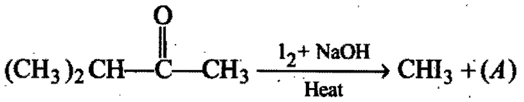
(xix) $(CH_3)_3C{-}CH_2OH \xrightarrow[\text{Heat, } 170^\circ C]{\text{Conc. } H_2SO_4} (A)$

(xx) 

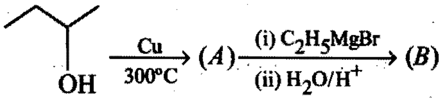
(xxi) 

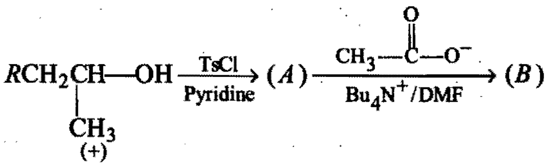
(xxii) 

$H{-}\overset{O}{\overset{\|}{C}}{-}OEt + 2CH_3CH_2MgI \xrightarrow{H_2O/H^+} (A)$

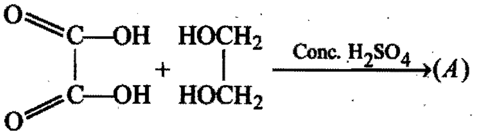
(xxiii) 

$(CH_3)_2CH{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xrightarrow[\text{Heat}]{I_2 + NaOH} CHI_3 + (A)$

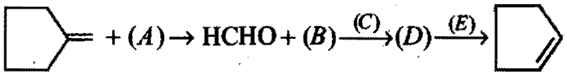
(xxiv) 

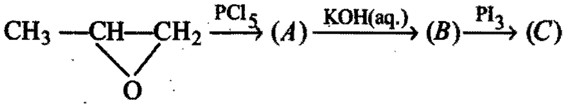
(xxv) 

$RCH_2\underset{\underset{(+)}{CH_3}}{\underset{|}{CH}}{-}OH \xrightarrow[\text{Pyridine}]{TsCl} (A) \xrightarrow[Bu_4N^+/DMF]{CH_3{-}\overset{O}{\overset{\|}{C}}{-}O^-} (B) \xrightarrow[\text{NaOH}]{\text{HOH}} (C)$

(xxvi) 

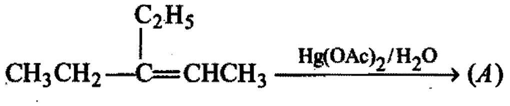
$HOOC{-}COOH + HOCH_2{-}CH_2OH \xrightarrow{\text{Conc. } H_2SO_4} (A)$

(xxvii) 

(xxviii) 

$CH_3{-}CH{-}CH_2\ (\text{epoxide, } O) \xrightarrow{PCl_5} (A) \xrightarrow{KOH(aq.)} (B) \xrightarrow{PI_3} (C)$

(xxix) $CH_3CH_2C{\equiv}CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} (A) \xrightarrow{H_2/Pd\text{-}BaSO_4} (B) \xrightarrow{\text{Alkaline } KMnO_4} (C)$ [IIT 2002]

(xxx) 

$CH_3CH_2{-}\overset{C_2H_5}{\overset{|}{C}}{=}CHCH_3 \xrightarrow{Hg(OAc)_2/H_2O} (A)$

$(A) \xrightarrow{NaBH_4} (B)$

5. What happens when?

(a) Sodium metal reacts with absolute alcohol.

(b) Vapour of ethyl alcohol is passed through heated aluminium oxide at 360°C.

(c) Glycerol is heated with $KHSO_4$.

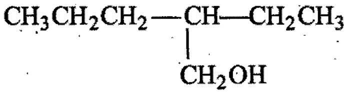
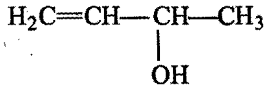
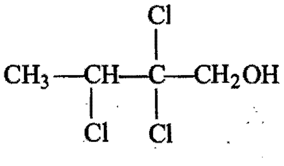
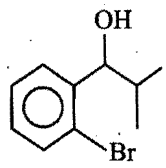
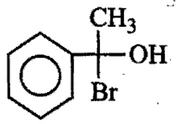
(d) Ethyl alcohol reacts with acetyl chloride.

(e) Ethyl alcohol is heated with iodine and NaOH.
(f) Ethyl alcohol is heated with bleaching powder.
(g) Ethylene glycol is heated with concentrated H_2SO_4.
(h) Isopropyl alcohol is oxidised with acidic potassium dichromate.
(i) Ethyl alcohol is treated with conc. H_2SO_4 under different conditions.
(j) Tertiary butyl alcohol is passed over heated copper at 300°C.

6. Answer the following:

(i) What are the functional groups of primary, secondary and tertiary alcohols?
(ii) Give the another name for rubbing alcohol.
(iii) Give the another name for grain alcohol.
(iv) What is the name of carbinol?
(v) What is the chief product when a solution of sodium chloride containing ethyl alcohol is electrolysed?
(vi) Name the enzyme which converts maltose to ethanol.
(vii) What is the name of the compound which is used as antifreeze in car radiators?
(viii) Which reagent is used to measure number of —OH groups in an alcohol?
(ix) Which alcohol is present in alcoholic beverages?
(x) Name the most acidic monohydric alcohol.

7. Write IUPAC names of the following:

(a) Tertiary butyl alcohol
(b) Secondary butyl alcohol
(c) 
$CH_3CH_2CH_2-\underset{\underset{CH_2OH}{|}}{CH}-CH_2CH_3$
(d) $HC\equiv C-CH_2OH$
(e) 
$H_2C=CH-\underset{\underset{OH}{|}}{CH}-CH_3$
(f) Chloral hydrate
(g) Isoamyl alcohol
(h) Diethyl carbinol
(i) Ethyl methyl isopropyl carbinol
(j) 
$CH_3-\underset{\underset{Cl}{|}}{CH}-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2OH$
(k) $CH_3CH=CHCH_2OH$
(l) $H_2C=CHCH_2OH$
(m) 
(n) 

Short Answer Type

8. (a) What are primary, secondary and tertiary alcohols? Give one example of each.
(b) How do primary, secondary and tertiary alcohols differ in their behaviour towards oxidation?
(c) Give Victor Meyer's method to identify primary, secondary and tertiary alcohols.
(d) What is the theoretical basis for Lucas test?
[**Hint:** $ZnCl_2$, a strong Lewis acid, encourages an S_N1 pathway for formation of the alkyl chlorides. Thus, the rate of reaction of the alcohols is 3° > 2° > 1°.]

9. Write the structural formula and IUPAC names of the alcoholic isomers with molecular formula $C_4H_{10}O$.

10. Write the equations of preparing ethyl alcohol in one step only from the following compounds:
(a) Ethyl iodide, (b) Ethylene, (c) Acetyl chloride,
(d) Acetic acid, (e) Ethylamine, (f) Acetaldehyde,
(g) Formaldehyde.

11. How does ethyl alcohol react with?
(a) Sodium, (b) PCl_5, (c) Conc. HBr, (d) Conc. H_2SO_4,
(e) Acetyl chloride, (f) Potassium dichromate in presence of dilute H_2SO_4.

12. How will you obtain the following compounds from ethyl alcohol?
(a) Ethyl chloride, (b) Ethyl acetate, (c) Acetaldehyde,
(d) Iodoform, (e) Ethylene, (f) Diethyl ether (g) Ethane,
(h) Ethylamine, (i) Chloroform.

13. (a) How is ethyl alcohol prepared from molasses?
(b) How is absolute alcohol obtained from rectified alcohol in the laboratory?
(c) How is glycerol obtained on a large scale?

14. Starting from glycerol, how will you obtain the following?
(a) Acrolein, (b) Allyl alcohol,
(c) 2-Iodopropane, (d) Nitroglycerine,
(e) 1,2,3-Trichloropropane, (f) Glyceric acid.

15. Starting from glycol, how the following compounds are obtained?
(a) Dioxane, (b) 1,2-Dichloroethane,
(c) Oxalic acid, (d) Ethylene oxide,
(e) Acetaldehyde.

16. Outline a synthesis of each alcohol from the indicated starting materials:
(a) Isopropyl alcohol from a hydrocarbon.
(b) *n*-Butyl alcohol from acetylene.
(c) Allyl alcohol from propene.
(d) Glycerol from acetone or isopropyl alcohol or propene.
(e) Glycerol from carbon and hydrogen or acetylene.
(f) *n*-Propyl alcohol from ethylene oxide.
(g) *Tert.* butyl alcohol from acetone.

(h) Isopropyl alcohol from acetaldehyde.
(i) 2-methyl propan-1-ol from formaldehyde.
(j) Cyclohexyl methanol from formaldehyde.
(k) 1-Phenylethanol from styrene (vinyl benzene).
(l) *Tert.* amyl alcohol from methyl magnesium iodide.
(m) 3,5-Dimethyl hexan-3-ol from butan-2-one.

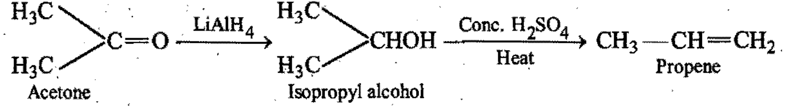
Hint: (a) $CH_3CH_2CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CHClCH_3 \xrightarrow{KOH(aq.)} CH_3CHOHCH_3$

(b)
$$\begin{tikzcd} H{-}C{\equiv}C{-}H \arrow[r, "H_2"] \arrow[d, "NaNH_2"] & H_2C{=}CH_2 \arrow[r, "HBr"] & CH_3CH_2Br \\ H{-}C{\equiv}C{-}Na \arrow[r, "CH_3CH_2Br"] & HC{\equiv}CCH_2CH_3 \arrow[r, "H_2", "\text{(Lindlar's catalyst)}"'] & H_2C{=}CHCH_2CH_3 \arrow[r, "HBr", "H_2O_2"'] & {} \end{tikzcd}$$

$$BrH_2CCH_2CH_2CH_3 \xrightarrow{KOH(aq.)} HOCH_2CH_2CH_2CH_3$$

Alternative $CH_3CH_2CH{=}CH_2 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} CH_3CH_2CH_2CH_2OH$

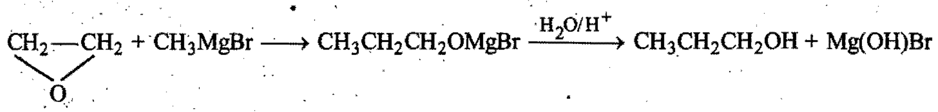
(c) $CH_3CH{=}CH_2 \xrightarrow[500°C]{Cl_2} CH_2ClCH{=}CH_2 \xrightarrow{KOH(aq.)} CH_2OH{-}CH{=}CH_2$

(d)


$$CH_3{-}CH{=}CH_2 \xrightarrow[500°C]{Cl_2} CH_2ClCH{=}CH_2 \xrightarrow{NaOH(aq.)} CH_2OHCH{=}CH_2 \xrightarrow{HOCl} CH_2OHCHClCH_2OH \xrightarrow{NaOH(aq.)} CH_2OHCHOHCH_2OH$$

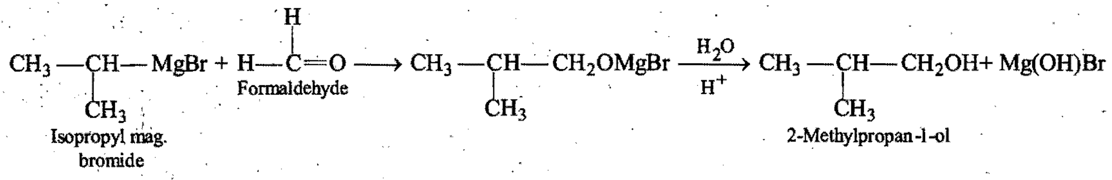
(e) $C + H_2 \xrightarrow[arc]{Elec.} HC{\equiv}CH \xrightarrow{NaNH_2} HC{\equiv}CNa \xrightarrow{CH_3I} HC{\equiv}C{-}CH_3 \xrightarrow[\text{Lindlar's catalyst}]{H_2} \underset{\text{Propene}}{H_2C{=}CH{-}CH_3}$

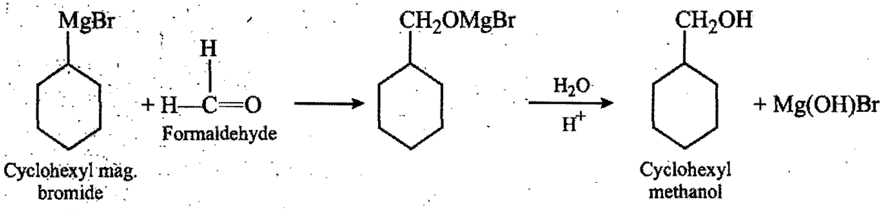
From propene, the glycerol is obtained as described in (d).

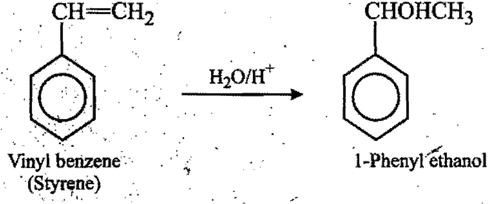
(f)

$$CH_2{-}CH_2(O) + CH_3MgBr \longrightarrow CH_3CH_2CH_2OMgBr \xrightarrow{H_2O/H^+} CH_3CH_2CH_2OH + Mg(OH)Br$$

(g) $(CH_3)_2CO + CH_3MgBr \longrightarrow (CH_3)_3COMgBr \xrightarrow{H_2O/H^+} (CH_3)_3COH + Mg(OH)Br$

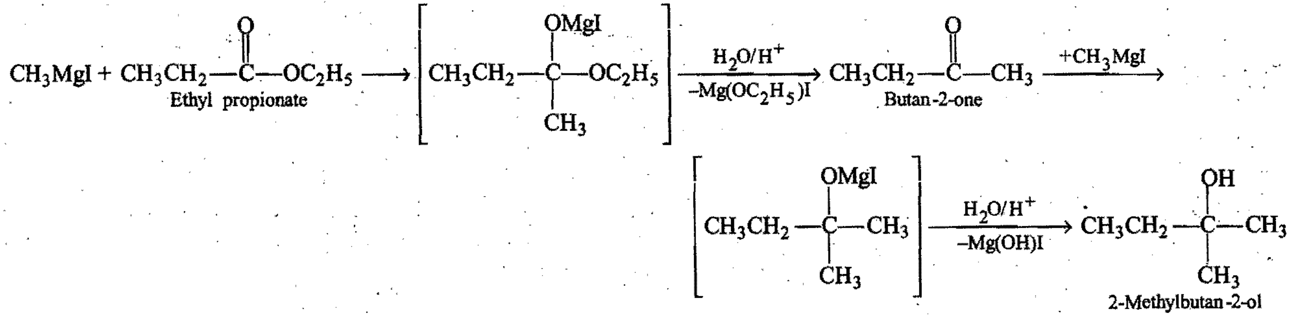
(h) $CH_3CHO + CH_3MgBr \longrightarrow (CH_3)_2CHOMgBr \xrightarrow{H_2O/H^+} (CH_3)_2CHOH + Mg(OH)Br$

(i)

$$\underset{\text{Isopropyl mag. bromide}}{CH_3{-}CH(CH_3){-}MgBr} + \underset{\text{Formaldehyde}}{H{-}C(H){=}O} \longrightarrow CH_3{-}CH(CH_3){-}CH_2OMgBr \xrightarrow[H^+]{H_2O} \underset{\text{2-Methylpropan-1-ol}}{CH_3{-}CH(CH_3){-}CH_2OH} + Mg(OH)Br$$

(j)


(k)


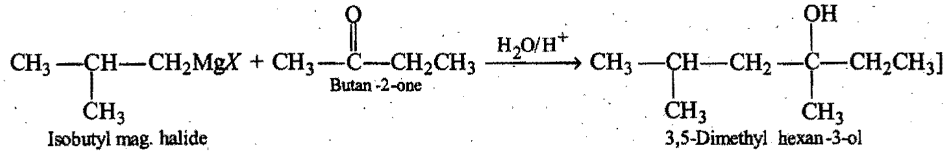
(l)



$$CH_3MgI + \underset{\text{Ethyl propionate}}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5} \longrightarrow \left[CH_3CH_2-\underset{CH_3}{\underset{|}{\overset{OMgI}{\overset{|}{C}}}}-OC_2H_5\right] \xrightarrow[-Mg(OC_2H_5)I]{H_2O/H^+} \underset{\text{Butan-2-one}}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{+CH_3MgI}$$

$$\left[CH_3CH_2-\underset{CH_3}{\underset{|}{\overset{OMgI}{\overset{|}{C}}}}-CH_3\right] \xrightarrow[-Mg(OH)I]{H_2O/H^+} \underset{\text{2-Methylbutan-2-ol}}{CH_3CH_2-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3}$$

(m)



$$\underset{\text{Isobutyl mag. halide}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2MgX} + \underset{\text{Butan-2-one}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3} \xrightarrow{H_2O/H^+} \underset{\text{3,5-Dimethyl hexan-3-ol}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2CH_3]}$$

17. How will you obtain?

(a) Propan-1-ol from propan-2-ol (three steps).

[**Hint:** $CH_3CHOHCH_3 \xrightarrow[170°C]{H_2SO_4} CH_3CH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2CH_2Br \xrightarrow{KOH(aq.)} CH_3CH_2CH_2OH$]

(b) Ethanol from methanol (three steps).

[**Hint:** $CH_3OH \xrightarrow{HI} CH_3I \xrightarrow[Et_2O]{Mg} CH_3MgI \xrightarrow[(ii)\ H_2O/H^+]{(i)\ HCHO} CH_3CH_2OH$]

(c) Vinyl acetate from ethyl alcohol.

[**Hint:** $C_2H_5OH \xrightarrow[170°C]{Conc.\ H_2SO_4} H_2C{=}CH_2 \xrightarrow{Br_2} CH_2Br-CH_2Br \xrightarrow[KOH]{(Alc.)} HC{\equiv}CH \xrightarrow{CH_3COOH} H_2C{=}CHOOCCH_3$]

(d) Ethanol from acetylene.

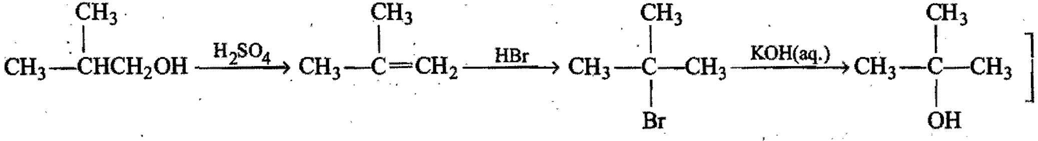
[**Hint:** $HC{\equiv}CH \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO \xrightarrow[LiAlH_4]{Reduction} C_2H_5OH$]

(e) *n*-Propyl alcohol from ethyl alcohol (four steps).

[**Hint:** $C_2H_5OH \xrightarrow{SOCl_2} C_2H_5Cl \xrightarrow{Mg} C_2H_5MgCl \xrightarrow{HCHO} C_2H_5CH_2OMgCl \xrightarrow[H^+]{H_2O} C_3H_7OH$]

(f) *Tert.* butyl alcohol from isobutyl alcohol.

[**Hint:**



$$CH_3-\overset{CH_3}{\overset{|}{C}}HCH_2OH \xrightarrow{H_2SO_4} CH_3-\overset{CH_3}{\overset{|}{C}}{=}CH_2 \xrightarrow{HBr} CH_3-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow{KOH(aq.)} CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

]

(g) Methyl alcohol from acetic acid.

[**Hint:** $CH_3COOH \xrightarrow{NaOH} CH_3COONa \xrightarrow[Heat]{Soda\ lime} CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow{NaOH(aq.)} CH_3OH$]

(h) Acetamide from ethyl alcohol.

[**Hint:** $C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow{Heat} CH_3CONH_2$]

(i) Formic acid from oxalic acid.

Hint: Heat oxalic acid with glycerol at 110°C.]

(j) Butan-1-ol from acetaldehyde.

[**Hint:** $CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow{NaOH} CH_3COONa \xrightarrow{Electrolysis} CH_3-CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2Cl \xrightarrow[Heat]{Na} CH_3CH_2CH_2CH_3 \xrightarrow[h\nu]{Cl_2}$

$CH_3CH_2CH_2CH_2Cl \xrightarrow{NaOH(aq.)} CH_3CH_2CH_2CH_2OH$]

(k) Acetylene from ethyl alcohol.

[**Hint:** $C_2H_5OH + I_2 + NaOH \longrightarrow CHI_3 \xrightarrow[\text{Heat}]{Ag} CH{\equiv}CH$]

18. How will you distinguish among the following pairs?

(a) *n*-Propyl alcohol and isopropyl alcohol.

[**Hint:** *n*-Propyl alcohol does not give iodoform test while isopropyl alcohol forms yellow crystalline iodoform when treated with I_2 and NaOH.]

(b) *n*-Butyl, *sec.* butyl and *tert.* butyl alcohols.

[**Hint:** Perform Lucas test. *Tert.* butyl alcohol reacts immediately with ($ZnCl_2$ + HCl) Lucas reagent to form cloudiness, secondary butyl alcohol reacts within 5 minutes while *n*-butyl alcohol does not react at all at room temperature.]

(c) Ethanol and chloroform.

[**Hint:** Chloroform gives isocyanide test. This test is not given by ethanol. Ethanol gives iodoform test. This test is not given by chloroform.]

(d) Ethanol and acetone.

[**Hint:** Ethanol undergoes oxidation with dilute acidified $K_2Cr_2O_7$ and gives pungent odour due to formation of acetaldehyde. Acetone gives a red colour with sodium nitroprusside in the presence of NaOH.]

(e) Ethanol and propan-1-ol.

[**Hint:** Ethyl alcohol (ethanol) gives iodoform test. This test is not given by propan-1-ol.]

(f) Glycerol and sugar solution.

[**Hint:** Glycerol on heating with $KHSO_4$ forms a pungent odour compound, acrolein. This test is not given by sugar solution. The pink colour of borax and phenolphthalein disappears when glycerol is added to it in cold but reappears on heating, however, it again disappears on cooling. This test is not given by sugar solution.]

(g) Allyl alcohol and *n*-propyl alcohol.

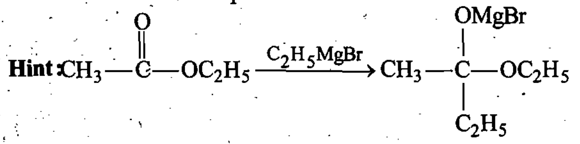
[**Hint:** Allyl alcohol reacts immediately with Lucas reagent and gives white turbidity in less than one minute while *n*-propyl alcohol does not react.]

19. Write short notes on:

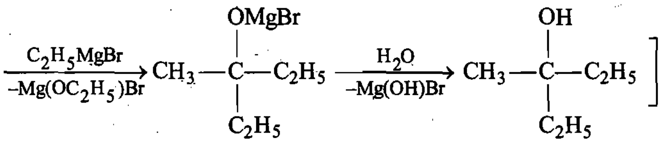
(a) Fermentation, (b) Enzymes, (c) Power alcohol,
(d) Iodoform test, (e) Methylated or denatured spirit,
(f) Destructive distillation of wood, (g) Absolute alcohol,
(h) Rectified spirit, (i) Proof-spirit, (j) Dynamite,
(k) Alcoholometry.

20. (a) Write the structural formula of the main organic product formed when ethyl acetate is treated with twice the molar quantity of ethyl magnesium bromide and the reaction mixture is poured into water.

[**Hint:**



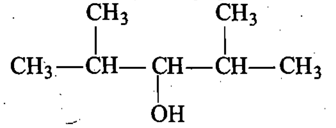
$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{C_2H_5MgBr} CH_3-\underset{C_2H_5}{\overset{OMgBr}{C}}-OC_2H_5$



$\xrightarrow[-Mg(OC_2H_5)Br]{C_2H_5MgBr} CH_3-\underset{C_2H_5}{\overset{OMgBr}{C}}-C_2H_5 \xrightarrow[-Mg(OH)Br]{H_2O} CH_3-\underset{C_2H_5}{\overset{OH}{C}}-C_2H_5$]

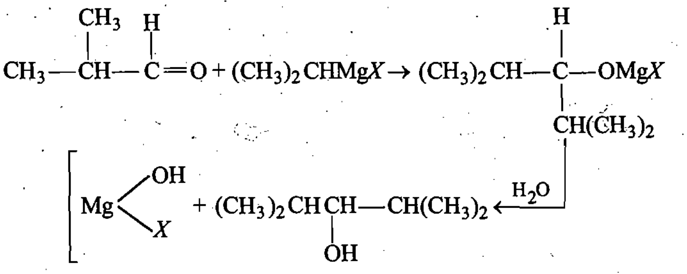
(b) Give the structures of Grignard reagent and the substrate (aldehyde or ketone) that would react to form 2,4-dimethyl pentan-3-ol.

[**Hint:** Structure of 2,4-dimethyl pentan-3-ol is,



$CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}-\overset{CH_3}{CH}-CH_3$]

This is formed by reacting $(CH_3)_2CHCHO$ with $(CH_3)_2CHMgX$.



$CH_3-\overset{CH_3}{CH}-\overset{H}{C}=O + (CH_3)_2CHMgX \rightarrow (CH_3)_2CH-\underset{CH(CH_3)_2}{\overset{H}{C}}-OMgX$

$\left[Mg\begin{matrix}OH\\X\end{matrix} + (CH_3)_2CH\underset{OH}{CH}-CH(CH_3)_2\right] \xleftarrow{H_2O}$

(c) By giving one chemical reaction prove that glycerol is an alcohol.

[**Hint:** Give reaction with acetyl chloride or PCl_5 or sodium. These reactions show that —OH groups are present in glycerol.]

(d) Give one specific example to prove that enzymes are very specific in their action.

(e) Write down the names and structures of two compounds obtained by dehydration of ethyl alcohol.

(f) List the reagents commonly used to reduce carbonyl functional groups to alcohols.

(g) Give the expected reduced product from the reaction of (a) CH_3COCH_2COOH, (b) $OHCCH_2COOCH_3$, (c) $CH_3CH_2COCH_2CH_2Br$, (d) p-$O_2N-C_6H_4CHO$ with (i) $NaBH_4$, (ii) $LiAlH_4$.

(h) Give the product of the oxidation with MnO_2 of:
(a) $CH_3CH_2CH{=}CHCH_2OH$
(b) $C_6H_5CH_2OH$
(c) $C_6H_5CH(OH)CH_2CH_2OH$
(d) $CH_3CH{=}CHCH_2CH_2CH_2OH$

(i) Give the product of the oxidation with Jones reagent of:
(a) $CH_3CH{=}CHCH(OH)CH_3$ (b) $C_6H_{11}CH_2OH$

(j) How can a primary alcohol be oxidised to an aldehyde?

21. (i) Arrange the following in order of their increasing basicity:

$H_2O, OH^-, CH_3OH, CH_3O^-$

(ii) Arrange the following in order of their increasing boiling point:
n-butane, ethanol, water, propane.

(iii) Arrange the following in order of their increasing boiling point:
n-butane, *n*-butanol, *n*-butyl chloride, isobutane.

(iv) Arrange the primary, secondary and tertiary alcohols into decreasing order of reactivity towards sodium.

(v) Arrange the primary, secondary and tertiary alcohols into decreasing order of acidity.

(vi) Arrange the following in order of their decreasing boiling point:
pentan-1-ol, 2-methyl butan-2-ol, 3-methyl butan-2-ol.

(vii) Arrange the following in decreasing order of rate of dehydration with conc. H_2SO_4:

$CH_3CH_2CH(OH)CH_2CH_2CH_3$ (*A*)
$(CH_3)_2C(OH)CH_2CH_2CH_3$ (*B*)
$(CH_3)_2C(OH)CH(CH_3)_2$ (*C*)
$CH_3CH_2CH(OH)CH(CH_3)_2$ (*D*)
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$ (*E*)

22. Give reasons for the following:

(i) Molecular mass of ethanol and dimethyl ether is the same, however ethanol is a liquid at room temperature but dimethyl ether is a gas.

Hint: Hydrogen bonding in ethanol.]

(ii) Anhydrous $CaCl_2$ cannot be used for drying ethanol.

Hint: Ethanol forms an addition compound with $CaCl_2$.]

(iii) Tertiary alcohols form the turbidity fastest in Lucas test while primary alcohols form slowest.

Hint: Positive inductive effect is maximum in tertiary alcohol and hence —OH removal is facilitated.]

(iv) Ethyl alcohol reacts with HI but not with HCN.

Hint: C_2H_5OH is a weak base and hence reacts with stronger acid.]

(v) Sodium metal can be used for drying diethyl ether but not ethanol.

Hint: Ethanol has active hydrogen atom which reacts with sodium.]

(vi) Propanol, unlike propane is soluble in water.

Hint: Propanol can form hydrogen bonding with water but propane does not possess this property.]

(vii) Propanol boils at a higher temperature than propane.

Hint: In propanol, there is intermolecular hydrogen bonding but in propane, there is no hydrogen bonding.]

(viii) Why glycerol has high viscosity and is miscible with water in all proportions?

Hint: Hydrogen bonding is responsible for high viscosity and solubility in water.]

(ix) Reactivity of H*X* with alcohols is in the order,
HI > HBr > HCl > HF.

Hint: Bond dissociation energy of H*X* is in the order,
HI < HBr < HCl < HF.]

(x) Why is it not possible to obtain a halide by reacting *R*OH with X^-?

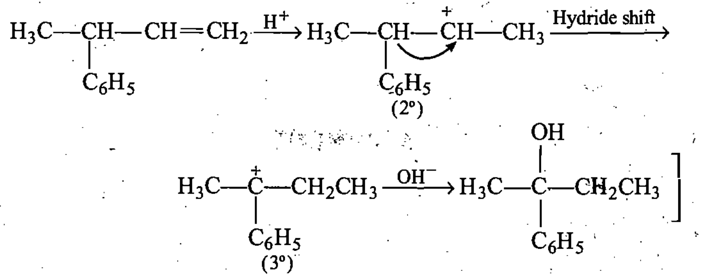
Hint: OH^- is a very poor leaving group. Acid converts it to H_2O, a better leaving group.]

(xi) $ClCH_2CH_2OH$ is stronger acid than CH_3CH_2OH.

Hint: The electron withdrawing Cl delocalises the negative charge on the oxygen atom of the OH group.]

(xii) Hydration of 3-phenylbut-1-ene in dil. H_2SO_4 forms 2-phenylbutan-2-ol instead of 3-phenylbutan-2-ol.

Hint: Hydration gives an intermediate 2° C^+, which undergoes a hydride shift to more stable 3° carbocation.



$$H_3C-\underset{C_6H_5}{CH}-CH=CH_2 \xrightarrow{H^+} H_3C-\underset{\underset{(2°)}{C_6H_5}}{CH}-\overset{+}{C}H-CH_3 \xrightarrow{\text{Hydride shift}}$$

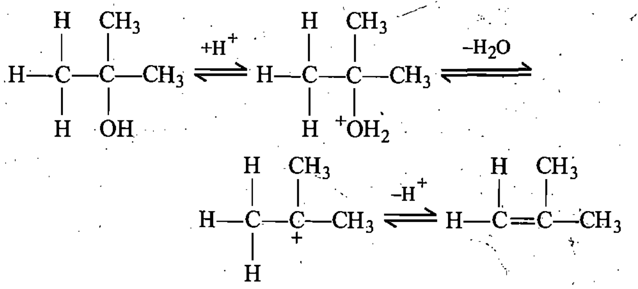
$$H_3C-\underset{\underset{(3°)}{C_6H_5}}{\overset{+}{C}}-CH_2CH_3 \xrightarrow{OH^-} H_3C-\underset{C_6H_5}{\overset{OH}{C}}-CH_2CH_3]$$

(xiii) The compound $(CH_3)_3C—CH(OH)CH_3$ on treatment with conc. HCl forms $(CH_3)_2C(Cl)—CH(CH_3)_2$ instead of $(CH_3)_3C—CH(Cl)CH_3$.

Hint: The first formed 2° C^+ rearranges by a CH_3 shift to more stable 3° C^+, which then gives the 3° chloride.]

(xiv) Acid catalysed dehydration of *t*-butanol is faster than that of *n*-butanol.

Hint: The acid catalysed dehydration of an alcohol proceeds *via* the formation of a carbocation:



$$H-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \underset{}{\overset{+H^+}{\rightleftharpoons}} H-\underset{H}{\overset{H}{C}}-\underset{^+OH_2}{\overset{CH_3}{C}}-CH_3 \overset{-H_2O}{\rightleftharpoons}$$

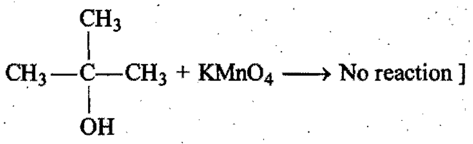
$$H-\underset{H}{\overset{H}{C}}-\underset{+}{\overset{CH_3}{C}}-CH_3 \overset{-H^+}{\rightleftharpoons} H-\overset{H}{C}=\overset{CH_3}{C}-CH_3$$

Since, 3° carbocation is more stable than 1°, the dehydration in 3° proceeds faster than 1°.]

(xv) When *t*-butanol and *n*-butanol are separately treated with a few drops of dilute $KMnO_4$, in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate?

Hint: *n*-Butanol is oxidised by $KMnO_4$ and not *t*-butanol as the latter does not contain H atom attached to carbinol carbon atom.

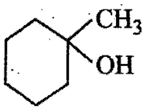
$$\underset{\substack{n\text{-Butanol} \\ (1° \text{ alcohol})}}{CH_3CH_2CH_2CH_2OH} + \underset{\text{Purple}}{KMnO_4} \rightarrow \underset{\substack{\text{Potassium} \\ \text{benzoate}}}{CH_3CH_2CH_2CO\overset{-}{O}\overset{+}{K}} + \underset{\substack{\text{Brown} \\ \text{ppt.}}}{MnO_2} + KOH$$

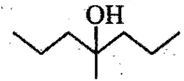


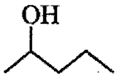
$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + KMnO_4 \longrightarrow$ No reaction]

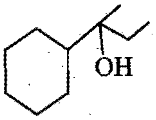
Tert.-butanol
(3° alcohol)

23. Show how would you synthesize the following alcohols from appropriate alkenes?

(i)


(ii)


(iii)


(iv)


ANSWERS

1. (a) alkane, different; (b) methyl alcohol; (c) $(CH_3)_2CHOMgBr$, H_2O/H^+; (d) zymase; (e) invertase; (f) ketone; (g) thioalcohol; (h) ethanol; (i) absolute alcohol; (j) two, secondary; (k) sweet, conc. HNO_3/conc. H_2SO_4; (l) decreases; (m) dehydration; (n) ketones; (o) distilled; (p) undistilled; (q) acetone; (r) acetaldehyde; (s) 95.57% ethyl alcohol and 4.43% water; (t) not be; (u) higher; (v) alcohol, esterification; (w) $C_2H_5HSO_4$; (x) unfit; (y) nitroglycerine; (z) tertiary, primary.

2. (a) False—gives tertiary butyl alcohol; (b) False—no reaction; (c) True; (d) False—does not give iodoform test; (e) False—contains methyl alcohol, acetic acid and acetone; (f) True; (g) True; (h) True; (i) False—secondary and tertiary alcohols are dehydrated easily than primary alcohols; (j) True; (k) True; (l) False—forms chloral; (m) True; (n) True; (o) False—weaker acids than water; (p) True; (q) True; (r) False—less acidic than primary alcohol; (s) False—it can act as a base; (t) False—is a dihydric alcohol; (u) False—miscibility decreases with increase in molecular mass and increases with branching of chains; (v) True; (w) False—forms acrolein; (x) False—contains two primary and one secondary alcoholic groups; (y) True; (z) True.

3. (i) (A—8); (B—5); (C—7); (D—6); (E—2); (F—3); (G—1); (H—4).
(ii) (A—7); (B—6); (C—1); (D—8); (E—3); (F—2); (G—5); (H—4).

4. (i) $C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$

(ii) $\underset{\text{Starch}}{2(C_6H_{12}O_5)_n} + nH_2O \xrightarrow[\text{(Diastase)}]{\text{Malt extract}} \underset{\text{Maltose}}{n(C_{12}H_{22}O_{11})}$

(iii) $CO + 2H_2 \xrightarrow[300°C,\ 200\ atm]{ZnO + Cr_2O_3} \underset{\text{Methyl alcohol}}{CH_3OH}$

(iv) $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

(v) $C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{I_2} CI_3CHO \xrightarrow{NaOH} CHI_3 + HCOONa$

(vi) At 110°C HCOOH and at 260°C allyl alcohol.

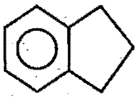
(vii) (*A*) $CH_3CH{=}CH_2$; (*B*) $CH_3CHBrCH_3$;
(*C*) $CH_3CHOHCH_3$.

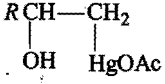
(viii) (*A*) C_2H_5Cl; (*B*) C_2H_5CN;
(*C*) C_2H_5COOH; (*D*) $C_2H_5COONH_4$;
(*E*) $C_2H_5CONH_2$.

(ix) (*A*) C_3H_7Br; (*B*) $CH_3CH{=}CH_2$;
(*C*) $CH_3CHBrCH_3$; (*D*) $CH_3CHNH_2CH_3$.

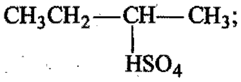
(x) (*A*) CH_3CH_2I; (*B*) CH_3CH_2MgI;
(*C*) $CH_3CH_2CH_2OH$.

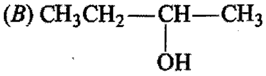
(xi) (*A*) cyclohexanol; (*B*) cyclohexene;
(*C*) adipic acid.

(xii) (*A*) $C_6H_5CH_2CH{=}CH_2$; (*B*) $C_6H_5CH_2CH_2CH_2OH$;
(*C*)


(xiii) (*A*)


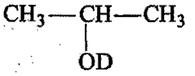
$R\underset{\underset{OH}{|}}{CH}-\underset{\underset{HgOAc}{|}}{CH_2}$; (*B*) $R-CHOHCH_3$.

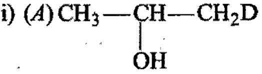
(xiv) (*A*)


$CH_3CH_2-\underset{\underset{HSO_4}{|}}{CH}-CH_3$; (*B*)


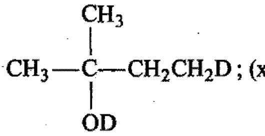
$CH_3CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$

(xv) (*A*) $(CH_3CH_2CH_2)_3B$; (*B*) $CH_3CH_2CH_2OH$

(xvi) (*A*)


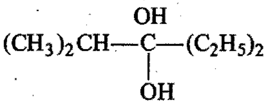
$CH_3-\underset{\underset{OD}{|}}{CH}-CH_3$; (xvii) (*A*)


$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2D$

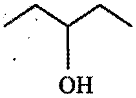
(xviii) (*A*)


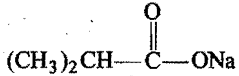
$CH_3-\underset{\underset{OD}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_2D$; (xix) (*A*) $(CH_3)_2C{=}CHCH_3$

(xx) (*A*)

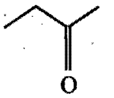

(xxi) (*A*)


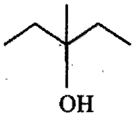
$(CH_3)_2CH-\underset{\underset{OH}{|}}{C}-(C_2H_5)_2$

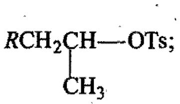
(xxii) (*A*)


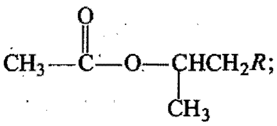
(xxiii) (*A*)


$(CH_3)_2CH-\overset{\overset{O}{\|}}{C}-ONa$

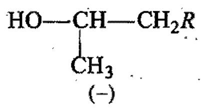
(xxiv) (*A*)


; (*B*)


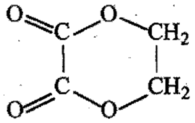
(xxv) (*A*)


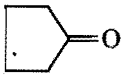
$RCH_2\underset{\underset{CH_3}{|}}{CH}-OTs$; (*B*)


$CH_3-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{CH_3}{|}}{CH}CH_2R$;

(*C*)


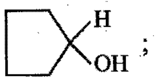
$HO-\underset{\underset{CH_3}{|}}{CH}-CH_2R$
(–)

(xxvi) (*A*)


(xxvii) (*A*) O_3/H_2O; (*B*)


;

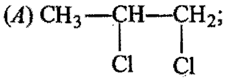
(*C*) $LiAlH_4$; (*D*)



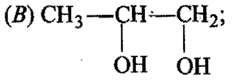
;

(*E*) Conc. H_2SO_4, 160°C

(xxviii) (*A*)



$CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2}$; (*B*)



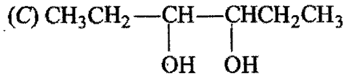
$CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}$;

(*C*) $CH_3CH=CH_2$

(xxix) (*A*) $CH_3CH_2C\equiv C-CH_2CH_3$;

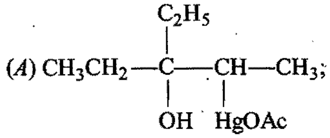
(*B*) $CH_3CH_2CH=CHCH_2CH_3$;

(*C*)



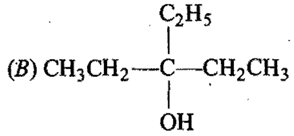
$CH_3CH_2-\underset{OH}{CH}-\underset{OH}{CH}CH_2CH_3$

(xxx) (*A*)



$CH_3CH_2-\underset{OH}{\overset{C_2H_5}{C}}-\underset{HgOAc}{CH}-CH_3$;

(*B*)



$CH_3CH_2-\underset{OH}{\overset{C_2H_5}{C}}-CH_2CH_3$

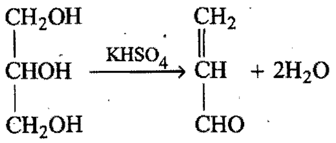
5. (a) Sodium ethoxide + hydrogen are formed.

$$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$$

(b) Dehydration occurs, ethylene is formed.

$$C_2H_5OH \xrightarrow[350°C]{Al_2O_3} CH_2=CH_2 + H_2O$$

(c) Dehydration occurs, acrolein is formed.



$$\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \xrightarrow{KHSO_4} \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CHO \end{matrix} + 2H_2O$$

(d) An ester, ethyl acetate is formed.

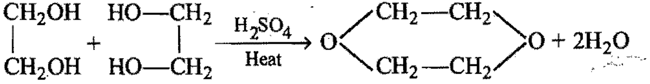
$$CH_3COCl + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + HCl$$

(e) Iodoform is formed.

$$C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{I_2} Cl_3CHO \xrightarrow{NaOH} CHI_3 + HCOONa$$

(f) Chloroform is formed.

(g) Dioxane is formed.



(h) $$(CH_3)_2CHOH \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \underset{\text{Acetone}}{(CH_3)_2CO}$$

(i) At room temperature, ethyl hydrogen sulphate is formed.

(1) $C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5HSO_4 + H_2O$

(2) At 140°C, diethyl ether is formed.

$$C_2H_5OH \xrightarrow{H_2SO_4} C_2H_5HSO_4 \xrightarrow{C_2H_5OH} C_2H_5OC_2H_5 + H_2SO_4$$

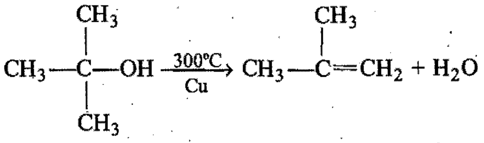
(3) At 170°C, ethylene is formed.

$$C_2H_5OH \xrightarrow{H_2SO_4} C_2H_5HSO_4 \xrightarrow{170°C} C_2H_4 + H_2SO_4$$

(4) While at 0°C, ethyl oxonium hydrogen sulphate is formed.

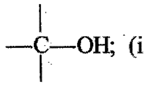
$$C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5OH_2^+HSO_4^-$$

(j) 2-Methyl propene is formed.



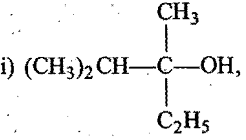
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[Cu]{300°C} CH_3-\overset{CH_3}{C}=CH_2 + H_2O$$

6. (i) Primary alcohol $-CH_2OH$, secondary alcohol $>CHOH$; tertiary alcohol



$-\overset{|}{\underset{|}{C}}-OH$; (ii) Isopropyl alcohol; (iii) Ethyl alcohol or spirit of wine; (iv) Methyl alcohol; (v) Chloroform; (vi) Maltase; (vii) Ethylene glycol; (viii) Acetyl chloride or acetic anhydride; (ix) Ethyl alcohol; (x) Methyl alcohol.

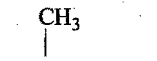
7. (a) 2-Methyl propan-2-ol; (b) Butan-2-ol; (c) 2-Ethyl pentan-1-ol; (d) Prop-2-yn-1-ol; (e) But-3-en-2-ol; (f) $CCl_3CH(OH)_2$; 2,2,2-Trichloroethane-1,1-diol; (g) $(CH_3)_2CHCH_2CH_2OH$, 3-Methyl butan-1-ol; (h) Pentan-3-ol; (i)



$(CH_3)_2CH-\underset{C_2H_5}{\overset{CH_3}{C}}-OH$,

2,3-Dimethyl pentan-3-ol; (j) 2,2,3-Trichlorobutan-1-ol; (k) 2-Buten-1-ol; (l) 2-Propen-1-ol; (m) 1-(2′-Bromophenyl) -2-methyl propan-1-ol; (n) 1-Bromo-1-phenyl ethanol

9. (i) $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH}$ (ii)



$\underset{\text{2-Methyl propan-1-ol}}{CH_3-\overset{CH_3}{C}HCH_2OH}$

(iii) $\underset{\text{Butan-2-ol}}{CH_3CH_2CHOHCH_3}$ (iv) $\underset{\text{2-Methyl propan-2-ol}}{(CH_3)_3COH}$

10. (a) $C_2H_5I + AgOH$ or aq. $NaOH \longrightarrow C_2H_5OH + AgI$ or NaI

(b) $C_2H_4 \xrightarrow[(ii)\ H_2O]{(i)\ H_2SO_4} C_2H_5OH$

(c) $CH_3COCl \xrightarrow[C_2H_5OH]{Na} C_2H_5OH$

(d) $CH_3COOH \xrightarrow{LiAlH_4} C_2H_5OH$

(e) $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$

(f) $CH_3CHO \xrightarrow[\text{or } Pt/H_2]{Na/C_2H_5OH} C_2H_5OH$

(g) $HCHO + CH_3MgBr \rightarrow CH_3CH_2OMgBr \xrightarrow[H^+]{H_2O} C_2H_5OH + Mg(OH)Br$

11. See properties of ethyl alcohol.

12. (a) $C_2H_5OH + PCl_5$

(b) $C_2H_5OH + CH_3COCl$

(c) $C_2H_5OH + K_2Cr_2O_7/H_2SO_4$

(d) $C_2H_5OH + I_2 + NaOH$

(e) C_2H_5OH + Conc. H_2SO_4 at 170°C

(f) $C_2H_5OH + H_2SO_4$ at 140°C

(g) $C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl \xrightarrow{[H]} C_2H_6$

(h) $C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl \xrightarrow{NaNH_2} C_2H_5NH_2$

(i) $C_2H_5OH + CaOCl_2$ (Bleaching powder).

14. (a) heat with $KHSO_4$ or P_2O_5, (b) heat with oxalic acid at 260°C, (c) treat with large amount of HI, (d) treat with a mixture of conc. H_2SO_4 and fuming nitric acid, (e) treat with PCl_5, (f) treat with conc. HNO_3.

15. (a) heat with conc. H_2SO_4, (b) treat with PCl_5, (c) oxidise with conc. HNO_3, (d) heat at 600°C, (e) heat with zinc chloride.

20. (e) (i) Ethylene, $CH_2{=}CH_2$ and (ii) Diethyl ether, $C_2H_5OC_2H_5$.

(f) H_2/catalyst, $LiAlH_4$, $NaBH_4$, NaH.

(g) (a) (i) $CH_3CH(OH)CH_2COOH$,
 (ii) $CH_3CH(OH)CH_2CH_2OH$
(b) (i) $HOH_2CCH_2COOCH_3$, (ii) $HOH_2CCH_2CH_2OH$
(c) (i) $CH_3CH_2CH(OH)CH_2CH_2Br$,
 (ii) $CH_3CH_2CH(OH)CH_2CH_3$
(d) (i) $p\text{-}O_2N—C_6H_4CH_2OH$, (ii) $p\text{-}H_2N—C_6H_4CH_2OH$

[$LiAlH_4$, being a more reactive reducing agent than $NaBH_4$, will also reduce —COOH and —COO*R* to corresponding primary alcohols. $LiAlH_4$ also reduces $—NO_2$ to $—NH_2$ and many alkyl halides are reduced to alkanes.]

(h) (a) $CH_3CH_2CH{=}CHCHO$ (b) C_6H_5CHO
(c) $C_6H_5COCH_2CH_2OH$ (d) No reaction

[MnO_2 is a weaker oxidising agent and it selectively oxidises the —OH group of only allylic and benzylic 1° and 2° alcohols to give aldehydes.]

(i) (a) $CH_3CH{=}CHCOCH_3$ (b) $C_6H_{11}CHO$

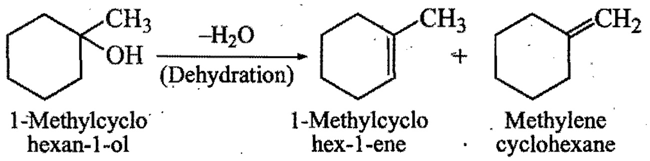
[The Jones reagent is a chromic acid in aqueous acetone solution and sufficiently mild to oxidise alcohols into $>C{=}O$ without affecting the double bonds.]

(j) By using selective oxidant like,
(i) $K_2Cr_2O_7$/dil. H_2SO_4 (ii) copper or silver catalyst at 250°C (iii) Pyridinium chlorochromate (PCC), made by mixing equimolar amounts of CrO_3, HCl and pyridine in CH_2Cl_2 (iv) Collins reagent, made up of 1 mole of CrO_3 to 2 mole of pyridine in CH_2Cl_2 (as in MnO_2).

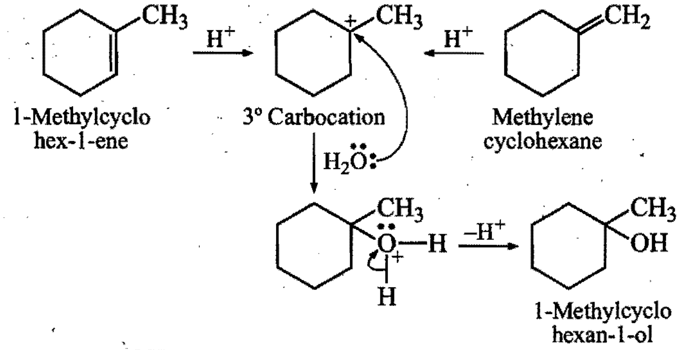
21. (i) $CH_3OH < H_2O < OH^- < CH_3O^-$
(ii) Propane < *n*-butane < ethanol < H_2O
(iii) Isobutane < *n*-butane < *n*-butyl chloride < *n*-butyl alcohol
(iv) Primary > secondary > tertiary
(v) Primary > secondary > tertiary
(vi) Pentan-1-ol > 3-methyl butan-2-ol > 2-methyl butan-2-ol
(vii) (*C*) > (*B*) > (*D*) > (*A*) > (*E*).

23. The alkenes for synthesising the alcohols can be obtained by first dehydrating the alcohol to give either a single alkene or a mixture of alkenes. If a mixture of alkenes is possible then find out which alkene gives the desired alcohol. The acid catalysed addition of H_2O to alkenes occurs in accordance with the Markownikoff's rule.

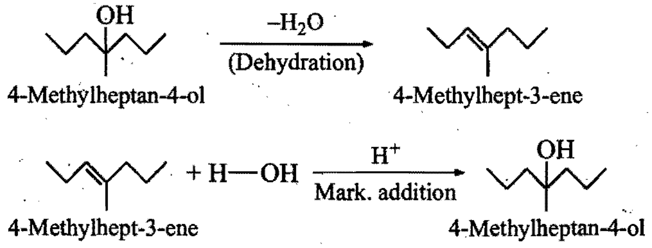
(i)



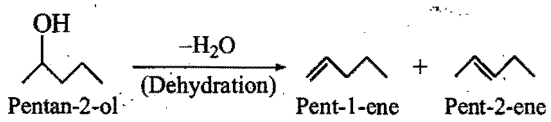
Addition of water to both these alkenes give the desired alcohol.



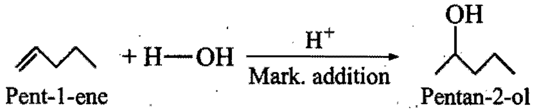
(ii)



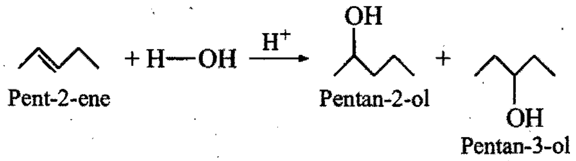
(iii)



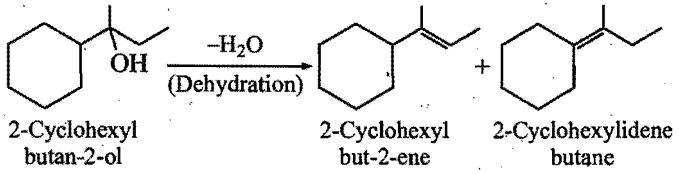
Addition of water to pent-1-ene gives the desired alcohol.



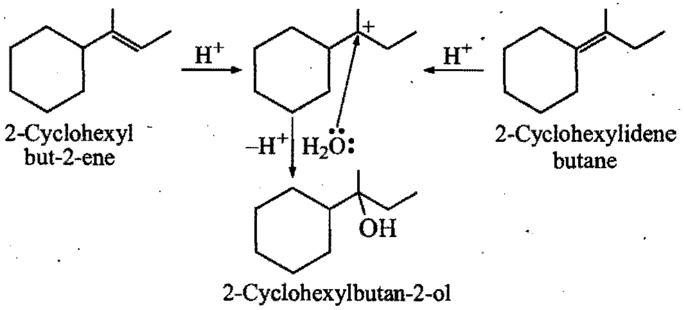
However Pent-2-ene will give two products.



(iv)



Addition of H_2O to both alkenes give the desired alcohol.



PROBLEMS BASED ON STRUCTURE AND PROPERTIES

1. A compound (*A*) with molecular formula $C_4H_{10}O$ reacts rapidly with metallic sodium but reacts very slowly with Lucas reagent. (*A*) when treated with hot concentrated H_2SO_4 gives a compound (*B*), C_4H_8. (*B*) on hydration with aqueous H_2SO_4 forms a compound (*C*) with molecular formula $C_4H_{10}O$. (*C*) is almost inert to metallic sodium but reacts readily with Lucas reagent. What are (*A*), (*B*) and (*C*)? Explain the reactions involved.

Ans. (*A*) $(CH_3)_2CHCH_2OH$; (*B*) $(CH_3)_2C{=}CH_2$; (*C*) $(CH_3)_2COHCH_3$]
Isobutyl alcohol — Isobutylene — *Tert.* butyl alcohol

2. Compound (*A*) reacts with sodium metal to produce hydrogen gas which is seen as bubbles. Compound (*A*) reacts with thionyl chloride to form (*B*), $C_6H_{13}Cl$. Compound (*B*) reacts with alcoholic KOH to form 1-hexene as the only product. Identify (*A*) and (*B*).

Ans. (*A*) Hexan-1-ol; (*B*) 1-Chlorohexane]

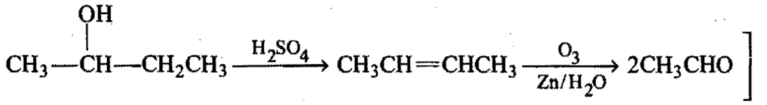
3. A compound of molecular formula $C_5H_{10}O_5$ is changed to $C_{13}H_{18}O_9$ by treatment with acetic anhydride. How many alcohol groups are indicated?

Ans. 4 —OH groups]

Hint: For every —OH group C_2OH_2 is added.]

4. An alcohol of unknown structure gave a positive Lucas test in about 5 minutes. When the alcohol was treated with hot conc. H_2SO_4, an alkene was formed which had the formula C_4H_8. Ozonolysis of this compound gave a single product C_2H_4O. What was the structure of the alcohol?

Hint: C_4H_8 on ozonolysis gave only a single product C_2H_4O, *i.e.*, CH_3CHO, hence C_4H_8 has the structure $CH_3CH{=}CHCH_3$. This can be obtained from a secondary alcohol. Hence, the unknown alcohol was Butan-2-ol ($CH_3CHOHCH_2CH_3$).



$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2CH_3 \xrightarrow{H_2SO_4} CH_3CH{=}CHCH_3 \xrightarrow[Zn/H_2O]{O_3} 2CH_3CHO$$]

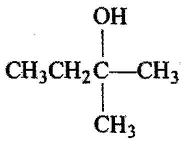
5. An organic compound gives hydrogen on reacting with sodium. It also gives iodoform test and forms an aldehyde of molecular formula C_2H_4O on oxidation. Name the compound.

Ans. Ethyl alcohol]

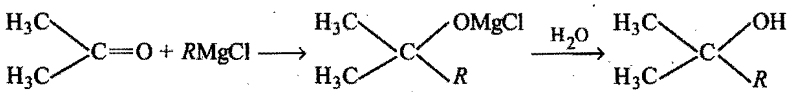
6. A compound (*A*) reacts with thionyl chloride to give a compound (*B*). (*B*) reacts with magnesium to form a Grignard reagent which is treated with acetone and the product is hydrolysed to give 2-methyl butan-2-ol. What are the structural formulae of (*A*) and (*B*)?

Ans. (*A*) Ethyl alcohol; (*B*) Ethyl chloride]

Hint: 2-Methyl butan-2-ol has the structure,



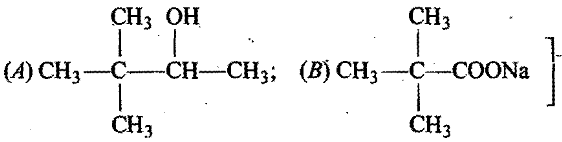
$$CH_3CH_2\overset{OH}{\underset{CH_3}{C}}-CH_3$$



Thus, *R* is CH_3CH_2—. Hence, (*B*) is CH_3CH_2Cl]

7. '*A*' ($C_6H_{14}O$) is an organic compound which gives blood red colour with ceric ammonium nitrate. It gives iodoform test on treatment with NaOH/I_2; salt of monobasic acid '*B*' is also formed during the reaction. Salt on acidification gives 2,2-dimethyl propanoic acid. What are '*A*' and '*B*'; give their structural formulae?

[**Ans.**

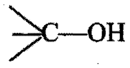
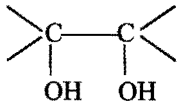


$$(A)\ CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{OH}{CH}-CH_3;\quad (B)\ CH_3-\overset{CH_3}{\underset{CH_3}{C}}-COONa$$]

OBJECTIVE QUESTIONS

Set I : This set contains the questions with single correct answer.

1. The general molecular formula, which represents the homologous series of alkanol is: **[CBSE (Med.) 2006]**
(a) $C_nH_{2n}O$ ☐ (b) $C_nH_{2n+1}O$ ☐
(c) $C_nH_{2n+2}O$ ☐ (d) $C_nH_{2n}O_2$ ☐

2. Which one is a primary alcoholic group?
(a) $—CH_2OH$ ☐ (b)  ☐
(c)  ☐ (d)  ☐

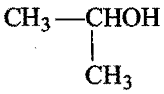
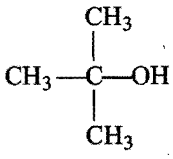
3. Butan-2-ol is a:
(a) primary alcohol ☐ (b) secondary alcohol ☐
(c) tertiary alcohol ☐ (d) dihydric alcohol ☐

4. Total number of isomeric alcohols with formula $C_4H_{10}O$ is:
(a) 2 ☐ (b) 1 ☐
(c) 3 ☐ (d) 4 ☐

5. Number of isomers represented by molecular formula $C_4H_{10}O$ is:
(a) 3 ☐ (b) 4 ☐
(c) 7 ☐ (d) 10 ☐

6. An isomer of ethanol is:
(a) methanol ☐ (b) dimethyl ether ☐
(c) acetone ☐ (d) diethyl ether ☐

7. Lucas reagent is: **[CET (Punjab) 2006; JIPMER (Med.) 2008]**
(a) anhydrous $ZnCl_2$ and conc. HCl ☐
(b) anhydrous $ZnCl_2$ and conc. HNO_3 ☐
(c) hydrous $ZnCl_2$ and conc. HNO_3 ☐
(d) hydrous $ZnCl_2$ and conc. HCl ☐

8. Which one of the following alcohols reacts most readily with Lucas reagent?
(a) $CH_3CH_2CH_2OH$ ☐ (b)  $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CHOH}}$ ☐
(c)  $CH_3—\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}—OH$ ☐ (d) CH_3CH_2OH ☐

9. Primary, secondary and tertiary alcohols are distinguished by:
(a) oxidation method ☐
(b) Lucas test ☐
(c) Victor Meyer's method ☐
(d) all of the above ☐

10. The product of reaction $CH_3CH_2OH \xrightarrow[Cu]{300°C} ?$ is:
(a) C_2H_6 ☐ (b) CH_3COCH_3 ☐
(c) CH_3COOH ☐ (d) CH_3CHO ☐

11. When vapours of secondary alcohol are passed over hot copper at 300°C, the product formed is:
(a) aldehyde ☐ (b) ketone ☐
(c) alkene ☐ (d) alkane ☐

12. Which of the following is soluble in water?
(a) CH_3OH ☐ (b) $CHCl_3$ ☐
(c) CCl_4 ☐ (d) CS_2 ☐

13. $CO + H_2 \xrightarrow[300°C/300\ atm]{X\ (catalyst)} CH_3OH$, the catalyst X is : **[JEE (Orissa) 2010]**
(a) Fe ☐ (b) Cr_2O_3/ZnO ☐
(c) V_2O_5 ☐ (d) Al_2O_3 ☐

14. Hydrogen bonding is maximum in:
(a) ethanol ☐ (b) diethyl ether ☐
(c) ethyl chloride ☐ (d) triethylamine ☐

15. Reason for excessive solubility of ethyl alcohol in water is due to:
(a) covalent bonding ☐
(b) ionic bonding ☐
(c) hydrogen bonding with water ☐
(d) none of the above ☐

16. Alcohols of high molecular masses are:
(a) soluble in water ☐
(b) soluble in water on heating ☐
(c) insoluble in all solvents ☐
(d) insoluble in water ☐

17. HBr reacts fastest with:
(a) 2-methyl propan-2-ol ☐ (b) propan-1-ol ☐
(c) propan-2-ol ☐ (d) 2-methyl propan-1-ol ☐

18. An industrial method for the preparation of methanol is:
(a) by reacting CH_4 with steam at 900°C with a nickel catalyst ☐
(b) by reduction of HCHO with $LiAlH_4$ ☐
(c) by catalytic reduction of CO in presence of $ZnO—Cr_2O_3$ ☐
(d) by reaction of HCHO with NaOH(aq.) ☐

19. Reaction, $\underbrace{CO + H_2}_{\text{Water gas}} + H_2 \xrightarrow[Cr_2O_3—ZnO]{673\ K,\ 300\ atm} ?$
may be used for manufacture of:
(a) HCHO ☐ (b) CH_3COOH ☐
(c) HCOOH ☐ (d) CH_3OH ☐

20. Which reagent can bring about,
$RCOOH \longrightarrow RCH_2OH$ transformation?
(a) Sn + HCl ☐ (b) $LiAlH_4$ in ether ☐
(c) Na and C_2H_5OH ☐ (d) H_2 and Pt ☐

21. Which of the following is an alkoxide?
(a) $CH_2{=}CH_2$ ☐ (b) CH_3MgI ☐
(c) $(CH_3CO)_2O$ ☐ (d) $CH_3CH_2CH_2ONa$ ☐

22. Rectified spirit contains:
(a) 75% alcohol ☐ (b) 95.5% alcohol ☐
(c) 56% alcohol ☐ (d) 100% alcohol ☐

23. Enzymes are:
(a) carbohydrates ☐ (b) lipids ☐
(c) proteins ☐ (d) none of these ☐

24. When wine is put in air, it becomes sour due to:
(a) oxidation of C_2H_5OH ☐
(b) reduction of C_2H_5OH ☐
(c) formation of $C_2H_5NH_2$ ☐
(d) dissolution of CO_2 ☐

25. Wine contains:
(a) CH_3OH ☐ (b) C_2H_5OH ☐
(c) C_6H_5OH ☐ (d) glucose ☐

26. Fermentation is an/a:
(a) endothermic reaction ☐
(b) exothermic reaction ☐
(c) polymerisation reaction ☐
(d) condensation reaction ☐

27. Glucose and fructose are converted into C_2H_5OH in presence of:
(a) invertase ☐ (b) diastase ☐
(c) zymase ☐ (d) lipids ☐

28. CH_3OH and C_2H_5OH may be distinguished chemically: **[BCECE (Med.) 2007]**
(a) by the action of HCl ☐
(b) by the action of $I_2 + Na_2CO_3$ ☐
(c) by the action of NH_3 ☐
(d) solubility in water ☐

29. Alcoholic fermentation is brought by:
(a) CO_2 ☐ (b) $NaHCO_3$ ☐
(c) yeast ☐ (d) bacteria ☐

30. Which of the following compounds is oxidised to prepare ethyl methyl ketone?
(a) Propan-2-ol ☐ (b) Butan-2-ol ☐
(c) Butan-l-ol ☐ (d) Tertiary butyl alcohol ☐

31. Grain alcohol is common name of:
(a) amyl alcohol ☐ (b) ethyl alcohol ☐
(c) methanol ☐ (d) none of these ☐

32. Pyroligneous acid obtained during destructive distillation of wood contains:
(a) acetone and methyl alcohol ☐
(b) methyl alcohol and ethyl alcohol ☐
(c) acetone and acetic acid ☐
(d) methyl alcohol, acetone and acetic acid ☐

33. The reason for high boiling points of alcohols as compared to isomeric ethers is:
(a) solubility of alcohols in water ☐
(b) higher reactivity ☐
(c) association in molecules due to hydrogen bonding ☐
(d) none of the above ☐

34. Starch is changed into disaccharide in presence of:
(a) diastase ☐ (b) maltase ☐
(c) laptase ☐ (d) zymase ☐

35. Absolute alcohol cannot be obtained by simple fractional distillation because:
(a) pure C_2H_5OH is unstable ☐
(b) C_2H_5OH forms hydrogen bonding with water ☐
(c) boiling point of C_2H_5OH is very close to that of water ☐
(d) constant boiling azeotropic mixture is formed with water ☐

36. Wood spirit is known as: **[AFMC 2004]**
(a) ethanol ☐ (b) methanol ☐
(c) acetone ☐ (d) benzene ☐

37. Isopropyl alcohol on oxidation forms:
(a) acetone ☐ (b) ether ☐
(c) methane ☐ (d) acetaldehyde ☐

38. Primary amine on treatment with $NaNO_2$ and HCl yields:
(a) nitro compound ☐ (b) ammonia ☐
(c) secondary alcohol ☐ (d) primary alcohol ☐

39. Identify (*Z*) in the reaction series,

$$H_2C{=}CH_2 \xrightarrow{HBr} (X) \xrightarrow{\text{Hydrolysis}} (Y) \xrightarrow[I_2(\text{excess})]{NaOH} (Z):$$

(a) C_2H_5I ☐ (b) C_2H_5OH ☐
(c) CHI_3 ☐ (d) CH_3CHO ☐

40. Which one is not characteristic of alcohols?
(a) They are lighter than water ☐
(b) Their boiling points rise uniformly with rising molecular weight ☐
(c) Lower members are insoluble in water but solubility increases regularly ☐
(d) Lower members have a pleasant odour and burning taste ☐

41. A compound (*X*) of the formula C_3H_8O yields a compound C_3H_6O on oxidation. To which of the following class of compounds could (*X*) belong?
(a) Aldehyde ☐ (b) Secondary alcohol ☐
(c) Alkene ☐ (d) *Tert.* alcohol ☐

42. Formaldehyde forms an addition product with CH_3MgI which on hydrolysis gives: **[BHU 2005; JIPMER (Med.) 2008]**
(a) ethyl iodide ☐ (b) ethyl alcohol ☐
(c) methyl alcohol ☐ (d) methyl iodide ☐

43. When CH_3MgI is made to react with acetone and the addition product is hydrolysed, we get: **[PMT (Raj.) 2002; AFMC 2004]**
(a) primary alcohol ☐ (b) secondary alcohol ☐
(c) tertiary alcohol ☐ (d) an aldehyde ☐

44. Identify (*Z*) in the following reaction series: **[CBSE (Med.) 2009]**

$$\text{Ethanol} \xrightarrow{PBr_3} (X) \xrightarrow{\text{Alc. KOH}} (Y) \xrightarrow[H_2O,\ \text{heat}]{H_2SO_4,\ \text{room temp.}} (Z)$$

(a) $H_2C{=}CH_2$ ☐ (b) CH_3CH_2OH ☐
(c) $CH_3CH_2OSO_3H$ ☐ (d) $C_2H_5OC_2H_5$ ☐

45. The compound (*B*) formed in the following sequence of reactions,

$CH_3CH_2CH_2OH \xrightarrow{PCl_5} (A) \xrightarrow{\text{Alc. KOH}} (B)$ is:

(a) propene ☐ (b) propyne ☐
(c) propane ☐ (d) propanal ☐

46. Ethanol containing some methanol is called:

(a) methylated spirit ☐ (b) rectified spirit ☐
(c) absolute spirit ☐ (d) none of these ☐

47. Rectified spirit can be dried with:

(a) conc. H_2SO_4 ☐ (b) CaO ☐
(c) anhydrous $CaCl_2$ ☐ (d) slaked lime ☐

48. When vapours of an alcohol are passed over hot reduced copper, alcohol is converted into alkene, the alcohol is:

(a) tertiary ☐ (b) primary ☐
(c) secondary ☐ (d) none of these ☐

49. Ethyl alcohol on oxidation with dil. acid $K_2Cr_2O_7$ gives:

(a) formic acid ☐ (b) formaldehyde ☐
(c) acetic acid ☐ (d) acetaldehyde ☐

50. Lucas reagent is used to distinguish among primary, secondary and tertiary:

(a) alkyl halides ☐ (b) aliphatic amines ☐
(c) aromatic amines ☐ (d) alcohols ☐

51. Lucas test is used for the determination of: **[CET (Karnataka) 2009]**

(a) aldehydes ☐ (b) phenols ☐
(c) carboxylic acids ☐ (d) alcohols ☐

52. Chlorine reacts with ethanol to give:

(a) ethyl chloride ☐ (b) chloroform ☐
(c) acetaldehyde ☐ (d) chloral ☐

53. The compound that will not give iodoform test with alkali and iodine is:

(a) diethyl ketone ☐ (b) ethanol ☐
(c) acetone ☐ (d) isopropyl alcohol ☐

54. To prepare propan-2-ol from methyl magnesium iodide, the chemical reagent required is:

(a) CH_3CHO ☐ (b) HCHO ☐
(c) CH_3COCH_3 ☐ (d) CO_2 ☐

55. For a given alcohol, the order of reactivity with halogen acids is:

(a) HI > HBr > HCl ☐ (b) HI > HCl > HBr ☐
(c) HCl > HBr > HI ☐ (d) HBr > HI > HCl ☐

56. Which is U.P. spirit (containing ethyl alcohol by volume)?

(a) 85% ☐ (b) 75% ☐
(c) 65% ☐ (d) 55% ☐

57. Power alcohol is:

(a) absolute alcohol + methyl alcohol ☐
(b) absolute alcohol + petrol ☐
(c) rectified alcohol + petrol ☐
(d) denatured alcohol + petrol ☐

58. If there be a compound of formula $CH_3C(OH)_3$ which one would be obtained without treatment with any reagent:

(a) methanol ☐ (b) formaldehyde ☐
(c) acetic acid ☐ (d) ethanol ☐

59. Out of *n*-butyl alcohol, *sec*. butyl alcohol, *tert*. butyl alcohol, the highest boiling point is expected for:

(a) *n*-butyl alcohol ☐ (b) *sec*. butyl alcohol ☐
(c) *tert*. butyl alcohol ☐ (d) same for all ☐

60. When ethyl alcohol is dissolved in water, it is accompanied with:

(a) absorption of heat and contraction in volume ☐
(b) evolution of heat and contraction in volume ☐
(c) absorption of heat and increase in volume ☐
(d) evolution of heat and increase in volume ☐

61. 23 g of sodium metal shall react with methyl alcohol to give:

(a) 1 mole of oxygen ☐
(b) 1 mole of hydrogen ☐
(c) 1/2 mole of hydrogen ☐
(d) 1/2 mole of oxygen ☐

62. Which one of the following statements is wrong?

(a) CH_3OH is used for drinking purposes ☐
(b) CH_3OH is highly poisonous compound ☐
(c) CH_3OH is most acidic alcohol ☐
(d) CH_3OH is soluble in water ☐

63. Which of the following alcohols is least soluble in water? **[BHU 2002]**

(a) CH_3OH ☐ (b) C_3H_7OH ☐
(c) $C_{10}H_{21}OH$ ☐ (d) C_4H_9OH ☐

64. In glycerol molecule, there is:

(a) one primary alcoholic group ☐
(b) one secondary alcoholic group ☐
(c) two secondary alcoholic groups ☐
(d) two primary and one secondary alcoholic groups ☐

65. For one mole of glycerol, moles of acetyl chloride required for complete acetylation are:

(a) one ☐ (b) two ☐
(c) three ☐ (d) four ☐

66. The alcohol which forms fats with fatty acids is:

(a) ethanol ☐ (b) methanol ☐
(c) isopropyl alcohol ☐ (d) glycerol ☐

67. Acrolein is formed when glycerol is heated with:

(a) acidified $KMnO_4$ ☐ (b) Br_2 water ☐
(c) $KHSO_4$ ☐ (d) HNO_3 ☐

68. Glycerol on treatment with oxalic acid at 110°C forms:

(a) allyl alcohol ☐ (b) formic acid ☐
(c) CO_2 and CO ☐ (d) glyceric acid ☐

69. The explosive nitroglycerine is:

(a) an ester ☐ (b) a salt ☐
(c) a soap ☐ (d) a complex compound ☐

70. Which of the following compounds is commonly used as antifreeze in automobile radiators?

(a) CH_3OH ☐ (b) C_2H_5OH ☐
(c) Glycerol ☐ (d) All of these ☐

71. In cold countries, ethylene glycol is added in the water used in the radiators of cars during winters. This results in:

(a) lowering in freezing point ☐
(b) reducing the viscosity ☐
(c) reducing the specific heat ☐
(d) making water a better conductor of electricity ☐

72. Which one of the following statements is wrong?
(a) Glycerol is used as sweetening agent in beverages ☐
(b) Glycerol is used for making cosmetics ☐
(c) Glycerol is used for making dynamite ☐
(d) Glycerol is used for making ethyl alcohol by fermentation ☐

73. Which of the following compounds is obtained when glycerol is heated with oxalic acid at 230°C?
(a) Formic acid ☐ (b) Allyl alcohol ☐
(c) Carbon dioxide ☐ (d) Glycerol dioxalate ☐

74. Impure glycerine can be purified by:
(a) steam distillation ☐ (b) simple distillation ☐
(c) vacuum distillation ☐ (d) solvent extraction ☐

75. The boiling point of ethanol is higher as compared to the boiling point of diethyl ether though both have the same molecular formula. This is due to: **[UPSEE (Engg.) 2010]**
(a) resonance ☐ (b) H-bonding ☐
(c) *R*-group ☐ (d) covalent bonding ☐

76. The product formed when glycerol reacts with PCl_5 is:
(a) 1,2,3-trichloropropane ☐
(b) glycerol monochlorohydrin ☐
(c) glycerol dichlorohydrin ☐
(d) all of the above ☐

77. Which one is not the byproduct of alcohol industry?
(a) Carbon dioxide ☐ (b) Argol ☐
(c) Fusel oil ☐ (d) Glycerol ☐

78. Following compounds are given
(i) CH_3CH_2OH (ii) CH_3COCH_3
(iii) $(CH_3)_2CHOH$ (iv) CH_3OH
Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform? **[AIPMT (Mains) 2010]**
(a) (i) and (ii) ☐ (b) (i), (iii) and (iv) ☐
(c) only (ii) ☐ (d) (i), (ii) and (iii) ☐

79. The group reagent for the test of alcohols is:
(a) ceric ammonium nitrate ☐
(b) Schiff's reagent ☐
(c) Molisch's reagent ☐
(d) bromine water ☐

80. The most important ingredient of dynamite is:
(a) nitrobenzene ☐ (b) picric acid ☐
(c) nitroglycerine ☐ (d) TNT ☐

81. The compound which reacts with oxalic acid at about 110°C to give formic acid is:
(a) acetone ☐ (b) butan-2-ol ☐
(c) glycerol ☐ (d) ethanol ☐

82. Glycerol is more viscous than ethanol due to: **[UPSEE (Engg.) 2008]**
(a) many hydrogen bonds per molecule ☐
(b) Fajan's rule ☐
(c) high boiling point ☐
(d) high molecular weight ☐

83. $X \xrightarrow{PCl_5} C_2H_5Cl$, $Y \xrightarrow{PCl_5} CH_3COCl$,
X and *Y* are: **[JEE (WB) 2010]**
(a) $(C_2H_5)_2O$ and CH_3CO_2H ☐
(b) C_2H_5I and C_2H_5CHO ☐
(c) C_2H_5OH and C_2H_5CHO ☐
(d) C_2H_5OH and CH_3CO_2H ☐

84. The compound which reacts fastest with Lucas reagent at room temperature is: **[JIPMER 2004]**
(a) butan-1-ol ☐ (b) butan-2-ol ☐
(c) 2-methyl propan-1-ol ☐ (d) 2-methyl propan-2-ol ☐

85. Which of the following compounds will form a hydrocarbon on reaction with a Grignard reagent?
(a) CH_3CH_2OH ☐ (b) CH_3CHO ☐
(c) CH_3COCH_3 ☐ (d) HCHO ☐

86. A compound obtained by heating glycerol with conc. H_2SO_4 or $KHSO_4$ or P_2O_5 is:
(a) glyceric acid ☐
(b) allyl alcohol ☐
(c) acrolein ☐
(d) glycerol hydrogen sulphate ☐

87. Boiling point of C_2H_5OH is higher as compared to C_2H_5SH on account of:
(a) association ☐ (b) dissociation ☐
(c) low molecular mass ☐ (d) none of these ☐

88. Ethyl alcohol is denatured by adding:
(a) glycerol ☐ (b) methanol and pyridine ☐
(c) aniline ☐ (d) ether and ethanol ☐

89. Propene can be converted into propan-1-ol. Which of the reagents among the following is ideal to affect the conversion?
(a) Alkaline $KMnO_4$ ☐
(b) B_2H_6 and alkaline H_2O_2 ☐
(c) O_3/Zn ☐
(d) OsO_4/CH_2Cl_2 ☐

90. Which of the following can work as dehydrating agent for alcohols?
(a) H_2SO_4 ☐ (b) Al_2O_3 ☐
(c) H_3PO_4 ☐ (d) All of these ☐

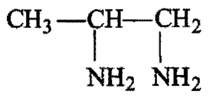
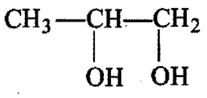
91. Which of the following reagents can convert acetic acid into ethanol? **[BCECE (Med.) 2006]**
(a) Sn + HCl ☐ (b) $H_2 + Pt$ ☐
(c) $LiAlH_4$ + ether ☐ (d) Na + alcohol ☐

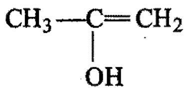
92. Which of the following is a tertiary alcohol? **[BCECE (Med.) 2008]**
(a) 2-Methylpropan-1-ol ☐
(b) 2-Methylpropan-2-ol ☐
(c) 3-Methylbutan-1-ol ☐
(d) 3-Methylbutan-2-ol ☐

93. A compound (*X*) with molecular formula C_3H_8O can be oxidised to (*Y*) with a molecular formula $C_3H_6O_2$. (*X*) is most likely:
(a) primary alcohol ☐ (b) secondary alcohol ☐
(c) aldehyde ☐ (d) ketone ☐

94. Identify (*Z*) in the series,

$$C_3H_7OH \xrightarrow[170^\circ C]{\text{Conc. } H_2SO_4} (X) \xrightarrow{Br_2} (Y) \xrightarrow[\text{Alc. KOH}]{\text{Excess of}} (Z)$$

(a) 
$CH_3-CH(NH_2)-CH_2(NH_2)$ ☐ (b) 
$CH_3-CH(OH)-CH_2(OH)$ ☐

(c) $CH_3-C\equiv CH$ ☐ (d) 
$CH_3-C(OH)=CH_2$ ☐

95. Denatured spirit is mainly used as a:
(a) drug ☐
(b) good fuel ☐
(c) material in preparing oils ☐
(d) solvent in preparing varnishes ☐

96. The product formed, when glycol is heated with zinc chloride, is:
(a) acetaldehyde ☐ (b) glyoxal ☐
(c) oxalic acid ☐ (d) ethylene oxide ☐

97. The product formed, when glycol is heated with conc. H_2SO_4, is:
(a) ethylene ☐ (b) dioxane ☐
(c) ethylene oxide ☐ (d) glyoxal ☐

98. Oxalic acid is formed when glycol is treated with:
(a) H_2SO_4 ☐ (b) H_3PO_4 ☐
(c) HCl ☐ (d) HNO_3 ☐

99. Which of the following is generally present in tonics?
(a) Ethanol ☐ (b) Ether ☐
(c) Ethanal ☐ (d) Chloral ☐

100. The compound formed by reaction of ethylene glycol and periodic acid (HIO_4) is: **[CBSE (Med.) 2009]**
(a) carbon dioxide ☐ (b) formic acid ☐
(c) formaldehyde ☐ (d) glyoxal ☐

101. Dynamite is prepared by mixing nitroglycerine with:
(a) saw dust and ammonium nitrate ☐
(b) cellulose nitrate ☐
(c) saw dust alone ☐
(d) conc. sulphuric acid ☐

102. When 3,3-dimethyl butan-2-ol is heated with conc. H_2SO_4 the major product obtained is: **[PMT (Kerala) 2007; Punjab CET (Engg.) 2008]**
(a) 2,3-dimethyl but-1-ene ☐
(b) 3,3-dimethyl but-1-ene ☐
(c) 2,3-dimethyl but-2-ene ☐
(d) *cis* and *trans* isomers of 2,3-dimethyl but-2-ene ☐
[Hint : See solved problem 13(c)]

103. Isobutyl alcohol is a:
(a) primary alcohol ☐ (b) secondary alcohol ☐
(c) tertiary alcohol ☐ (d) diethyl ether ☐

104. The hydrolysis of oils and fats with alkali is called:
(a) esterification ☐ (b) saponification ☐
(c) dehydration ☐ (d) acetylation ☐

105. Which is used in alcoholic beverages? **[CPMT 2008]**
(a) Phenol ☐ (b) Glycerol ☐
(c) Methanol ☐ (d) Ethanol ☐

106. When ethyl alcohol reacts with nitric acid, it forms:
(a) nitromethane ☐ (b) nitroethane ☐
(c) ethyl nitrate ☐ (d) diethyl ether ☐

107. Dehydration of methyl alcohol gives:
(a) methane ☐
(b) ethane ☐
(c) methyl hydrogen sulphate ☐
(d) dimethyl ether ☐

108. Upon oxidation, an alcohol gave a carbonyl compound containing same number of carbon atoms. The alcohol is a:
(a) primary alcohol ☐
(b) secondary alcohol ☐
(c) tertiary alcohol ☐
(d) primary or secondary alcohol ☐

109. Liquor poisoning is due to the presence of:
(a) methyl alcohol ☐
(b) ethyl alcohol ☐
(c) carbonic acid ☐
(d) bad compound in liquor ☐

110. An enzyme which changes cane sugar into glucose and fructose, is known as:
(a) zymase ☐ (b) maltase ☐
(c) invertase ☐ (d) diastase ☐

111. An enzyme which changes maltose into glucose is known as:
(a) zymase ☐ (b) maltase ☐
(c) invertase ☐ (d) diastase ☐

112. Methylated spirit is:
(a) 100% alcohol ☐
(b) 95.6% alcohol + 4.4% water ☐
(c) 90% alcohol + 9% methanol + pyridine, etc. ☐
(d) power alcohol ☐

113. Denatured spirit is a mixture of ethyl alcohol, methyl alcohol and:
(a) acetic acid ☐ (b) pyridine ☐
(c) acetone ☐ (d) water ☐

114. Ethanol is used for the preparation of:
(a) Tincture iodine ☐ (b) Toluene ☐
(c) DDT ☐ (d) Carbon tetrachloride ☐

115. In the following reaction, what is (X)?

$$(X) \xrightarrow{Na_2SO_3} \text{Glycerol} + \text{acetaldehyde} + CO_2$$

(a) Ethyl alcohol ☐ (b) Glucose ☐
(c) Glycol ☐ (d) Allyl alcohol ☐

116. Glycerol on oxidation with bromine water or sodium hypobromite or Fenton's reagent yields:
(a) oxalic acid ☐ (b) meso-oxalic acid ☐
(c) formic acid ☐ (d) glycerose ☐

117. When glycerol is treated with phosphorus tri-iodide, the main product obtained is:
(a) glyceryl tri-iodide ☐ (b) propene ☐
(c) allyl iodide ☐ (d) isopropyl iodide ☐

118. Glycol on treatment with PI_3 gives mainly:
(a) ethylene ☐ (b) ethylene iodide ☐
(c) ethyl iodide ☐ (d) ethane ☐

119. Glycol may be obtained:
(a) by the oxidation of ethylene with cold, dilute, alkaline permanganate solution ☐
(b) by the hydrolysis of ethylene bromide under reflux with aqueous sodium carbonate solution ☐
(c) by the hydrolysis of ethylene chlorohydrin on boiling with aqueous sodium bicarbonate ☐
(d) by any of the above methods ☐

120. If two —OH groups are attached to 1,4-carbon atoms, it is called:
(a) α-glycol ☐ (b) β-glycol ☐
(c) γ-glycol ☐ (d) Δ-glycol ☐

121. Ethyl alcohol is manufactured by:
(a) fermentation of sugars ☐
(b) hydration of ethylene ☐
(c) catalytic reduction of acetaldehyde ☐
(d) all of the above ☐

122. The factor adversely affecting the fermentation process is:
(a) presence of air ☐
(b) low concentration of sugars ☐
(c) high concentration of sugars ☐
(d) presence of an enzyme ☐

123. The optimum temperature for carrying out fermentation of molasses is:
(a) 0°C ☐ (b) 30°C ☐
(c) 60°C ☐ (d) 100°C ☐

124. Fermentation of starch solution to ethyl alcohol does not require:
(a) zymase ☐ (b) maltase ☐
(c) invertase ☐ (d) diastase ☐

125. Power alcohol is:
(a) rectified spirit ☐
(b) a mixture of petrol and ethanol ☐
(c) absolute alcohol ☐
(d) a mixture of methanol and ethanol ☐

126. The compound which gives the most stable carbonium ion on dehydration is:
(a) $(CH_3)_2CH{-}CH_2OH$ ☐
(b) $CH_3CH_2CH_2CH_2OH$ ☐
(c) $CH_3{-}CH(OH){-}CH_2CH_3$ ☐
(d) $(CH_3)_3C{-}OH$ ☐

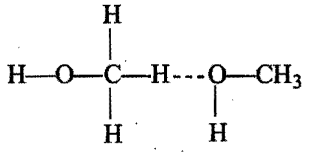
127. Alkenes are converted into alcohols by:
(a) hydrolysis with dil. H_2SO_4 ☐
(b) hydration of alkene with alkaline $KMnO_4$ ☐
(c) hydrolysis with water vapours and conc. H_2SO_4 ☐
(d) hydration of alkene with aq. KOH ☐

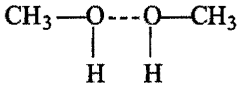
128. Which one of the following will produce a primary alcohol by reacting with CH_3MgI?
(a) Ethylene oxide ☐ (b) Ethyl acetate ☐
(c) Methyl cyanide ☐ (d) Acetone ☐

129. Which of the following are the starting materials for the Grignard's synthesis of *tert*. butyl alcohol?
(a) $CH_3MgI + CH_3COCH_3$ ☐
(b) $CH_3MgI + CH_3CHOHCH_3$ ☐
(c) $CH_3CH_2MgBr + CH_3COCH_3$ ☐
(d) $CH_3CH_2MgBr + CH_3CHO$ ☐

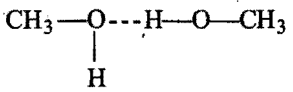
130. How many isomers of $C_5H_{11}OH$ will be primary alcohols? **[BHU (S) 2006]**
(a) 5 ☐ (b) 4 ☐
(c) 3 ☐ (d) 2 ☐

131. The dimer of methanol will have the structure:

(a) 
$H{-}O{-}\overset{H}{\underset{H}{C}}{-}H\cdots\underset{H}{O}{-}CH_3$ ☐

(b) 
$CH_3{-}\underset{H}{O}\cdots\underset{H}{O}{-}CH_3$ ☐

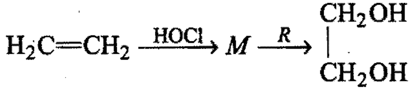
(c) $H{-}O{-}CH_3\cdots CH_3{-}O{-}H$ ☐

(d) 
$CH_3{-}\underset{H}{O}\cdots H{-}O{-}CH_3$ ☐

132. An alcohol on oxidation is found to give CH_3COOH and CH_3CH_2COOH. The structure of the alcohol is:
(a) $CH_3CH_2CH_2OH$ ☐
(b) $CH_3CH_2CH(OH)CH_3$ ☐
(c) $CH_3CH(OH)CH_2CH_2CH_3$ ☐
(d) $(CH_3)_2C(OH)CH_2CH_3$ ☐

133. A compound with molecular formula $C_4H_{10}O_3$ is converted by the action of acetyl chloride to a compound with molecular weight 190. The original compound has:
(a) one —OH group ☐ (b) two —OH groups ☐
(c) three — OH groups ☐ (d) no —OH group ☐

134. In reaction sequence,

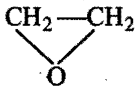

$$H_2C{=}CH_2 \xrightarrow{HOCl} M \xrightarrow{R} \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$$

molecule *M* and reagent *R*, respectively are:
(a) CH_3CH_2Cl and NaOH ☐
(b) CH_3CH_2OH and H_2SO_4 ☐
(c) $CH_2Cl{-}CH_2OH$ and aq. $NaHCO_3$ ☐
(d) $CH_3{-}CH_3$ and heat ☐

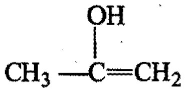
135. Which of the following represents neo-pentyl alcohol? **[AMU (Engg.) 2009]**
(a) $CH_3CH(CH_3)CH_2CH_2OH$ ☐
(b) $CH_3(CH_2)_3OH$ ☐
(c) $(CH_3)_3C{-}CH_2OH$ ☐
(d) $CH_3CH_2CH(OH)C_2H_5$ ☐

136. Propan-1-ol and propan-2-ol can be distinguished by: **[IIT (S) 2001]**
(a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution ☐
(b) oxidation with acidic dichromate followed by reaction with Fehling solution ☐
(c) oxidation by heating with copper followed by reaction with Fehling solution ☐
(d) oxidation with conc. H_2SO_4 followed by reaction with Fehling solution ☐

137. 2-Phenylethanol may be prepared by the reaction of phenyl magnesium bromide with: **[GATE 2001]**
(a) HCHO ☐ (b) CH_3CHO ☐
(c) CH_3COCH_3 ☐ (d) ☐



138. Vinyl carbinol is: **[UPSEAT 2001]**
(a) $HO—CH_2—CH=CH_2$ ☐
(b) ☐



$CH_3—\overset{OH}{\overset{|}{C}}=CH_2$

(c) $CH_3—CH=CH—OH$ ☐
(d) $CH_3—C(CH_2OH)=CH_2$ ☐

139. *n*-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent: **[CBSE (Med.) 2002]**
(a) PCl_5 ☐
(b) reduction ☐
(c) oxidation with potassium dichromate ☐
(d) ozonolysis ☐

140. In the synthesis of glycerol from propene, the steps involved are: **[TEE (Tamil Nadu) 2002]**
(a) glycerol β-chlorohydrin and allyl chloride ☐
(b) glycerol trichloride and glycerol α-chlorohydrin ☐
(c) allyl alcohol and α-chlorohydrin ☐
(d) allyl alcohol and monosodium glycerolate ☐

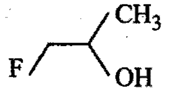
141. Order of esterification of alcohol is: **[PMT (Raj.) 2002]**
(a) $T > S > P$ ☐ (b) $S > T > P$ ☐
(c) $P > S > T$ ☐ (d) none of these ☐

142. An organic compound (*A*) reacts with methyl magnesium iodide to form an addition product which on hydrolysis forms the compound (*B*). Compound (*B*) gives blue colour salt in Victor Meyer's test. The compounds (*A*) and (*B*) are respectively: **[TEE (Tamil Nadu) 2002]**
(a) acetaldehyde, tertiary butyl alcohol ☐
(b) acetaldehyde, ethyl alcohol ☐
(c) acetaldehyde, isopropyl alcohol ☐
(d) acetone, isopropyl alcohol ☐

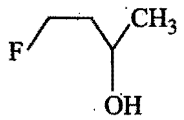
143. An organic compound '*X*' on treatment with acidified $K_2Cr_2O_7$ gives a compound '*Y*' which reacts with I_2 and Na_2CO_3 to form tri-iodomethane. The compound '*X*' is:
(a) CH_3OH ☐ (b) CH_3COCH_3 ☐
(c) CH_3CHO ☐ (d) $CH_3CHOHCH_3$ ☐

144. How many optically active stereoisomers are possible for butan-2,3-diol?
(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) 4 ☐

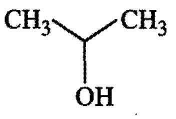
145. The order of reactivity of the following alcohols towards conc. HCl is:



(I)



(II)



(III)

(IV)

(a) I > II > III > IV ☐ (b) I > III > II > IV ☐
(c) IV > III > II > I ☐ (d) IV > III > I > II ☐

146. $(CH_3)_3CMgBr$ on reaction with D_2O produces:
(a) $(CH_3)_3CD$ ☐ (b) $(CH_3)_3COD$ ☐
(c) $(CD_3)_3CD$ ☐ (d) $(CD_3)_3OD$ ☐

147. In the reaction given below, *X* is:

Neo-pentylalcohol $\xrightarrow{H_2SO_4} X$ **[DPMT 2009]**

(a) 2-methylpentane ☐ (b) Neo-pentane ☐
(c) 2-methylpent-2-ene ☐ (d) 2-methylbut-2-ene ☐

148. Which one/ones of the following reactions will yield 2-propanol?

(i) $CH_3CH=CH_2 + H_2O \xrightarrow{H^+}$

(ii) $CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgI}$

(iii) $HCHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } C_2H_5MgI}$

(iv) $CH_3CH=CH_2 \xrightarrow{\text{Neutral } KMnO_4}$

Choose the right answer:
(a) (i) and (ii) ☐ (b) (ii) and (iii) ☐
(c) (iii) and (i) ☐ (d) (ii) and (iv) ☐

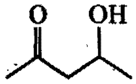
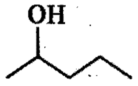
149. Which of the following enzymes convert glucose into ethyl alcohol? **[BHU 2002; JIPMER (Med.) 2008]**
(a) Diastase ☐ (b) Invertase ☐
(c) Maltase ☐ (d) Zymase ☐

150. Ethyl acetate reacts with CH_3MgBr to form:
(a) secondary alcohol ☐
(b) tertiary alcohol ☐
(c) primary alcohol and an acid ☐
(d) an acid ☐

151. The correct order of boiling points for primary (1°), secondary (2°) and tertiary alcohol (3°) is: **[PMT (Raj.) 2002]**
(a) 1° > 2° > 3° ☐ (b) 3° > 2° > 1° ☐
(c) 2° > 1° > 3° ☐ (d) 2° > 3° > 1° ☐

152. Which of the following is the most suitable method for removing the traces of water from ethanol?
(a) Heating with Na metal ☐
(b) Distilling it ☐
(c) Passing dry HCl gas through it ☐
(d) Reacting with Mg ☐

153. Which one of the following will most readily be dehydrated in acidic condition? **[IIT (S) 2000; CPMT 2006; BCECE (Med.) 2008]**

(a)

☐ (b)

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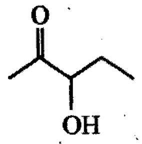
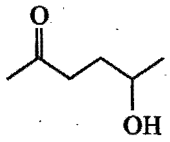
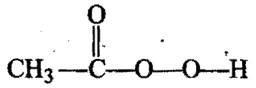
(c)

☐ (d)

☐

154. The reaction of Lucas reagent is fastest with: **[PMT (MP) 2000]**

(a) $(CH_3)_3C—OH$ ☐ (b) $(CH_3)_2CHOH$ ☐
(c) $CH_3(CH_2)_2OH$ ☐ (d) CH_3CH_2OH ☐

155. Propan-l-ol may be prepared by the reaction of propene with: **[CBSE (Med.) 2000; AIIMS (Med.) 2003]**

(a) H_3BO_3 ☐ (b) $B_2H_6/NaOH—H_2O_2$ ☐
(c) H_2SO_4/H_2O ☐ (d)

$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—O—O—H$ ☐

156. What is formed when glycerol reacts with HIO_4? **[DPMT 2000]**

(a) Two molecules of formic acid and one molecule of formaldehyde ☐
(b) Two molecules of formaldehyde and one molecule of formic acid ☐
(c) Three molecules of formic acid ☐
(d) Three molecules of formaldehyde ☐

157. The compound that will react most readily with NaOH to form methanol is: **[IIT (S) 2001]**

(a) $(CH_3)_4\overset{+}{N}I^-$ ☐ (b) $CH_3—O—CH_3$ ☐
(c) $(CH_3)_3\overset{+}{S}I^-$ ☐ (d) $(CH_3)_3C—Cl$ ☐

158. Ethanol when reacted with PCl_5 gives (*A*), $POCl_3$ and HCl. (*A*) reacts with silver nitrite to form (*B*) (major product) and AgCl. (*A*) and (*B*) are respectively: **[EAMCET 2001]**

(a) C_2H_5Cl and $C_2H_5OC_2H_5$ ☐
(b) C_2H_6 and $C_2H_5OC_2H_5$ ☐
(c) C_2H_5Cl and $C_2H_5NO_2$ ☐
(d) C_2H_6 and $C_2H_5NO_2$ ☐

159. Given are cyclohexanol (I), acetic acid (II), 2,4,6-trinitrophenol (III) and phenol (IV). In these the order of decreasing acidic character will be : **[CBSE (PMT) Prelims 2010]**

(a) II > III > IV > I ☐ (b) II > III > I > IV ☐
(c) III > II > IV > I ☐ (d) III > IV > II > I ☐

160. Excess of ethanol when heated with conc. H_2SO_4 at 140°C, the compound obtained is: **[AFMC 2002]**

(a) ethene ☐
(b) diethyl sulphate ☐
(c) ethoxy ethane ☐
(d) ethyl hydrogen sulphate ☐

161. When glycerol is treated with excess of HI, it produces : **[AIPMT (Mains) 2010]**

(a) 2-iodopropane ☐ (b) allyl iodide ☐
(c) propene ☐ (d) glycerol tri-iodide ☐

162. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4, the initiation step is: **[AIEEE 2003]**

(a) elimination of water ☐
(b) formation of an ester ☐
(c) formation of carbocation ☐
(d) protonation of alcohol molecule ☐

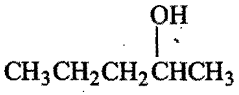
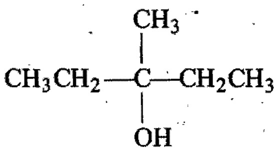
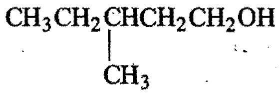
163. Which of the following functional groups, cannot be reduced to alcohol using $NaBH_4$ in ethanolic solution? **[UPSEAT 2004]**

(a) *R*—O—*R* ☐ (b) *R*COCl ☐
(c) *R*—COOH ☐ (d) *R*—CHO ☐

164. Acetyl bromide when reacts with excess of CH_3MgI followed by treatment with saturated solution of NH_4Cl it gives: **[AIEEE 2004]**

(a) acetone ☐
(b) acetamide ☐
(c) 2-methyl-2-propanol ☐
(d) acetyl iodide ☐

165. Among the following compounds which can be dehydrated very easily? **[AIEEE 2004]**

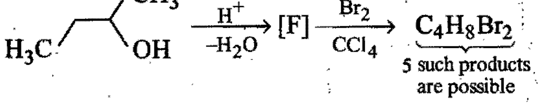
(a) $CH_3CH_2CH_2CH_2CH_2OH$ ☐
(b)

$CH_3CH_2CH_2\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$ ☐
(c)

$CH_3CH_2—\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}—CH_2CH_3$ ☐
(d)

$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_2OH$ ☐

166. Which of the following is industrially prepared by passing ethylene into hypochlorous acid? **[BHU 2004]**

(a) Ethylene glycol ☐
(b) Ethylene oxide ☐
(c) Ethylene dinitrate ☐
(d) Ethane ☐

167. The —OH group of an alcohol or the —COOH (carboxylic acid) can be replaced by —Cl using: **[CBSE (Med.) 2004; UGET (Med.) 2007]**

(a) phosphorus pentachloride ☐
(b) hypochlorous acid ☐
(c) chlorine ☐
(d) hydrochloric acid ☐

168.


How many structures of [F] are possible? **[IIT (S) 2003]**

(a) 2 ☐ (b) 5 ☐
(c) 6 ☐ (d) 3 ☐

169. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is: **[AIEEE 2005]**

(a) acidic permanganate ☐
(b) acidic dichromate ☐
(c) chromic anhydride in glacial acetic acid ☐
(d) pyridinium chlorochromate ☐

170. Acid catalysed hydration of alkenes except ethene leads to the formation of: **[AIEEE 2005]**

(a) primary alcohol ☐
(b) secondary or tertiary alcohol ☐
(c) mixture of primary and secondary alcohols ☐
(d) mixture of secondary and tertiary alcohols ☐

171. When alcohol reacts with conc. H_2SO_4, intermediate compound formed is: **[AFMC 2005]**

(a) carbonium ion ☐
(b) alkoxy ion ☐
(c) alkyl hydrogen sulphate ☐
(d) none of the above ☐

172. The only alcohol that can be prepared by the indirect hydration of alkene is: **[AFMC 2005]**

(a) methyl alcohol ☐
(b) ethyl alcohol ☐
(c) propyl alcohol ☐
(d) isobutyl alcohol ☐

173. Among the following the most stable compound is: **[AIIMS 2005]**

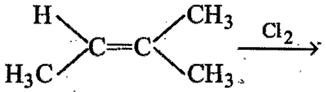
(a) *cis*-1, 2-cyclohexanediol ☐
(b) *trans*-1, 2-cyclohexanediol ☐
(c) *cis*-1, 3-cyclohexanediol ☐
(d) *trans*-1, 3-cyclohexanediol ☐

174. Which will give chiral molecule? **[DPMT 2005]**

(a) $CH_3COCl \xrightarrow{LiAlH_4}$ ☐

(b) $C_2H_5CHO \xrightarrow[H^+/H_2O]{CH_3MgBr}$ ☐

(c) $(CH_3)_2CHC_2H_5 \xrightarrow{Cu}$ ☐

(d)  ☐

175. A compound '*X*' undergoes reduction with $LiAlH_4$ to yield '*Y*'. When vapours of '*Y*' are passed over freshly reduced copper at 300°C, '*X*' is formed. What is '*Y*'? **[EAMCET (Med.) 2005; DCE (Engg.) 2008]**

(a) CH_3COCH_3 ☐ (b) CH_3CHO ☐
(c) CH_3CH_2OH ☐ (d) $CH_3—O—CH_3$ ☐

176. 3-Hydroxy butanal is formed when (*X*) reacts with (*Y*) in dilute (*Z*) solution. What are *X*, *Y* and *Z*? **[EAMCET (Engg.) 2005]**

	(*X*)	(*Y*)	(*Z*)	
(a)	CH_3CHO	$(CH_3CO)_2O$	NaOH	☐
(b)	CH_3CHO	CH_3CHO	NaCl	☐
(c)	$(CH_3CO)_2O$	$(CH_3CO)_2O$	HCl	☐
(d)	CH_3CHO	CH_3CHO	NaOH	☐

177. When phenyl magnesium bromide reacts with tertiary butanol, the product formed will be: **[IIT (S) 2005]**

(a) phenol ☐
(b) benzene ☐
(c) tertiary butyl phenyl ether ☐
(d) tertiary butyl benzene ☐

178. Which is the best reagent to convert cyclohexanol into cyclohexene? **[IIT (S) 2005]**

(a) Conc. HCl ☐
(b) Conc. HBr ☐
(c) Conc. H_3PO_4 ☐
(d) Conc. HCl with $ZnCl_2$ ☐

179. Match the List I with List II and pick the correct matching from the codes as given below: **[PMT (Kerala) 2006]**

List I		List II	
A.	Propane-1,2,3-triol	1.	Cyclic ether
B.	Ethane-1,2-diol	2.	Absolute ethanol + petrol
C.	Tetrahydrofuran	3.	Dynamite
D.	Power alcohol	4.	Denatured alcohol
E.	Methylated spirit	5.	Terylene

Codes:

(a) A—1, B—2, C—3, D—4, E—5 ☐
(b) A—1, B—3, C—5, D—4, E—2 ☐
(c) A—3, B—2, C—4, D—5, E—1 ☐
(d) A—3, B—5, C—1, D—2, E—4 ☐
(e) A—4, B—1, C—5, D—3, E—2 ☐

180. In the Victor Meyer's test, the colours given by 1°, 2° and 3° alcohols are respectively: **[PMT (Kerala) 2006]**

(a) red, colourless, blue ☐ (b) red, blue, colourless ☐
(c) colourless, red, blue ☐ (d) red, blue, violet ☐
(e) blue, red, violet ☐

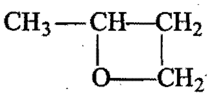
181. Phenol can be distinguished from ethanol by the following reagents except: **[PET (Kerala) 2006]**

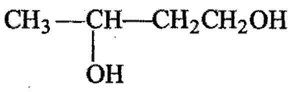
(a) sodium ☐ (b) $NaOH/I_2$ ☐
(c) neutral $FeCl_3$ ☐ (d) Br_2/H_2O ☐
(e) phthalic anhydride/conc. H_2SO_4 and NaOH ☐

182. The major product formed in the following reaction is:

$$CH_3CH(Cl)CH_2CH_2OH \xrightarrow{Aq.\ KOH}$$

[AIIMS 2006]

(a) $CH_3CH{=}CHCH_2OH$ ☐
(b) $CH_2{=}CHCH_2CH_2OH$ ☐
(c)  ☐

(d)  ☐

$CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2CH_2OH$

183. Phenyl magnesium bromide reacts with methanol to give: **[AIEEE 2006]**

(a) a mixture of anisole and Mg(OH)Br ☐
(b) a mixture of benzene and Mg(OMe)Br ☐
(c) a mixture of toluene and Mg(OH)Br ☐
(d) a mixture of phenol and Mg(Me)Br ☐

184. Reaction of esters with Grignard reagents give rise to: **[PMT (HP) 2006]**

(a) primary alcohols ☐ (b) secondary alcohols ☐
(c) tertiary alcohols ☐ (d) ketones ☐

185. Glycerol on oxidation with bismuth nitrate produces: **[BHU 2006]**

(a) glyceric acid ☐ (b) glyoxalic acid ☐
(c) oxalic acid ☐ (d) meso oxalic acid ☐

186. The end product of the reaction is: **[BHU 2006]**

$$C_2H_5OH \xrightarrow{PCl_5} (A) \xrightarrow{KCN} (B) \xrightarrow{H_3O^+} (C)$$

(a) propanol ☐ (b) propanoic acid ☐
(c) propanamide ☐ (d) none of these ☐

187. When compound '*X*' is oxidised by acidified potassium dichromate, compound '*Y*' is formed. Compound '*Y*' on reduction with $LiAlH_4$ gives '*X*'. '*X*' and '*Y*' respectively are: **[EAMCET (Engg.) 2006]**

(a) C_2H_5OH, CH_3COOH ☐
(b) CH_3COCH_3, CH_3COOH ☐
(c) C_2H_5OH, CH_3COCH_3 ☐
(d) CH_3CHO, CH_3COCH_3 ☐

188. $$CH_3CH_2OH \xrightarrow[\text{Step 1}]{Cl_2} CH_3CHO \xrightarrow[\text{Step 2}]{3Cl_2} Cl_3CCHO$$

In the above reaction, the role of Cl_2 in step 1 and step 2 respectively is: **[EAMCET (Engg.) 2006]**

(a) oxidation, chlorination ☐
(b) reduction, chlorination ☐
(c) oxidation, addition ☐
(d) reduction, substitution ☐

189. Starch is converted to ethanol by fermentation, the sequence of enzymes used is: **[DPMT 2006]**

(a) amylase, maltase, zymase ☐
(b) diastase, maltase, zymase ☐
(c) amylase, invertase, zymase ☐
(d) amylase, zymase, maltase ☐

190. Ethylene oxide when treated with Grignard reagent yields: **[CBSE (Med.) 2006]**

(a) cyclopropyl alcohol ☐ (b) primary alcohol ☐
(c) secondary alcohol ☐ (d) tertiary alcohol ☐

191. *Tert.* butyl alcohol is: **[CPMT 2006]**

(a) 2-methyl propan-2-ol ☐
(b) 2-methyl propan-1-ol ☐
(c) 3-methyl butan-1-ol ☐
(d) 3-methyl butan-2-ol ☐

192. Which of the following is dihydric alcohol? **[PMT (Haryana) 2006; Ludhiana CMC (Med.) 2008]**

(a) Glycerol ☐ (b) Ethylene glycol ☐
(c) Catechol ☐ (d) Resorcinol ☐

193. An organic compound '*A*' containing C, H and O has a pleasant odour with boiling point 78°C. On boiling '*A*' with conc. H_2SO_4, a colourless gas is produced which decolourises bromine water and alkaline $KMnO_4$. The organic liquid '*A*' is: **[GGS (Indraprastha Univ.) EE 2006]**

(a) C_2H_5Cl ☐ (b) $C_2H_5COOCH_3$ ☐
(c) C_2H_5OH ☐ (d) C_2H_6 ☐

194. In the following sequence of reactions,

$$CH_3CH_2OH \xrightarrow{P + I_2} (A) \xrightarrow[\text{ether}]{Mg} (B) \xrightarrow{HCHO} (C) \xrightarrow{H_2O} (D)$$

the compound *D* is: **[AIEEE 2007]**

(a) propanal ☐ (b) butanal ☐
(c) *n*-butyl alcohol ☐ (d) *n*-propyl alcohol ☐

195. A fruity smell is obtained by the reaction of ethanol with: **[BCECE (Med.) 2007; JIPMER (Med.) 2008]**

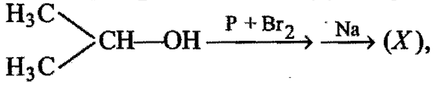
(a) CH_3COCH_3 ☐ (b) PCl_5 ☐
(c) CH_3COOH ☐ (d) CH_3CHO ☐

196. An organic compound '*X*' on treatment with pyridinium chlorochromate in dichloromethane gives compound '*Y*'. Compound '*Y*', reacts with I_2 and alkali to form tri-iodomethane. The compound '*X*' is: **[EAMCET (Engg.) 2007; AIIMS 2008]**

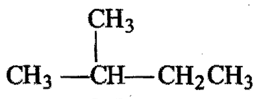
(a) C_2H_5OH ☐ (b) CH_3CHO ☐
(c) CH_3COCH_3 ☐ (d) CH_3COOH ☐

197. Methyl alcohol when reacted with carbon monoxide using cobalt or rhodium as catalyst, compound '*A*' is formed. '*A*' on heating with HI in the presence of red phosphorus as catalyst '*B*' is formed. Identify '*B*': **[EAMCET (Med.) 2007; CPMT 2008]**

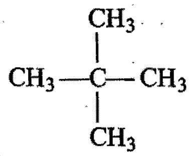
(a) CH_3COOH ☐ (b) CH_3CHO ☐
(c) CH_3CH_2I ☐ (d) CH_3CH_3 ☐

198. 

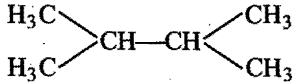
(*X*) is: **[AMU (Engg.) 2007]**

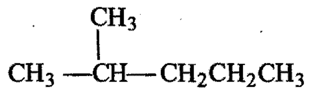
(a)  ☐

$CH_3-CH(CH_3)-CH_2CH_3$

(b)  ☐

$CH_3-C(CH_3)_2-CH_3$

(c)  ☐

(d)  ☐

$CH_3-CH(CH_3)-CH_2CH_2CH_3$

199. $$CH_3COOH \xrightarrow{LiAlH_4} (A),$$

$$(A) + CH_3COOH \xrightarrow{H_3O^+} (B) + H_2O$$

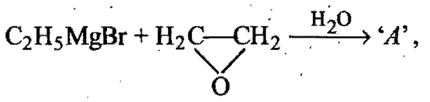
In the above reaction '*A*' and '*B*' respectively are: **[EAMCET (Engg.) 2007]**

(a) $CH_3COOC_2H_5, C_2H_5OH$ ☐
(b) CH_3CHO, C_2H_5OH ☐
(c) C_2H_5OH, CH_3CHO ☐
(d) $C_2H_5OH, CH_3COOC_2H_5$ ☐

200. Which among the following compounds will give a secondary alcohol on reacting with Grignard reagent followed by acid hydrolysis? **[PMT (Kerala) 2007]**
(i) HCHO ☐ (ii) C_2H_5CHO ☐
(iii) CH_3COCH_3 ☐ (iv) $HCOOC_2H_5$ ☐
Select the correct answer using the codes given below:
(a) (ii) only ☐ (b) (iii) only ☐
(c) (i) and (iv) ☐ (d) (ii) and (iii) ☐
(e) (ii) and (iv) ☐

201. The most suitable reagent for the conversion of primary alcohol into aldehyde with the same number of carbon is: **[PET (Kerala) 2007]**
(a) acidified $K_2Cr_2O_7$ ☐
(b) acidified $KMnO_4$ ☐
(c) alkaline $KMnO_4$ ☐
(d) pyridinium chlorochromate ☐
(e) CrO_3 ☐

202. In the following reaction,



$$C_2H_5MgBr + H_2C\!-\!CH_2\ (\text{O}) \xrightarrow{H_2O} \text{'}A\text{'},$$

'*A*' is: **[AFMC 2007]**
(a) $C_2H_5CH_2CHO$ ☐ (b) $C_2H_5CH_2CH_2OH$ ☐
(c) $C_2H_5CH_2OH$ ☐ (d) C_2H_5CHO ☐

203. When $H_2C{=}CH{-}COOH$ is reduced with $LiAlH_4$, the compound obtained will be: **[UPSEE (Engg.) 2007]**
(a) CH_3CH_2COOH ☐ (b) $H_2C{=}CHCH_2OH$ ☐
(c) $CH_3CH_2CH_2OH$ ☐ (d) CH_3CH_2CHO ☐

204. Catalytic dehydrogenation of primary alcohol gives a: **[CET (Karnataka) 2008]**
(a) ketone ☐ (b) ester ☐
(c) secondary alcohol ☐ (d) aldehyde ☐

205. The compound on dehydrogenation gives a ketone. The original compound is: **[CET (Karnataka) 2008]**
(a) tertiary alcohol ☐ (b) secondary alcohol ☐
(c) primary alcohol ☐ (d) carboxylic acid ☐

206. RCH_2CH_2OH can be converted to RCH_2CH_2COOH by the following sequence of steps: **[JEE (WB) 2008]**
(a) PBr_3, KCN, H_3O^+ ☐ (b) $PBr_3, KCN, H_2/P^+$ ☐
(c) KCN, H_3O^+ ☐ (d) HCN, PBr_3, H_3O^+ ☐

207. Which of the following will produce only one product on reduction with $LiAlH_4$? **[JEE (WB) 2008]**
(a) $CH_3COOCH_2CH_3$ ☐
(b) $CH_3CH_2OCOCH_2CH_3$ ☐
(c) $CH_3CH_2OCOCH_3$ ☐
(d) $CH_3CH_2OCOCH_2CH_2CH_3$ ☐

208. The hydrolysis of 2-bromo-3-methyl butane by S_N1 mechanism gives mainly: **[PMT (Kerala) 2008]**
(a) 3-methyl-2-butanol ☐
(b) 2-methyl-2-butanol ☐
(c) 2.2-dimethyl-2-propanol ☐
(d) 2-methyl-1-butanol ☐
(e) 1-pentanol ☐

209. The strongest acid is: **[BHU (Screening) 2008]**
(a) $HC{\equiv}CH$ ☐ (b) C_6H_6 ☐
(c) C_2H_6 ☐ (d) CH_3OH ☐

210. An organic compound '*X*' is oxidised by using acidified $K_2Cr_2O_7$. The product obtained reacts with phenyl hydrazine but does not answer silver mirror test. The possible structure of '*X*' is: **[CET (Karnataka) 2009]**
(a) CH_3COCH_3 ☐ (b) $(CH_3)_2CHOH$ ☐
(c) CH_3CHO ☐ (d) CH_3CH_2OH ☐

211. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was: **[AIEEE 2009]**
(a) CH_3OH ☐ (b) HCHO ☐
(c) CH_3COCH_3 ☐ (d) CH_3COOH ☐

212. The reaction involved in the oil of winter Green test is salicylic acid $\xrightarrow[\text{Conc. } H_2SO_4]{\text{'}X\text{', }\Delta}$ product. The product is treated with Na_2CO_3 solution. The missing reagent '*X*' in the above reaction is: **[CET (Karnataka) 2009]**
(a) NaOH ☐ (b) ethanol ☐
(c) methanol ☐ (d) phenol ☐

213. The function of $ZnCl_2$ in Lucas test for alcohols is: **[DCE 2009]**
(a) to act as an acid catalyst and react with HCl to form H_2ZnCl_4 ☐
(b) to act as a base catalyst and react with NaOH to form $Na_2Zn(OH)_4$ ☐
(c) to act as an amphoteric catalyst ☐
(d) to act as a neutral catalyst ☐

214. What are *X* and *Y* in the following reaction sequence:

$$C_2H_5OH \xrightarrow{Cl_2} (X) \xrightarrow{Cl_2} Y$$

[EAMCET (Engg.) 2009]
(a) C_2H_5Cl, CH_3CHO ☐
(b) CH_3CHO, CH_3CO_2H ☐
(c) CH_3CHO, CCl_3CHO ☐
(d) C_2H_5Cl, CCl_3CHO ☐

Set II : This set contains the questions with two or more correct answers.

215. Grignard reagents give alkane, on reaction with:
(a) phenol ☐ (b) ether ☐
(c) alcohol ☐ (d) water ☐

216. Isobutyl alcohol cannot be obtained by the reaction between:
(a) C_2H_5MgBr and CH_3CHO ☐
(b) CH_3MgBr and CH_3CH_2CHO ☐
(c) $(CH_3)_2CHMgBr$ and HCHO ☐
(d) CH_3MgBr and CH_3COCH_3 ☐

217. Alcohols act as:
(a) oxidising agent ☐ (b) reducing agent ☐
(c) Lewis base ☐ (d) Brorsted acid ☐

218. Glycerol can be converted to acrolein by dehydration in presence of:

(a) conc. H_2SO_4 ☐ (b) anhydrous $ZnCl_2$ ☐
(c) $KHSO_4$ ☐ (d) anhydrous $CaCl_2$ ☐

219. Which of the following chemicals are used for the denaturation of ethyl alcohol?
(a) CH_3OH ☐ (b) Pyridine ☐
(c) Anhydrous $CaCl_2$ ☐ (d) Naphtha ☐

220. Which of the following compounds will give yellow precipitate with iodine and alkali?
(a) 2-Hydroxy propane ☐ (b) Acetophenone ☐
(c) Methyl acetate ☐ (d) Acetamide ☐

221. Ethanol can be converted to propane nitrile (CH_3CH_2CN) by the following reaction(s):

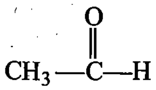
(a) $CH_3CH_2CH_2OH + KCN \xrightarrow{\Delta}$ ☐

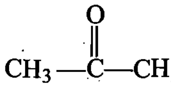
(b) $CH_3CH_2OH + HCN \xrightarrow{\Delta}$ ☐

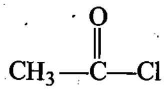
(c) $CH_3CH_2OH \xrightarrow[\text{Pyridine}]{TsCl} CH_3CH_2OTs \xrightarrow{KCN}$ ☐

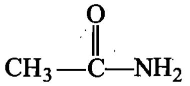
(d) $CH_3CH_2OH \xrightarrow[-POCl_3,\ -HCl]{PCl_5} CH_3CH_2Cl \xrightarrow[-NaCl]{NaCN} CH_3CH_2CN$ ☐

222. Which of the following compounds will give iodoform test?

(a) 
$CH_3-\overset{\overset{\large O}{\|}}{C}-H$ ☐

(b) 
$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3$ ☐

(c) 
$CH_3-\overset{\overset{\large O}{\|}}{C}-Cl$ ☐

(d) 
$CH_3-\overset{\overset{\large O}{\|}}{C}-NH_2$ ☐

223. Alcohol can be prepared by which of the following methods?
(a) By hydration of alkene ☐
(b) By reduction of carbonyl compounds ☐
(c) By reaction of primary aliphatic amines with nitrous acid ☐
(d) By hydrolysis of esters ☐

224. 1°, 2° and 3° alcohols can be distinguished by:
(a) Cu/573 K ☐ (b) Victor Meyer's test ☐
(c) conc. $HCl/ZnCl_2$ ☐ (d) Br_2 water ☐

225. Alcoholic group can be replaced by —Cl group by the following reagents:
(a) Cl_2 ☐ (b) $SOCl_2$ ☐
(c) PCl_5 ☐ (d) HCl and $ZnCl_2$ ☐

ASSERTION-REASON TYPE QUESTIONS

The questions given below consist of an **Assertion (A)** and the **Reason (R).** Use the following keys to choose the appropriate answer:
(a) If both (A) and (R) are correct and (R) is correct explanation of (A).
(b) If both (A) and (R) are correct but (R) is not correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) Solubility of *n*-alcohols in water decreases with increase in molecular weight.
(R) The relative proportion of the hydrocarbon part in alcohol increases with increasing molecular weight which permits enhanced hydrogen bond with water.

2. (A) Di-*tert.* butyl ether cannot be prepared by Williamson's ether synthesis.
(R) *Tert.* butyl bromide on treatment with sodium *tert.* butoxide preferentially undergoes elimination to form isobutylene and *tert.* butyl alcohol.

3. (A) The boiling point of ethanol is much higher than that of diethyl ether.
(R) In ethanol, the molecules are associated due to intermolecular hydrogen bonding, whereas in diethyl ether it is not possible.

4. (A) The acidity of alcohols follows the order 1° > 2° > 3°.
(R) The $+I$ effect of alkyl groups (3° > 2° > 1°) favours the dissociation of —O—H group.

5. (A) Alcohols can be dried over anhydrous $CaCl_2$.
(R) Anhydrous $CaCl_2$ absorbs moisture of aqueous ethyl alcohol.

6. (A) CH_3OH is a nucleophile.
(R) CH_3OH forms sodium methoxide on treatment with NaOH.

7. (A) HIO_4, decomposes, 1,2-glycols but not 1,3- or higher glycols.
(R) Only 1,2-glycols form cyclic esters which subsequently undergo cleavage to form carbonyl compounds.

8. (A) 3° Alcohols show turbidity within 5 minutes, when treated with Lucas reagent.
(R) Conc. HCl and anhydrous $ZnCl_2$ in 1 : 1 mixture is called Lucas reagent.

9. (A) Grignard reagent reacts with aldehydes and ketones to form alcohol.
(R) Alcohols have acidic hydrogen.

10. (A) Glycerol does not react with HI.
(R) 2-Iodopropane can be produced by treatment of glycerol with HI.

11. (A) Glycol $\begin{pmatrix} CH_2OH \\ | \\ CH_2OH \end{pmatrix}$ reacts with HI to give ethylene.
(R) Initially ethylene di-iodide is formed which being unstable loses a molecule of I_2 and forms ethylene.

ANSWERS

OBJECTIVE QUESTIONS

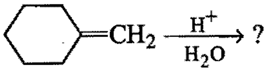
1. (c)	**2.** (a)	**3.** (b)	**4.** (d)	**5.** (c)	**6.** (b)	**7.** (a)	**8.** (c)	**9.** (d)	**10.** (d)
11. (b)	**12.** (a)	**13.** (b)	**14.** (a)	**15.** (c)	**16.** (d)	**17.** (a)	**18.** (c)	**19.** (d)	**20.** (b)
21. (d)	**22.** (b)	**23.** (c)	**24.** (a)	**25.** (b)	**26.** (b)	**27.** (c)	**28.** (b)	**29.** (c)	**30.** (b)
31. (b)	**32.** (d)	**33.** (c)	**34.** (a)	**35.** (d)	**36.** (b)	**37.** (a)	**38.** (d)	**39.** (c)	**40.** (c)
41. (b)	**42.** (b)	**43.** (c)	**44.** (b)	**45.** (a)	**46.** (a)	**47.** (b)	**48.** (a)	**49.** (d)	**50.** (d)
51. (d)	**52.** (d)	**53.** (a)	**54.** (a)	**55.** (a)	**56.** (d)	**57.** (b)	**58.** (c)	**59.** (a)	**60.** (b)
61. (c)	**62.** (a)	**63.** (c)	**64.** (d)	**65.** (c)	**66.** (d)	**67.** (c)	**68.** (b)	**69.** (a)	**70.** (c)
71. (a)	**72.** (d)	**73.** (b)	**74.** (c)	**75.** (b)	**76.** (a)	**77.** (d)	**78.** (d)	**79.** (a)	**80.** (c)
81. (c)	**82.** (a)	**83.** (d)	**84.** (d)	**85.** (a)	**86.** (c)	**87.** (a)	**88.** (b)	**89.** (b)	**90.** (d)
91. (c)	**92.** (b)	**93.** (a)	**94.** (c)	**95.** (d)	**96.** (a)	**97.** (b)	**98.** (d)	**99.** (a)	**100.** (c)
101. (a)	**102.** (c)	**103.** (a)	**104.** (b)	**105.** (d)	**106.** (c)	**107.** (d)	**108.** (d)	**109.** (a)	**110.** (c)
111. (b)	**112.** (c)	**113.** (b)	**114.** (a)	**115.** (b)	**116.** (d)	**117.** (c)	**118.** (a)	**119.** (d)	**120.** (c)
121. (d)	**122.** (c)	**123.** (b)	**124.** (c)	**125.** (b)	**126.** (d)	**127.** (c)	**128.** (a)	**129.** (a)	**130.** (b)
131. (d)	**132.** (c)	**133.** (b)	**134.** (c)	**135.** (c)	**136.** (c)	**137.** (d)	**138.** (a)	**139.** (c)	**140.** (a)
141. (c)	**142.** (c)	**143.** (d)	**144.** (b)	**145.** (c)	**146.** (a)	**147.** (d)	**148.** (a)	**149.** (d)	**150.** (b)
151. (a)	**152.** (d)	**153.** (a)	**154.** (a)	**155.** (b)	**156.** (b)	**157.** (a)	**158.** (c)	**159.** (c)	**160.** (c)
161. (a)	**162.** (d)	**163.** (a)	**164.** (c)	**165.** (c)	**166.** (a)	**167.** (a)	**168.** (d)	**169.** (d)	**170.** (b)
171. (a)	**172.** (b)	**173.** (d)	**174.** (b)	**175.** (c)	**176.** (d)	**177.** (b)	**178.** (c)	**179.** (d)	**180.** (b)
181. (a)	**182.** (d)	**183.** (b)	**184.** (c)	**185.** (d)	**186.** (b)	**187.** (a)	**188.** (a)	**189.** (b)	**190.** (b)
191. (a)	**192.** (b)	**193.** (c)	**194.** (d)	**195.** (c)	**196.** (a)	**197.** (d)	**198.** (c)	**199.** (d)	**200.** (e)
201. (d)	**202.** (b)	**203.** (b)	**204.** (d)	**205.** (b)	**206.** (a)	**207.** (a)	**208.** (b)	**209.** (d)	**210.** (b)
211. (d)	**212.** (c)	**213.** (a)	**214.** (c)	**215.** (a,c,d)	**216.** (a,b,d)	**217.** (c,d)	**218.** (a,b,c)	**219.** (a,b)	**220.** (a,b)
221. (c,d)	**222.** (a,b)	**223.** (a,b,c,d)	**224.** (a,b,c)	**225.** (b,c,d)					

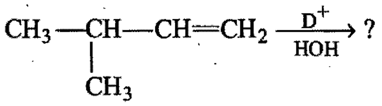
ASSERTION-REASON TYPE QUESTIONS

1. (c)	**2.** (a)	**3.** (a)	**4.** (c)	**5.** (d)	**6.** (b)	**7.** (a)	**8.** (d)	**9.** (a)	**10.** (d)
11. (a)									

BRAIN STORMING PROBLEMS

1. Give the major products of hydration of the following alkenes:

(i) 

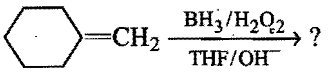
(ii) 

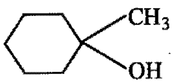
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2\xrightarrow[HOH]{D^+}?$

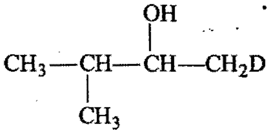
(iii) $C_3H_6(CH_3-CH=CH_2)\xrightarrow[HOH]{D^+}?$

(iv) $C_3H_6(CH_3-CH=CH_2)\xrightarrow[D_2O]{D^+}?$

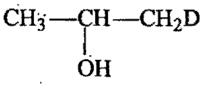
(v) $C_3H_6(CH_3-CH=CH_2)\xrightarrow[D_2O]{H^+}?$

(vi) 

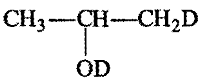
[**Hint :** (i) 

(ii) 

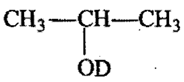
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{OH}{|}}{CH}-CH_2D$

(iii) 

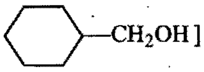
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2D$

(iv) 

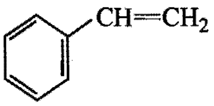
$CH_3-\underset{\underset{OD}{|}}{CH}-CH_2D$

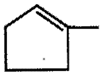
(v) 

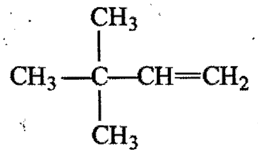
$CH_3-\underset{\underset{OD}{|}}{CH}-CH_3$

(vi) ]

2. Write down product of hydroboration oxidation of the following alkenes:

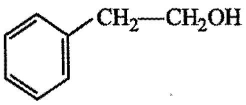
(i) 

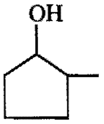
(ii) 

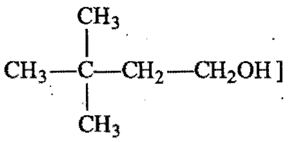
(iii) 

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2$

[**Hint :** Anti-Markownikoff's addition takes place.

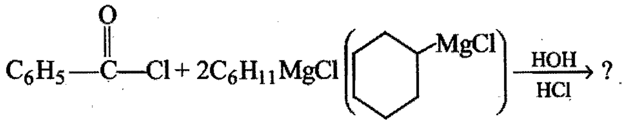
(i) 

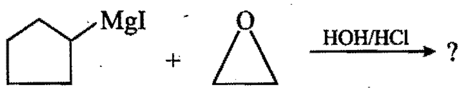
(ii) 

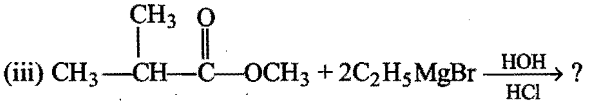
(iii) 

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2OH$]

3. Complete the following reactions:

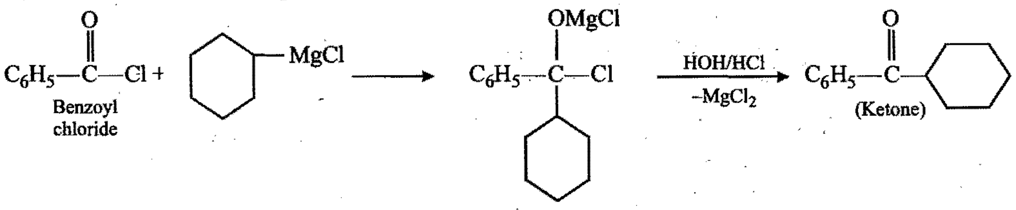
(i) 

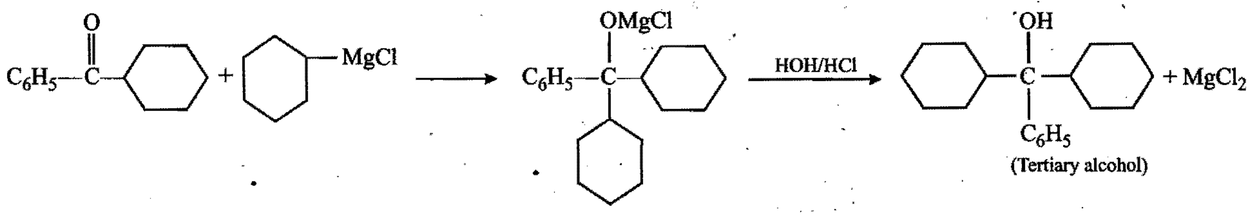
(ii) 

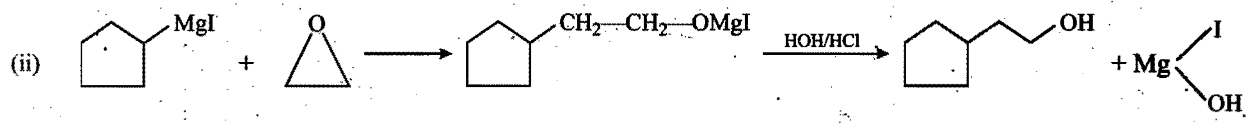
(iii) 

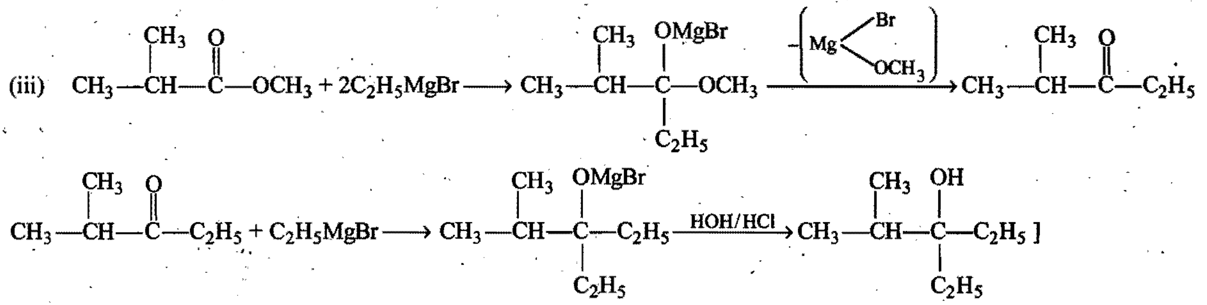
$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OCH_3+2C_2H_5MgBr\xrightarrow[HCl]{HOH}?$

[**Hint :** (i) Reaction involves two steps:





(ii) 

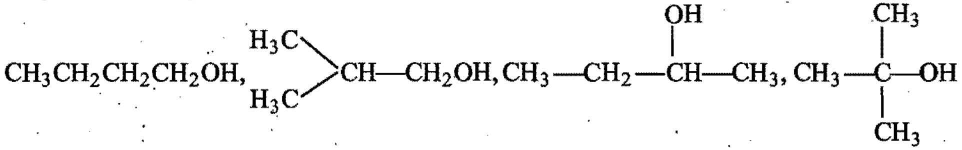
(iii) 

$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{||}{C}}-OCH_3 + 2C_2H_5MgBr \longrightarrow CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{C_2H_5}{\underset{|}{\overset{OMgBr}{\overset{|}{C}}}}-OCH_3 \xrightarrow{-\left(Mg\genfrac{}{}{0pt}{}{Br}{OCH_3}\right)} CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{||}{C}}-C_2H_5$$

$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{||}{C}}-C_2H_5 + C_2H_5MgBr \longrightarrow CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{C_2H_5}{\underset{|}{\overset{OMgBr}{\overset{|}{C}}}}-C_2H_5 \xrightarrow{HOH/HCl} CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{C_2H_5}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-C_2H_5\ ]$$

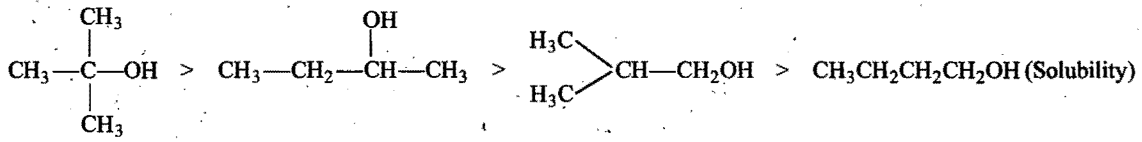
4. Arrange the following compounds in decreasing order of solubility and boiling point:

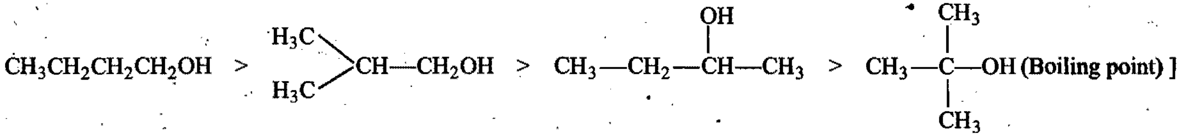
(i) $CH_3CH_2OH, CH_3CH_2CH_2OH, CH_3CH_2CH_2CH_2OH$

(ii) 

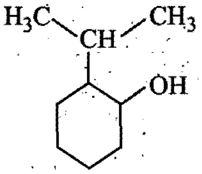
[Hint : (i) $CH_3CH_2OH > CH_3CH_2CH_2OH > CH_3CH_2CH_2CH_2OH$ (Solubility)

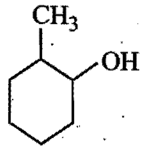
$CH_3CH_2OH < CH_3CH_2CH_2OH < CH_3CH_2CH_2CH_2OH$ (Boiling point)

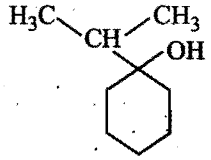
(ii) 



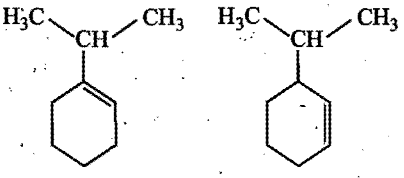
5. Write down the dehydration products of the following:

(i) 

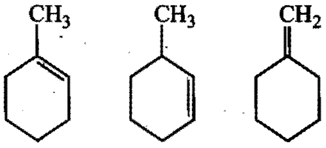
(ii) 

(iii) 

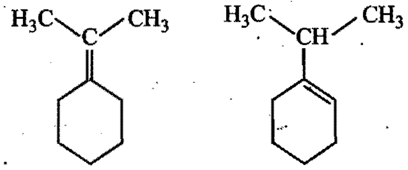
[Hint : Dehydration follows Saytzeff's rule:

(i) 

(Major) (Minor)

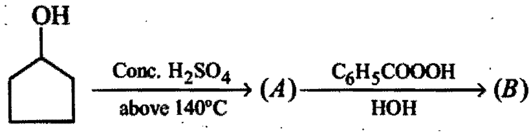
(ii) 

(Major) (Minor) (Trace)

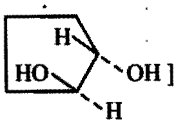
(iii) 

(Major) (Minor)]

6. Complete the following reaction:

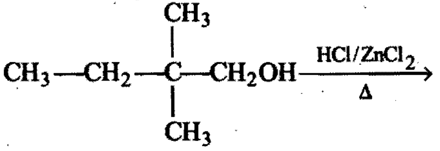


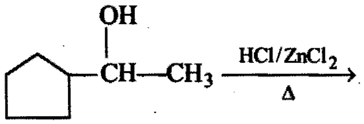
[Ans. (*A*) =

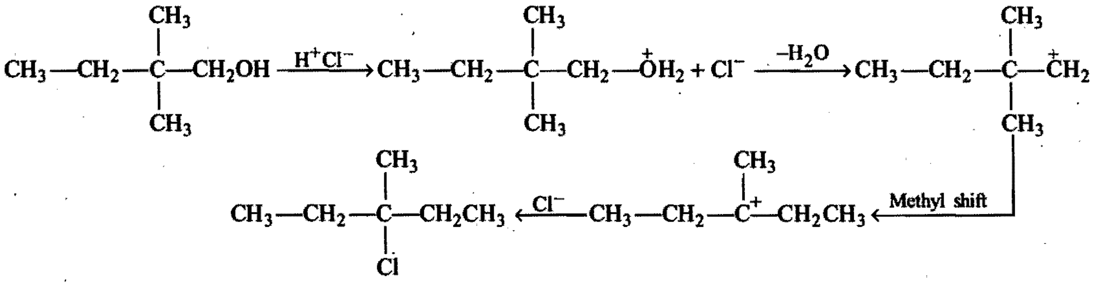
(*B*) =


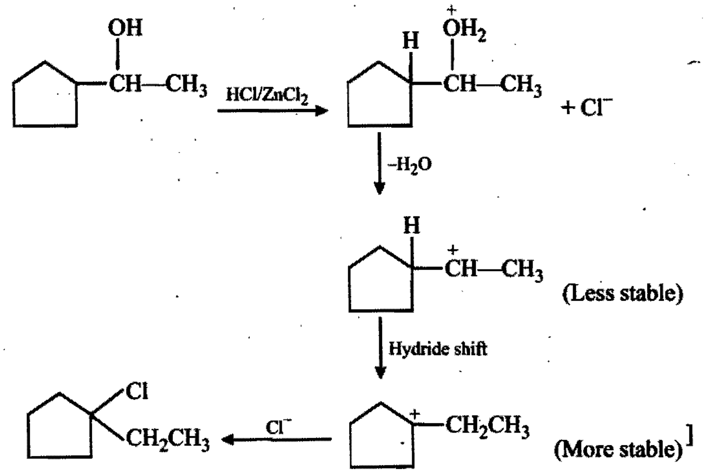
]

7. Explain and complete the following reactions:

(a)

$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH \xrightarrow[\Delta]{HCl/ZnCl_2}$

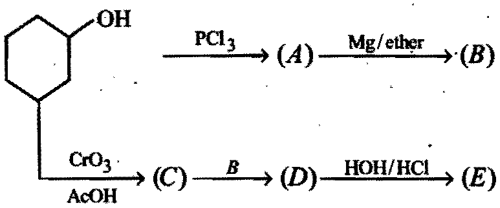
(b)


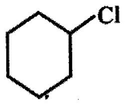
[Hint : (a)

$$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH \xrightarrow{H^+Cl^-} CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{+}{O}H_2 + Cl^- \xrightarrow{-H_2O} CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{C}H_2$$
$$CH_3-CH_2-\overset{CH_3}{\underset{Cl}{C}}-CH_2CH_3 \xleftarrow{Cl^-} CH_3-CH_2-\overset{CH_3}{\overset{+}{C}}-CH_2CH_3 \xleftarrow{\text{Methyl shift}}$$

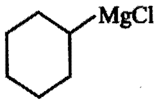
(b)


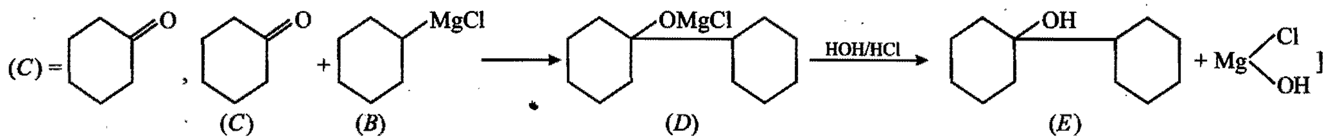
]

8. Complete the following chain of reactions:



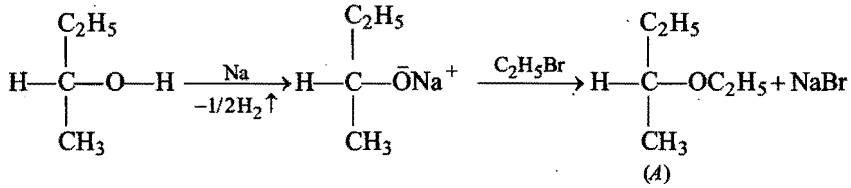
[Hint : (*A*) =


(*B*) =




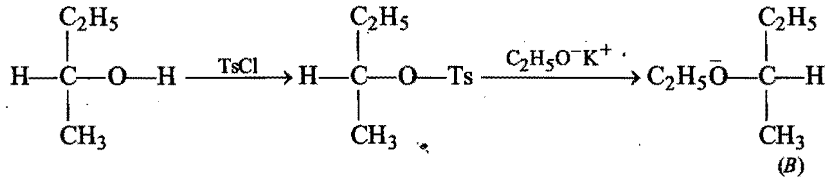
9. Discuss the stereochemistry of following reactions:

(i)



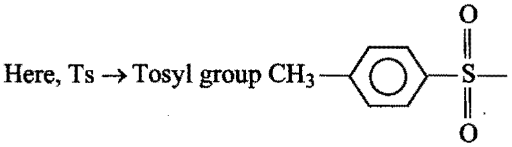
$$\mathrm{H-\underset{\textstyle CH_3}{\overset{\textstyle C_2H_5}{C}}-O-H \xrightarrow[-1/2H_2\uparrow]{Na} H-\underset{\textstyle CH_3}{\overset{\textstyle C_2H_5}{C}}-\bar{O}Na^+ \xrightarrow{C_2H_5Br} \underset{(A)}{H-\underset{\textstyle CH_3}{\overset{\textstyle C_2H_5}{C}}-OC_2H_5} + NaBr}$$

(ii)



$$\mathrm{H-\underset{\textstyle CH_3}{\overset{\textstyle C_2H_5}{C}}-O-H \xrightarrow{TsCl} H-\underset{\textstyle CH_3}{\overset{\textstyle C_2H_5}{C}}-O-Ts \xrightarrow{C_2H_5O^-K^+} \underset{(B)}{C_2H_5\bar{O}-\underset{\textstyle CH_3}{\overset{\textstyle C_2H_5}{C}}-H}}$$

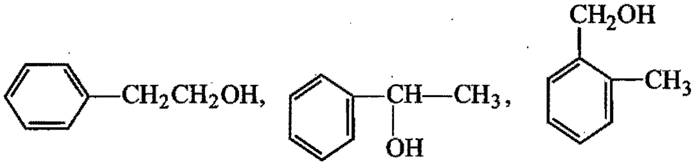
Here, Ts → Tosyl group



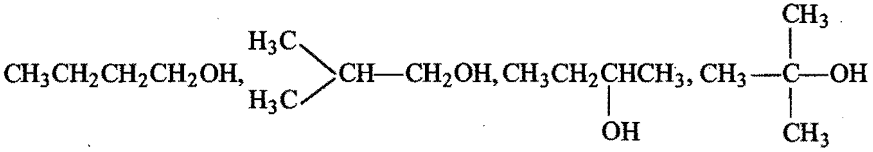
[**Hint:** In (i) reaction, —O—H bond of alcohol is broken and the configuration of product around chiral carbon is retained. In (ii) reaction, first step involves decomposition of —O—H bond, in the second step —C—O— bond is broken. In this reaction, inversion of configuration takes place. Tosyl group is better leaving group hence (C—O) bond is broken.]

10. Arrange the following alcohols in the increasing order of tendency towards esterification:

(a)

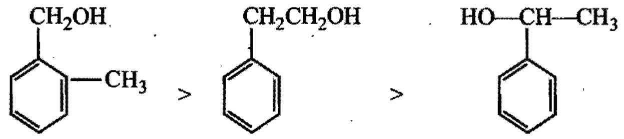


(b)

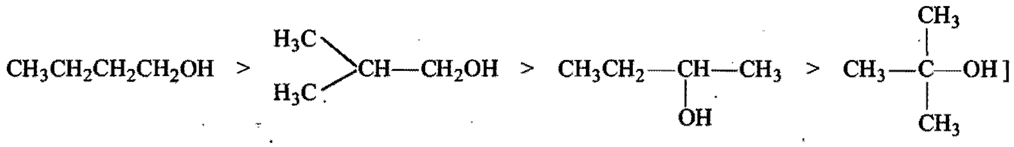


$$\mathrm{CH_3CH_2CH_2CH_2OH,\ (H_3C)_2CH-CH_2OH,\ CH_3CH_2\underset{\textstyle OH}{CH}CH_3,\ CH_3-\underset{\textstyle CH_3}{\overset{\textstyle CH_3}{C}}-OH}$$

[**Hint:** (a)

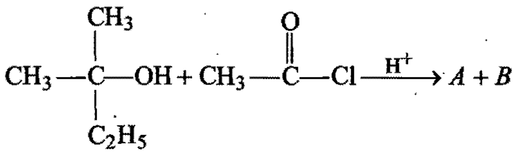


(b)



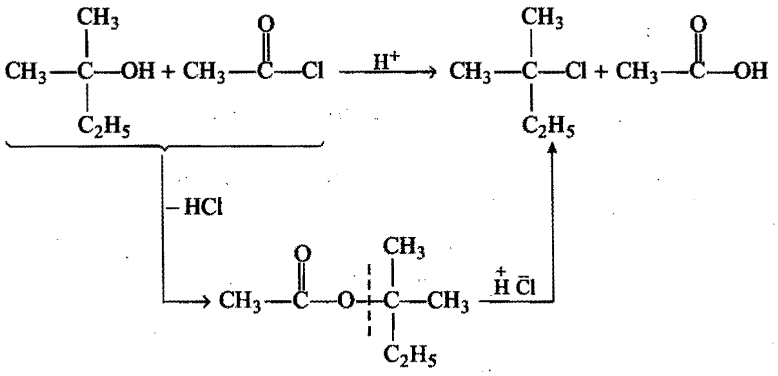
$$\mathrm{CH_3CH_2CH_2CH_2OH > (H_3C)_2CH-CH_2OH > CH_3CH_2-\underset{\textstyle OH}{CH}-CH_3 > CH_3-\underset{\textstyle CH_3}{\overset{\textstyle CH_3}{C}}-OH}$$]

11. Complete the following reaction and give its mechanism in short:



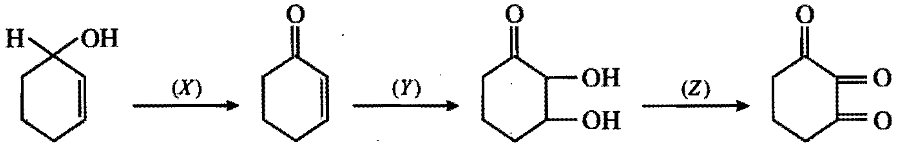
$$\mathrm{CH_3-\underset{\textstyle C_2H_5}{\overset{\textstyle CH_3}{C}}-OH + CH_3-\overset{\textstyle O}{\overset{\|}{C}}-Cl \xrightarrow{H^+} A + B}$$

[Hint :

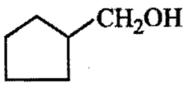


In this reaction, first of all, an ester is formed which undergoes decomposition in presence of dil. HCl.]

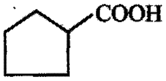
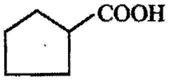
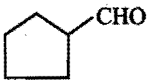
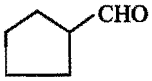
12. Give the reagents for following oxidation products:



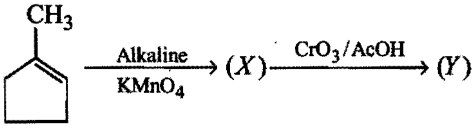
[Hint : (*X*) = $Na_2Cr_2O_7/H_2SO_4$ or CrO_3/Pyridine, (*Y*) = Baeyer's Reagent (Alkaline $KMnO_4$), (*Z*) = CrO_3/Pyridine]

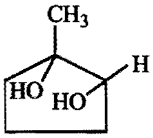
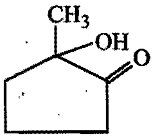
13. Give the products when  is oxidised using following reagents:

(i) $K_2Cr_2O_7/H_2SO_4$ (ii) CrO_3/H_2SO_4, acetone (iii) CrO_3/Pyridine (iv) Pyridinium chlorochromate

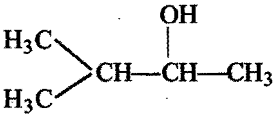
[Ans. (i)  (ii)  (iii)  (iv) ]

14. Complete the following reaction:

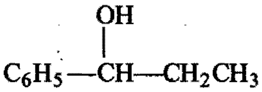


[Hint : (*X*) =  Baeyer's reagent (alkaline $KMnO_4$) forms glycol with alkene. (*Y*) =  3° alcoholic group is unaffected in this oxidation.]

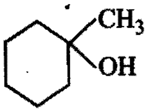
15. Which of the following compounds will give positive iodoform test?

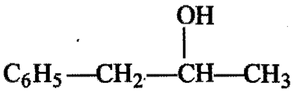
(a) 

$$(H_3C)_2CH-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_3$$

(b) 

$$C_6H_5-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_2CH_3$$

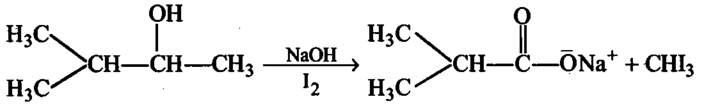
(c) 

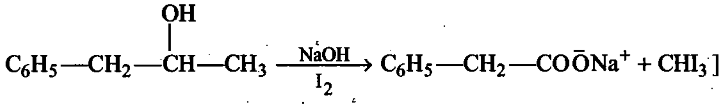
(d) 

$$C_6H_5-CH_2-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_3$$

Give the reactions involved.

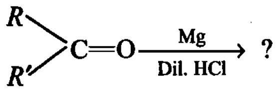
[**Hint :** (a) and (d) will give positive iodoform test.

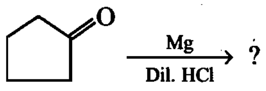
(a)


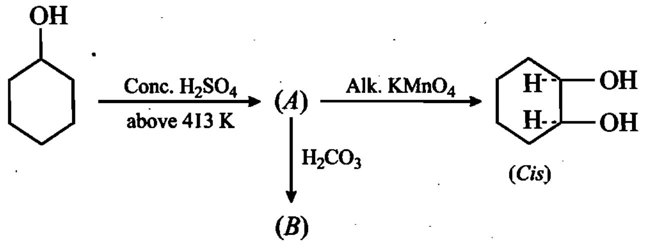
(d)


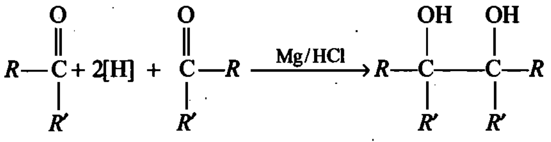
$$C_6H_5-CH_2-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[I_2]{NaOH} C_6H_5-CH_2-CO\bar{O}Na^+ + CHI_3]$$

16. Complete the following reactions:

(i)


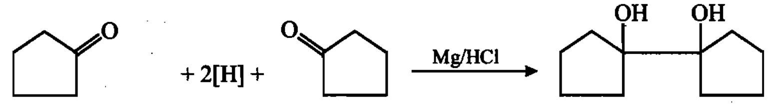
(ii)


(iii)


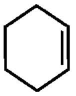
[**Hint :** (i)


$$R-\underset{R'}{\underset{|}{\overset{\overset{O}{\|}}{C}}}+2[H]+\underset{R'}{\underset{|}{\overset{\overset{O}{\|}}{C}}}-R \xrightarrow{Mg/HCl} R-\underset{R'}{\underset{|}{\overset{\overset{OH}{|}}{C}}}-\underset{R'}{\underset{|}{\overset{\overset{OH}{|}}{C}}}-R$$

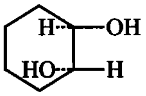
(Pinacol reduction)

(ii)


(Pinacol reduction)

(iii) (A) =


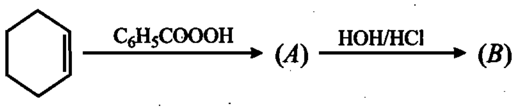
Cyclohexene

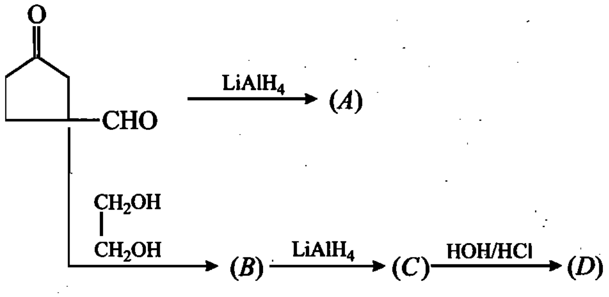
(B) =


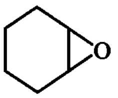
+ Enatiomer]

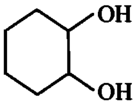
Racemic mixture

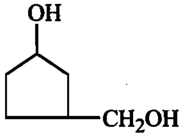
17. Identify (A), (B), (C) and (D) in the following reactions:

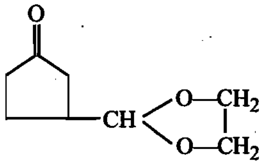
(i)


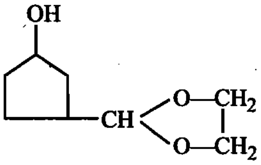
(ii)


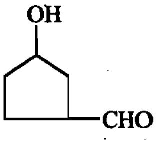
[**Hint :** (i) (A) =


(B) =


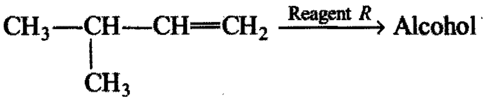
(ii) (A) =


(B) =


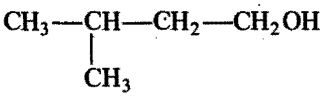
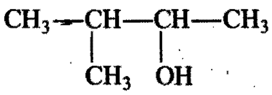
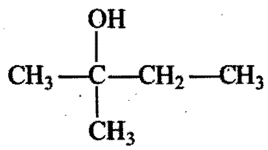
(C) =


(D) =


]

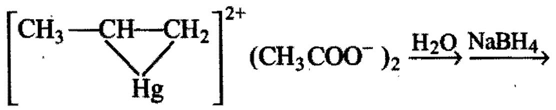
18. 
$CH_3-\underset{\substack{|\\CH_3}}{CH}-CH=CH_2 \xrightarrow{\text{Reagent } R} \text{Alcohol}$

which is/are true about alcohol and R?

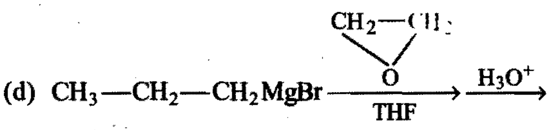
	Alcohol	**Reagent (R)**	
(a)	 $CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2-CH_2OH$	BH_3 / THF H_2O_2 / OH^-	☐
(b)	 $CH_3-\underset{\substack{|\\CH_3}}{CH}-\underset{\substack{|\\OH}}{CH}-CH_3$	$Hg(OAc)_2$ / $NaBH_4-H_2O$	☐
(c)	 $CH_3-\overset{\substack{OH\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-CH_3$	$H_3\overset{+}{O}$	☐
(d)	None of the above		☐

19. In which of the following reactions, alcohol will be formed as final product?

(a) $(CH_3-CH_2-\bar{CH_2})_3B \xrightarrow{H_2O_2 + NaOH}$ ☐

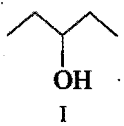
(b) 
$(CH_3COO^-)_2 \xrightarrow{H_2O} \xrightarrow{NaBH_4}$ ☐

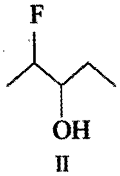
(c) $CH_3-CH=CHMgBr \xrightarrow{O_2,\Delta} \xrightarrow{H_2O}$ ☐

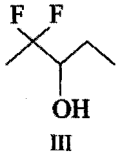
(d) 
$CH_3-CH_2-CH_2MgBr \xrightarrow[\text{THF}]{} \xrightarrow{H_3O^+}$ ☐

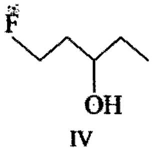
20. When neopentyl alcohol is treated with H_2SO_4, a mixture of two alkenes (85 : 15) is formed. Which statement(s) is/are correct about these alkenes?
(a) Both give same major products on treatment with HBr ☐
(b) Both give different major products on treatment with HBr in presence of peroxide ☐
(c) The alkene which is formed in 85% concentration has higher heat of hydrogenation than other alkene ☐
(d) Both alkenes, on ozonolysis give same product ☐

21. Arrange the following alcohols in order of reactivity towards gaseous HBr:


I

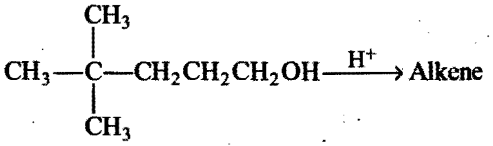

II


III

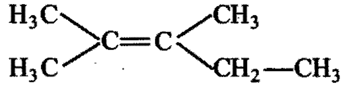

IV

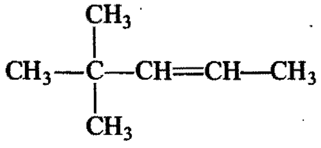
(a) II > III > IV > I ☐
(b) I > IV > II > III ☐
(c) I > II > III > IV ☐
(d) III > II > IV > I ☐

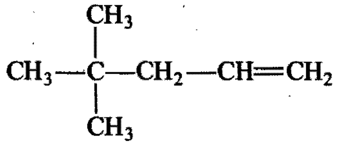
[**Hint:** $-I$ effect of the substituents will decrease the reactivity of alcoholic group towards HBr.]

22. 
$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2CH_2CH_2OH \xrightarrow{H^+} \text{Alkene}$

The alkene formed in the above reaction will be:

(a)  ☐

(b) 
$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH=CH-CH_3$ ☐

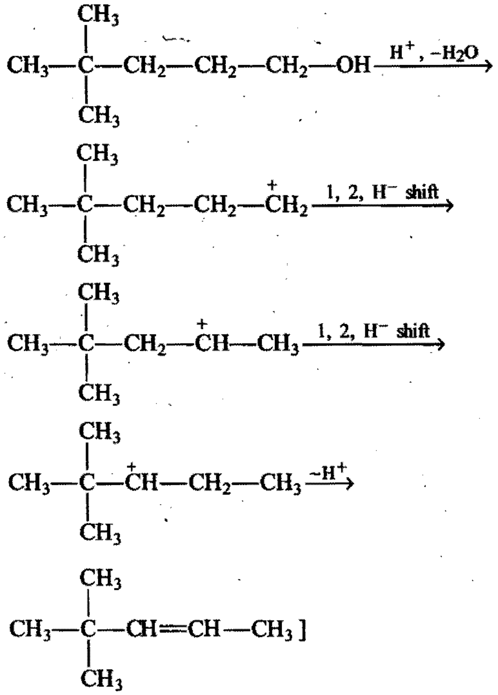
(c) 
$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-CH=CH_2$ ☐

(d) none of the above ☐

23. When  undergoes dehydration reaction in presence of concentrated H_2SO_4 then what will be the major product?

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

[**Hint:** 
$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-CH_2-CH_2-OH \xrightarrow{H^+,\,-H_2O}$

$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-CH_2-\overset{+}{C}H_2 \xrightarrow{1,\,2,\,H^-\ \text{shift}}$

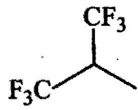
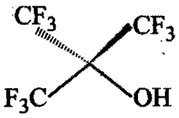
$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-\overset{+}{C}H-CH_3 \xrightarrow{1,\,2,\,H^-\ \text{shift}}$

$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-\overset{+}{C}H-CH_2-CH_3 \xrightarrow{-H^+}$

$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH=CH-CH_3$]

24. Which of the following is the most acidic alcohol?

(a) CH_3OH ☐ (b) CF_3-CH_2-OH ☐

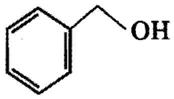
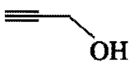
(c)

☐ (d)

☐

25. Which of the following is the most acidic alcohol?

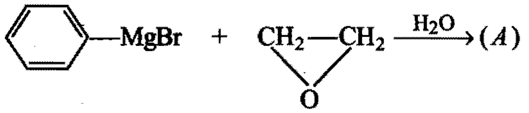
(a)

☐ (b)

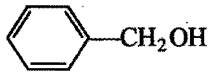
☐

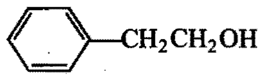
(c)

☐ (d)

☐

26. In the reaction,



the compound (A) is:

(a)

☐

(b)

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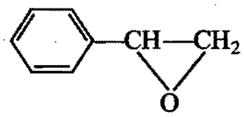
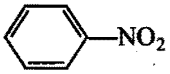
(c)

☐

(d) no reaction ☐

27. Which compound gives red colour in the following reaction?

$$\text{Compound} \xrightarrow[\text{(ii) NaOH}]{\text{(i) HNO}_2}$$

(a) $CH_3-CH_2-NO_2$ ☐ (b) $(CH_3)_2CHNO_2$ ☐

(c) $(CH_3)_3C-NO_2$ ☐ (d)

☐

28. An alcohol (A) on heating with concentrated H_2SO_4 gives alkene (B) as major product and (B) can show the geometrical isomerism. The compound (A) is:

(a) $(CH_3)_2C(OH)CH(CH_3)_2$ ☐
(b) $(CH_3)_2C(OH)CH_2Me$ ☐
(c) $CH_3CH_2CH(OH)CH_3$ ☐
(d) all of the above ☐

29. Tertiary alcohol is obtained as major product in:

(a) $(CH_3)_2CH-CH=CH_2 \xrightarrow[\text{demercuration}]{\text{Oxymercuration}}$ ☐

(b) $(CH_3)_3C-CH=CH_2 \xrightarrow{\text{Dil. } H_2SO_4}$ ☐

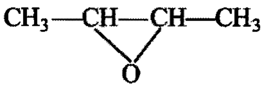
(c) $(CH_3)_2CH-CH=CH_2 \xrightarrow[\text{oxidation}]{\text{Hydroboration}}$ ☐

(d) all of the above ☐

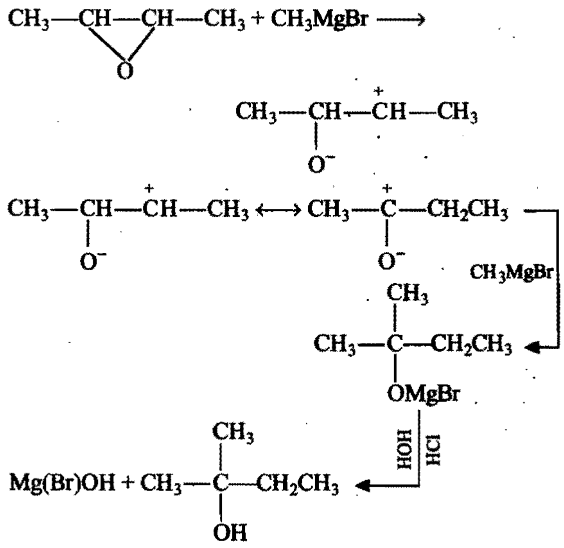
30. The substance(s) which is/are added to make liquor poisonous is/are:

(a) methanol ☐ (b) pyridine ☐
(c) $CuSO_4$ ☐ (d) formaldehyde ☐

31. Which of the following compounds on reaction with CH_3MgBr will give a tertiary alcohol?

(a) C_2H_5CHO ☐
(b) $C_2H_5COOCH_3$ ☐
(c) C_2H_5COOH ☐
(d)

$CH_3-\underset{\diagdown\, O\, \diagup}{CH-CH}-CH_3$ ☐

[**Hint :**

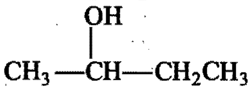


2-Methyl butan-2-ol

32. Which of the following alcohol(s) can be prepared by the action of Grignard reagents with aldehydes?

(a) Primary alcohols ☐
(b) Secondary alcohols ☐
(c) Tertiary alcohols ☐
(d) Both primary and tertiary alcohols ☐

33. The alcohol which gives the most stable carbonium ion on dehydration is:

(a) $(CH_3)_2CHCH_2OH$ ☐
(b) $(CH_3)_3C-OH$ ☐
(c) $CH_3CH_2CH_2CH_2OH$ ☐
(d)

$CH_3-\overset{OH}{\overset{|}{CH}}-CH_2CH_3$ ☐

34. 0.037 g of an alcohol, R—OH was added to CH_3MgBr and the gas evolved measured 11.2 mL at STP. The molecular mass of R—OH will be:

(a) 47 ☐ (b) 79 ☐
(c) 74 ☐ (d) 77 ☐

[**Hint :** $\underset{\text{1 mol}}{R-OH} + CH_3MgBr \longrightarrow \underset{\substack{\text{1 mol}\\ \text{or}\\ \text{22400 mL at STP}}}{CH_4} + Mg(Br)OR$

11.2 mL CH_4 at STP is formed by 0.037 g ROH

∴ 22400 mL CH_4 at STP will be formed by

$$\frac{0.037}{11.2} \times 22400\,\text{g}\ ROH$$
$$= 74\ \text{g}\ ROH$$

∴ Molar mass of $ROH = 74$]

35. Which of the following reactions will yield propan-2-ol?

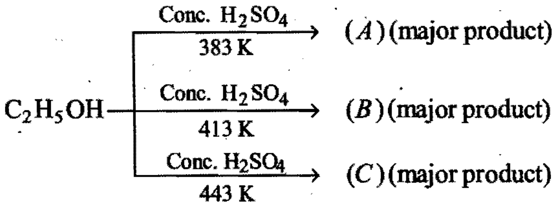
(a) $H_2C{=}CH{-}CH_3 + HOH \xrightarrow{H^+}$ ☐

(b) $CH_3{-}CHO \xrightarrow[HOH]{CH_3MgBr}$ ☐

(c) $CH_2O \xrightarrow[\text{(ii) } HOH]{\text{(i) } C_2H_5MgI}$ ☐

(d) $H_2C{=}CH{-}CH_3 \xrightarrow{\text{Neutral } KMnO_4}$ ☐

36. Ethanol is dehydrated as,

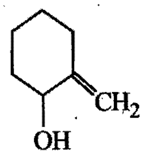


$$C_2H_5OH \begin{cases} \xrightarrow[383\,K]{\text{Conc. } H_2SO_4} (A)\text{ (major product)} \\ \xrightarrow[413\,K]{\text{Conc. } H_2SO_4} (B)\text{ (major product)} \\ \xrightarrow[443\,K]{\text{Conc. } H_2SO_4} (C)\text{ (major product)} \end{cases}$$

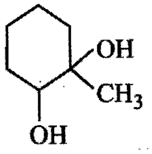
Major products (*A*), (*B*) and (*C*) are respectively:

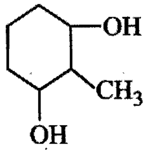
	(*A*)	(*B*)	(*C*)	
(a)	$C_2H_5HSO_4$	$C_2H_5OC_2H_5$	C_2H_4	☐
(b)	C_2H_4	$C_2H_5OC_2H_5$	$C_2H_5HSO_4$	☐
(c)	$C_2H_5HSO_4$	C_2H_4	$C_2H_5OC_2H_5$	☐
(d)	C_2H_4	$C_2H_5HSO_4$	$C_2H_5OC_2H_5$	☐

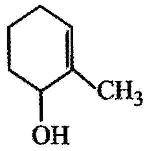
37. Which of the following will be the major product when

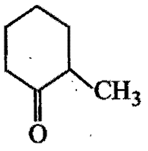


is treated with dil. H_2SO_4 in the presence of $HgSO_4$?

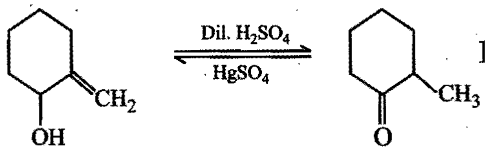
(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

[**Hint :**



(keto-enol tautomerism)

38. Ethyl alcohol can be manufactured from starch by the process of fermentation. Which enzymes stepwise complete the fermentation reaction?

(a) Diastase, invertase, zymase ☐

(b) Maltase, zymase, invertase ☐

(c) Diastase, maltase, zymase ☐

(d) Diastase, zymase and lactase ☐

39. If, ethanol dissolves in water, then which of the following would be happened?

(a) Absorption of heat and decrease in volume ☐

(b) Emission of heat and decrease in volume ☐

(c) Absorption of heat and increase in volume ☐

(d) Emission of heat and increase in volume ☐

[**Hint :** When alcohol is dissolved in water then the solution shows the positive deviation from Raoult's law.

∴ $\Delta H = +\text{ve}$: endothermic, heat absorbed

$\Delta V = +\text{ve}$: increase in volume]

40. Aliphatic primary amines on reaction with $NaNO_2/HCl$ give:

(a) only primary alcohol ☐

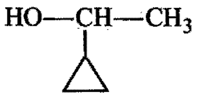
(b) only secondary alcohol ☐

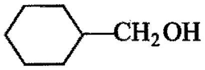
(c) only tertiary alcohol ☐

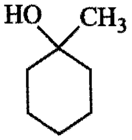
(d) primary, secondary and tertiary alcohol ☐

41. Which of the following alcohols will be oxidised by Br_2/KOH?

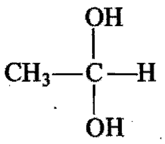
(a) CH_3OH ☐

(b)  ☐

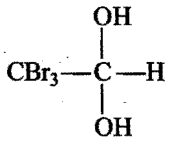
(c)  ☐

(d)  ☐

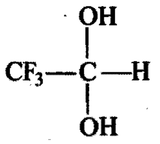
42. Which of the following 'gem' diols is stable?

(a) 

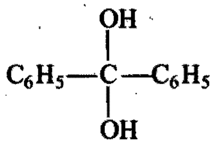
$$CH_3{-}\underset{OH}{\overset{OH}{C}}{-}H$$ ☐

(b) 

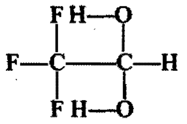
$$CBr_3{-}\underset{OH}{\overset{OH}{C}}{-}H$$ ☐

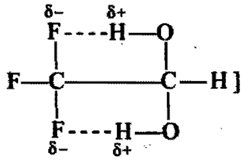
(c)  ☐

$CF_3-C(OH)_2-H$

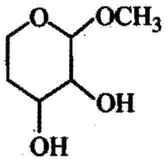
(d)  ☐

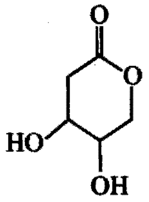
$C_6H_5-C(OH)_2-C_6H_5$

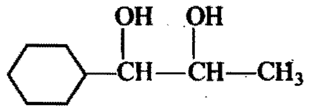
[Hint:  is stabilised by intramolecular hydrogen bonding.

]

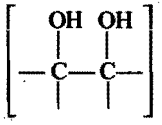
43. Which of the following compounds undergo periodate oxidation?

(a)  ☐

(b)  ☐

(c)  ☐

(d) All of the above ☐

[Hint: All these compounds have  glycolic groups, hence, they are oxidised by periodic acid (HIO_4).]

44. Glycerol forms salt with sodium metal at 110°C. The sodium salt is:

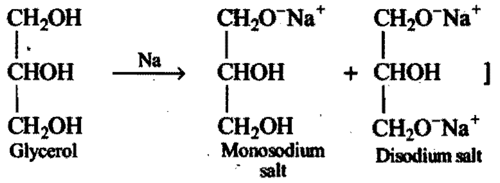
(a) monosalt ☐

(b) disalt ☐

(c) trisalt ☐

(d) mixture of mono and disalt ☐

[Hint: Primary alcoholic groups of glycerol form salt with sodium metal.



]

45. Surgical spirit is:

(a) absolute alcohol ☐

(b) rectified spirit ☐

(c) 95% rectified spirit and 5% methyl alcohol ☐

(d) 90% rectified spirit and 10% methyl alcohol ☐

46. The reaction of glycerol with HIO_4 gives:

(a) formaldehyde ☐

(b) formic acid ☐

(c) iodic acid ☐

(d) oxalic acid ☐

47. Which of the following will result in the formation of an ether?

(a) $(CH_3)_3CO^-Na^+ + C_2H_5Br \longrightarrow$ ☐

(b) $(CH_3)_3CBr + C_2H_5O^-Na^+ \longrightarrow$ ☐

(c) $C_6H_5O^-Na^+ + CH_3Br \longrightarrow$ ☐

(d) $C_6H_5Br + CH_3O^-Na^+ \longrightarrow$ ☐

[Hint: Tertiary halide and aromatic halide do not give Williamson's ether synthesis.]

48. How many isomers of $C_5H_{11}OH$ will be primary alcohols?

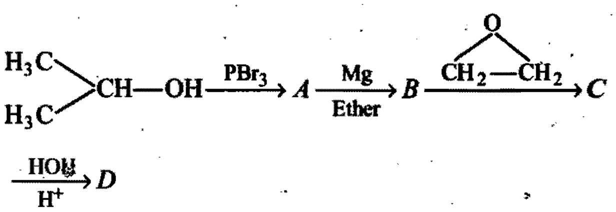
(a) Four ☐

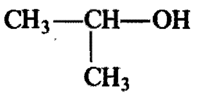
(b) Five ☐

(c) Three ☐

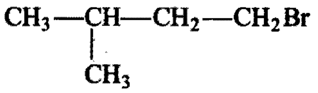
(d) Two ☐

49. Final product (D) in the sequence of reactions is:

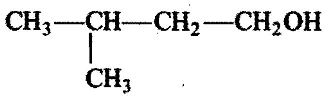


(a)  ☐

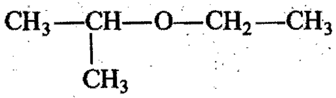
$CH_3-CH(CH_3)-OH$

(b)  ☐

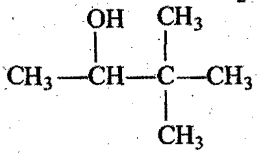
$CH_3-CH(CH_3)-CH_2-CH_2Br$

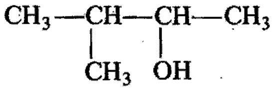
(c)  ☐

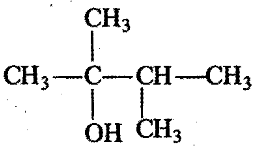
$CH_3-CH(CH_3)-CH_2-CH_2OH$

(d) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-O-CH_2-CH_3$ ☐

50. Which of the following alcohols will dehydrate most rapidly when treated with conc. H_2SO_4?

(a) 
$CH_3-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$ ☐

(b) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3$ ☐

(c) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$ ☐

(d) $CH_3-CH_2-CH_2-CH_2-OH$ ☐

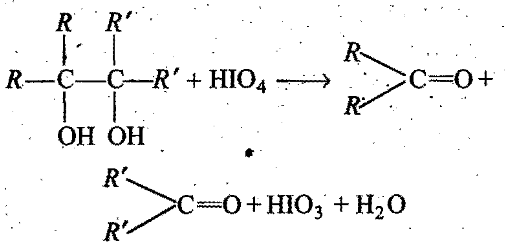
ANSWERS : BRAIN STORMING PROBLEMS

18. (a,b,c) **19.** (a,b,d) **20.** (a,b) **21.** (b) **22.** (b) **23.** (d) **24.** (d) **25.** (d) **26.** (b) **27.** (a)
28. (c) **29.** (b) **30.** (a,b,c) **31.** (d) **32.** (a,b) **33.** (b) **34.** (c) **35.** (a,b) **36.** (a) **37.** (d)
38. (c) **39.** (c) **40.** (d) **41.** (b) **42.** (c) **43.** (d) **44.** (d) **45.** (c) **46.** (a,b,c) **47.** (a,c)
48. (a) **49.** (c) **50.** (c)

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

A reaction characteristic of vicinal diols is their oxidative cleavage on treatment with periodic acid (HIO_4). The carbon-carbon bond of the vicinal diol unit is broken and two carbonyl groups result. Periodic acid is reduced to iodic acid (HIO_3).

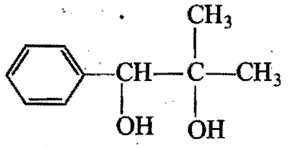


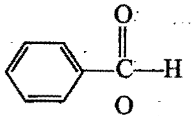
$$R-\underset{OH}{\overset{R}{C}}-\underset{OH}{\overset{R'}{C}}-R' + HIO_4 \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>C=O + \begin{matrix}R'\\R'\end{matrix}\!\!>C=O + HIO_3 + H_2O$$

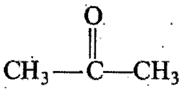
Cyclic diols react to give dicarbonyl compounds. The reactions are faster when the hydroxyl groups are *cis* than when they are *trans* but both stereoisomers are oxidised by periodic acid. Periodic acid cleavage of vicinal diols is often used for analytic purposes as an aid in structure determination. By identifying the carbonyl compounds produced, the constitution of the diol may be deduced.

Answer the following questions:

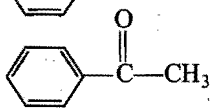
1. Which of the following compound(s) is/are obtained when the following compound is oxidised by HIO_4?

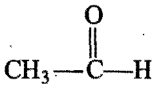


(a) 

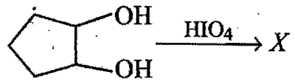
(b) 

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

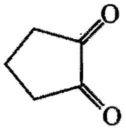
(c) 

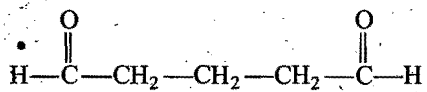
(d) 

$$CH_3-\overset{O}{\overset{\|}{C}}-H$$

2. 

The compound 'X' in above reaction is:

(a) 

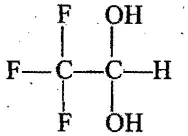
(b) 

$$H-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$$

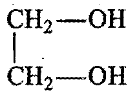
(c) both of these

(d) none of the above

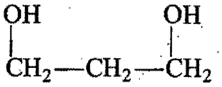
3. Which of the following diols will be oxidised by HIO_4?

(a) 

$$F-\underset{F}{\overset{F}{C}}-\underset{OH}{\overset{OH}{C}}-H$$

(b) 

$$\begin{array}{l}CH_2-OH\\|\\CH_2-OH\end{array}$$

(c) 

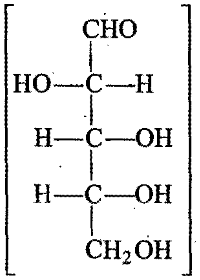
$$\overset{OH}{\overset{|}{C}H_2}-CH_2-\overset{OH}{\overset{|}{C}H_2}$$

(d) All of these

4. Which of the following products is/are obtained when glycerol is treated with HIO_4?

(a) HCHO (b) HCOOH

(c) HIO_3 (d) All of these

5. When arabinose 

$$\left[\begin{array}{c}CHO\\|\\HO-C-H\\|\\H-C-OH\\|\\H-C-OH\\|\\CH_2OH\end{array}\right]$$

is oxidised by HIO_4, then formaldehyde and formic acid are obtained. Number of molecules of formic acid and formaldehyde obtained respectively are:

(a) 3, 2 (b) 4, 1

(c) 1, 4 (d) 2, 3

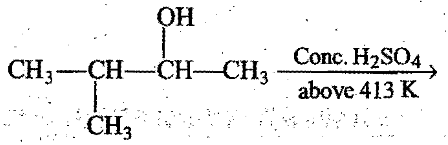
Passage 2

Secondary and tertiary alcohols always give E_1 reaction in dehydration. Primary alcohols whose β-carbon is 3° or 4° also give E_1 reaction. However, the primary alcohols whose β-carbon is 1° or 2° give E_2 reaction. Dehydrating agents like conc. H_2SO_4, Al_2O_3, anhydrous $ZnCl_2$ are used.

The reactivity of alcohols for elimination reaction lies in following sequence:

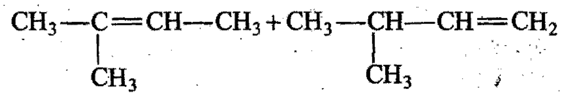
Tertiary alcohol > secondary alcohol > primary alcohol

Electron attracting groups present in alcohols increase the reactivity for dehydration. Greater is the $-I$ effect of the group present in alcohol, more will be its reactivity. Both E_1 and E_2 mechanism give the product according to Saytzeff's rule, *i.e.*, major product is the most substituted alkene.



$$CH_3-\underset{CH_3}{\underset{|}{C}H}-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow[\text{above 413 K}]{\text{Conc. } H_2SO_4}$$

3-Methyl butan-2-ol

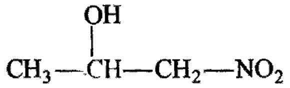


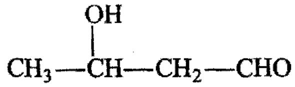
$CH_3—\underset{CH_3}{\underset{|}{C}}=CH—CH_3 + CH_3—\underset{CH_3}{\underset{|}{CH}}—CH=CH_2$

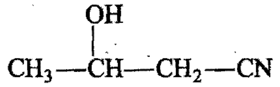
2-Methyl but-2-ene (Major product) 3-Methyl but-1-ene (Minor product)

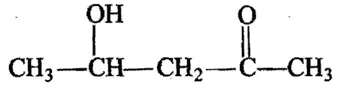
Answer the following questions:

1. Which among the following alcohols will be the most reactive for dehydration?

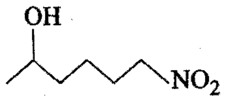
(a) 
$CH_3—\overset{OH}{\overset{|}{C}H}—CH_2—NO_2$

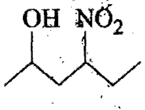
(b) 
$CH_3—\overset{OH}{\overset{|}{C}H}—CH_2—CHO$

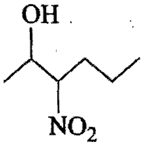
(c) 
$CH_3—\overset{OH}{\overset{|}{C}H}—CH_2—CN$

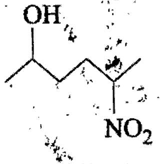
(d) 
$CH_3—\overset{OH}{\overset{|}{C}H}—CH_2—\overset{O}{\overset{||}{C}}—CH_3$

2. Arrange the reactivity of given four alcohols in decreasing order for dehydration.


(*A*)

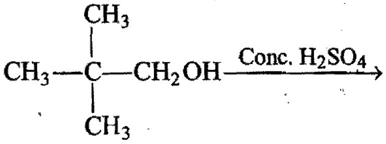

(*B*)

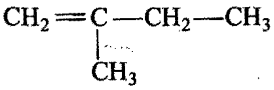

(*C*)

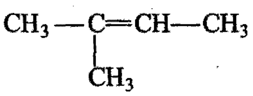

(*D*)

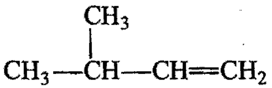
(a) $A > B > C > D$ (b) $D > C > B > A$
(c) $C > B > D > A$ (d) $B > C > A > D$.

[**Hint :** Nearer is the $-I$ group to the alcoholic group, greater is its reactivity for dehydration.]

3. In the reaction,  $CH_3—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—CH_2OH \xrightarrow{\text{Conc. } H_2SO_4}$ the product(s) obtained will be:

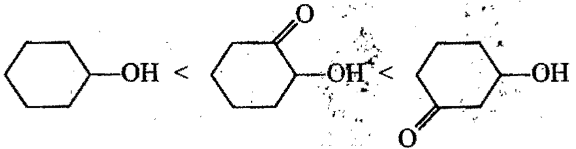
(a) 
$CH_2=\underset{CH_3}{\underset{|}{C}}—CH_2—CH_3$

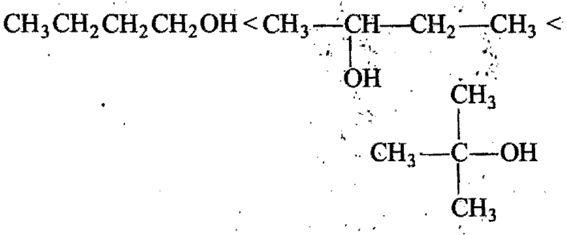
(b) 
$CH_3—\underset{CH_3}{\underset{|}{C}}=CH—CH_3$

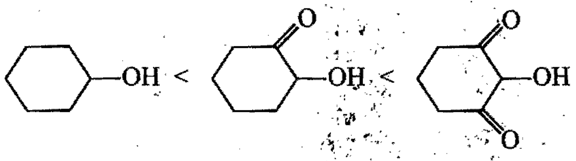
(c) 
$CH_3—\overset{CH_3}{\overset{|}{C}H}—CH=CH_2$

(d) this alcohol cannot be dehydrated

4. Which among the following sequences of reactivity for dehydration is incorrect?

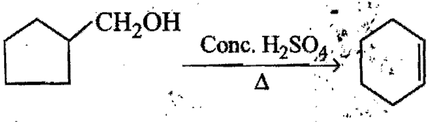
(a) 

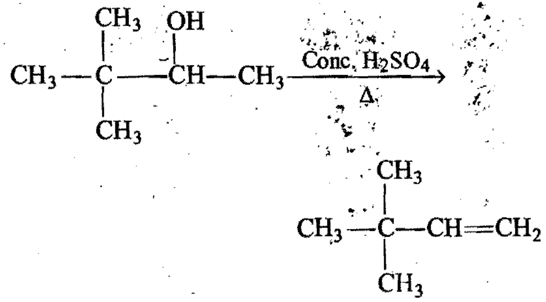
(b) 
$CH_3CH_2CH_2CH_2OH < CH_3—\underset{OH}{\underset{|}{C}H}—CH_2—CH_3 < CH_3—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—OH$

(c) 

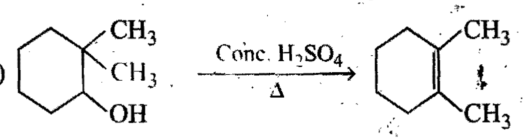
(d) 

5. Which of the following dehydration products is incorrect?

(a) 

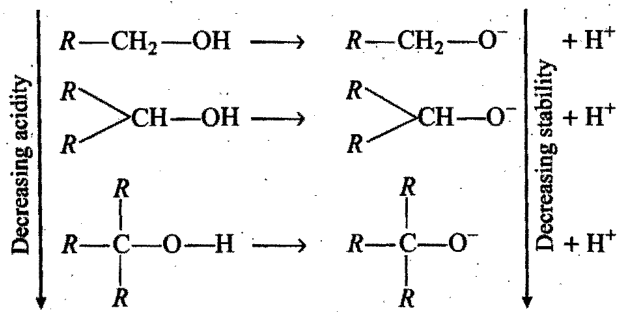
(b) 
$CH_3—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—\overset{OH}{\overset{|}{C}H}—CH_3 \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_3—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—CH=CH_2$

(c) $CH_3CH_2CH_2CH_2OH \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_3—CH=CH—CH_3$

(d) 

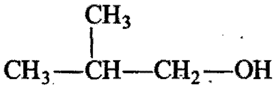
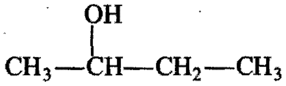
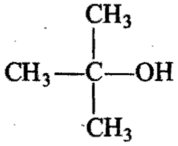
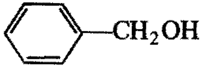
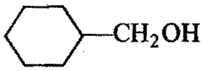
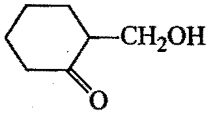
Passage 3

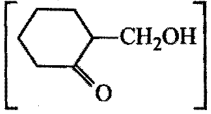
Alcohols are acidic in nature because hydrogen is attached to oxygen which is an electronegative element. Alcohol is weaker acid than water because OH^- ion is more stable than $R—O^-$ ion. $R—O^-$ is less stable, due to $+I$ effect of the alkyl group. Acidity of alcohols increases with increase in the stability of acid anion.



Some alcohols like $CH_3—OH$, $CF_3—CH_2—OH$, $(CF_3)_3C—OH$ are more acidic than water.

Answer the following questions:

1. Which among the following is the most acidic?
   (a) HOH
   (b) CH_3OH
   (c) $CH_3—CH_2—OH$
   (d) $CH_3—CH_2—CH_2—OH$
2. Which among the following alcohols has highest pK_a value?
   (a) $CH_3—CH_2—CH_2—CH_2—OH$
   (b)
   
   $CH_3—\overset{CH_3}{\overset{|}{C}H}—CH_2—OH$
   (c)
   
   $CH_3—\overset{OH}{\overset{|}{C}H}—CH_2—CH_3$
   (d)
   
   $CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—OH$
3. The strongest conjugate base out of the following is :
   (a) $(CF_3)_3CO^-$ (b) $(CBr_3)_3CO^-$
   (c) $(CCl_3)_3CO^-$ (d) $(CI_3)_3CO^-$
4. Which of the following will react fastest with sodium?
   (a)
   
   (b)
   
   (c)
   
   (d) $(CH_3)_3C—OH$

   [Hint : Keto group increases the acidic character hence,
   
   will react fastest with sodium.]
5. Lucas test of alcohols involves following reaction:

$$R—OH + \underset{\text{Conc.}}{HCl} \xrightarrow[ZnCl_2]{\text{Anhydrous}} \underset{\substack{\text{white}\\\text{turbidity}}}{RCl} + H_2O$$

   Select the correct statements for the Lucas test.
   (a) ROH behaves as a base
   (b) Lesser is the acidic character of alcohol, greater is its reactivity towards Lucas reagent
   (c) Reactivity of 1°, 2°, 3° alcohol, lies in the following sequence (for Lucas reaction) 3° > 2° > 1°
   (d) CH_3OH gives Lucas test most quickly

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	1. (a,b)	2. (b)	3. (b)	4. (d)	5. (b)*
Passage 2	1. (a)	2. (c)	3. (a,b)	4. (c)	5. (a)
Passage 3	1. (a)	2. (d)	3. (d)	4. (c)	5. (a,b,c)

10

ETHERS

10.1 INTRODUCTION

Ethers are a class of compounds which contain one divalent oxygen atom bonded to two monovalent alkyl groups (same or different). When both the alkyl groups are same, they are designated as **simple** or **symmetrical ethers** and when both are different, they are called **mixed** or **unsymmetrical ethers.**

$R—O—R$	$R—O—R'$
$CH_3—O—CH_3$	$CH_3—O—C_2H_5$
$C_2H_5—O—C_2H_5$	$C_2H_5—O—C_3H_7$
Symmetrical or Simple ethers	Unsymmetrical or Mixed ethers

Ethers form a homologous series with the general formula $\mathbf{C_nH_{2n+2}O}$ (same as monohydric alcohols), where the value of 'n' is always more than 1. The functional group of ethers is (C—O—C).

Ethers may be regarded as **anhydrides of alcohols** as they may be obtained by elimination of a water molecule from two alcohol molecules.

$$\underset{\text{Alcohol}}{R—O}\boxed{H + HO}\underset{\text{Alcohol}}{—R} \longrightarrow \underset{\text{Ether}}{R—O—R} + H_2O$$

Just as alcohols are considered as monoalkyl derivatives of water, ethers may be considered as dialkyl derivatives of water.

$$\underset{\text{Water}}{H—O—H} \qquad \underset{\text{Alcohol}}{R—O—H} \qquad \underset{\text{Ether}}{R—O—R}$$

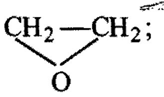
Structure : The oxygen atom in ethers is sp^3-hybridized. Two of the hybrid orbitals overlap with hybrid orbitals (one each) of two carbon atoms to form sigma bonds $\left(>C \overset{\sigma}{—} O \overset{\sigma}{—} C<\right)$. The bond angle is 110°, $\begin{matrix} R \\ & \overset{110°}{>}O \\ R \end{matrix}$ while H—O—H bond angle is 104.5°. This is because of greater size of alkyl groups resulting in greater forces of repulsion.

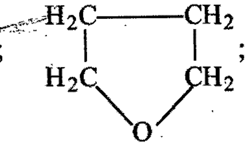
Thus, ethers have a **bent structure** and are **dipolar in nature.**

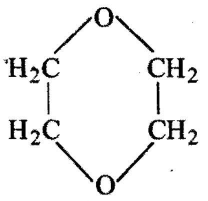
For example, the net dipole moment of dimethyl ether is 1.30 D and that of diethyl ether is 1.18 D.

[Besides the open chain saturated homologous series, $C_nH_{2n+2}O$, there are numerous organic compounds in which —O— functional group is present. These compounds are also termed ethers.]

$CH_3OCH{=}CH_2$;
Methyl vinyl ether
(Unsaturated)


Ethylene oxide
(Cyclic)


Tetrahydrofuran
(THF)


Dioxane

$C_6H_5OCH_3$;
Anisole
(Methyl phenyl ether)

$C_6H_5OC_2H_5$
Phenetole
(Ethylphenyl ether)

10.2 NOMENCLATURE

There are two systems for naming ethers:

1. Common names : In this system, ethers are named after the alkyl groups attached to oxygen atom and adding the word ether. When both the alkyl groups are same, the prefix di- is used. In case of unsymmetrical ethers two alkyl groups are named in alphabetical order.

CH_3OCH_3 ; Dimethyl ether

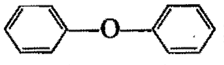
$C_2H_5OC_2H_5$; Diethyl ether

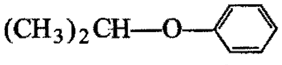
$CH_3OC_2H_5$; Ethyl methyl ether

$C_2H_5OC_3H_7$; Ethyl propyl ether

$CH_3—O—C(CH_3)_3$; Methyl *tert.* butyl ether

$CH_3CH_2CH_2—O—CH(CH_3)_2$; Isopropyl *n*-propyl ether

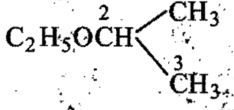
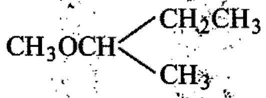
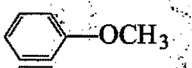
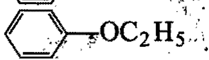

Diphenyl ether


Isopropyl phenyl ether

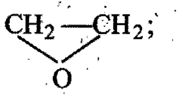
2. IUPAC system : In this system, ethers are named as **alkoxy alkanes.** The smaller alkyl group plus the oxygen atom is called an alkoxy substituent, *i.e.*, in case of mixed ethers, the etheral oxygen is taken with the smaller alkyl group and forms a part of the alkoxy group while the larger alkyl group is considered to be a part of the alkane. Names of some common alkoxy groups are:

$CH_3O—$;	$CH_3CH_2O—$;	$CH_3CH_2CH_2O—$;	$(CH_3)_2CHO—$
Methoxy	Ethoxy	*n*-Propoxy	Isopropoxy

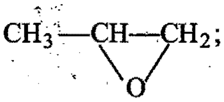
The name of the alkane is prefixed by the name of alkoxy group and position number.

Formula	IUPAC name
CH_3OCH_3	Methoxy methane
$CH_3OC_2H_5$	Methoxy ethane
$C_2H_5OC_2H_5$	Ethoxy ethane
$C_2H_5OC_3H_7$	Ethoxy propane
 $C_2H_5OCH(CH_3)_2$	2-Ethoxy propane
 $CH_3OCH(CH_2CH_3)CH_3$	2-Methoxy butane
	Methoxy benzene (Anisole)
	Ethoxy benzene (Phenetole)

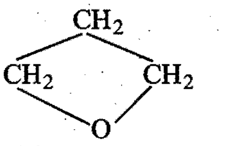
Cyclic ethers



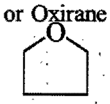
Ethylene oxide (Epoxyethane) or Oxirane



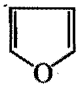
Propylene oxide (1,2-Epoxypropane)



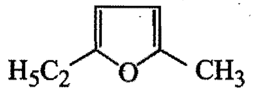
1,3-Epoxypropane (Oxetane)



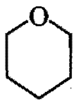
Oxolane (Tetrahydrofuran) or THF



Furan

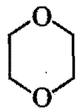


2-Ethyl-5-methyl furan

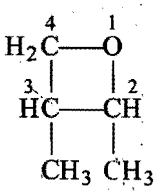


Oxane (Tetrahydropyran)

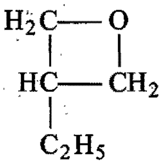
Pyran



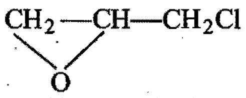
1,4-Dioxan (Diethylene dioxide)



2,3-Dimethyl oxetane



3-Ethyl oxetane



2-Chloromethyl oxirane (3-Chloro-1,2-epoxy propane or Epichlorohydrin)

Note : In case of simple ethers common names are also accepted in IUPAC system.

10.3 ISOMERISM

Ethers exhibit following types of structural isomerism:

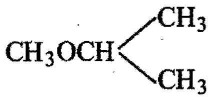
1. Functional isomerism : Ethers are isomeric with alcohols (monohydric) since both have same general formula, $C_nH_{2n+2}O$, but different functional groups.

Molecular formula	Alcohol	Ether
C_2H_6O	CH_3CH_2OH Ethyl alcohol	CH_3OCH_3 Dimethyl ether
C_3H_8O	C_3H_7OH Propyl alcohol	$CH_3OC_2H_5$ Ethyl methyl ether
$C_4H_{10}O$	C_4H_9OH Butyl alcohol	$C_2H_5OC_2H_5$ Diethyl ether
C_7H_8O	$C_6H_5CH_2OH$ Benzyl alcohol	$C_6H_5OCH_3$ Methyl phenyl ether

are functional isomers.

2. Metamerism : Ethers show isomerism among themselves due to different alkyl groups attached to polyvalent oxygen atom.

For example, the molecular formula $C_4H_{10}O$ exhibits three isomers.

$C_2H_5OC_2H_5$;	$CH_3OCH_2CH_2CH_3$;	 $CH_3OCH(CH_3)_2$
Diethyl ether (i)	Methyl *n*-propyl ether (ii)	Methyl isopropyl ether (iii)

(i) and (ii) are metamers; similarly (i) and (iii) are metamers.

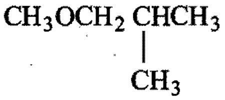
Only those ethers which contain more than three carbon atoms exhibit this type of isomerism. For example,

$C_8H_{10}O$	$C_6H_5OCH_2CH_3$;	$C_6H_5CH_2OCH_3$
	Ethyl phenyl ether	Benzyl methyl ether

are metamers.

3. Chain isomerism : These have the same alkyl groups on either side of the oxygen atom but different arrangements of the carbon chain within the alkyl group(s). For example,

$C_5H_{12}O$, $CH_3OCH_2CH_2CH_2CH_3$, 1-Methoxybutane



$CH_3OCH_2CH(CH_3)CH_3$

1-Methoxy 2-methyl propane

10.4 GENERAL METHODS OF PREPARATION

1. Dehydration of alcohols : When an excess of alcohol is heated at 140°C in presence of protic acids, (H_2SO_4, H_3PO_4, *i.e.*, concentrated sulphuric acid or phosphoric acid) two molecules of alcohol eliminate one molecule of water to form symmetrical ether. Lower ethers are prepared **industrially** by this method.

(a) Acid catalysed dehydration

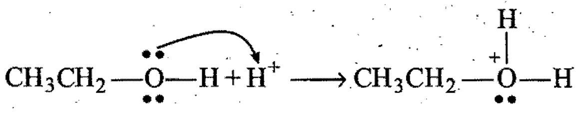
$$\underset{\text{2 Molecules of alcohol}}{ROH + HOR} \xrightarrow[140°C]{H_2SO_4(\text{conc.})} \underset{\text{Ether}}{ROR} + H_2O$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH + HOC_2H_5} \xrightarrow[140°C]{H_2SO_4(\text{conc.})} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2O$$

Mechanism

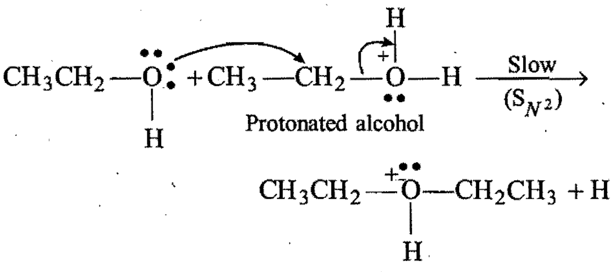
Acid catalysed dehydration of 1° alcohol to ether is a nucleophilic bimolecular substitution (S_N2) reaction involving the attack of alcohol molecule on a protonated alcohol, as shown below in three steps:

Step 1. Protonation of alcohol to form oxonium salt.



$$\underset{\text{Ethanol (Base)}}{CH_3CH_2-\ddot{O}-H} + \underset{\text{Acid}}{H^+} \longrightarrow \underset{\text{Protonated ethanol}}{CH_3CH_2-\overset{\overset{H}{|}}{\overset{+}{\ddot{O}}}-H}$$

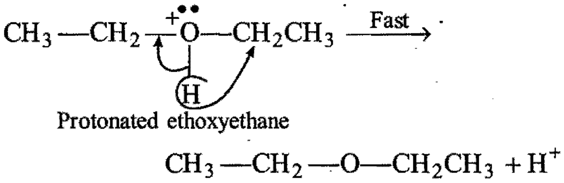
Step 2. Nucleophilic attack by unprotonated alcohol on protonated alcohol to form protonated ethoxyethane with the elimination of a water molecule.



$$CH_3CH_2-\underset{\underset{H}{|}}{\ddot{O}}: + \underset{\text{Protonated alcohol}}{CH_3-CH_2-\overset{\overset{H}{|}}{\overset{+}{\ddot{O}}}-H} \xrightarrow[(S_N2)]{\text{Slow}} \underset{\text{Protonated ethoxyethane}}{CH_3CH_2-\underset{\underset{H}{|}}{\overset{+}{\ddot{O}}}-CH_2CH_3} + H_2O$$

This step is slow and hence is the rate determining step of the reaction.

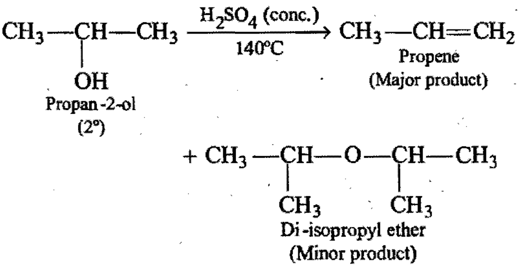
Step 3. Loss of a proton to form ethoxyethane.



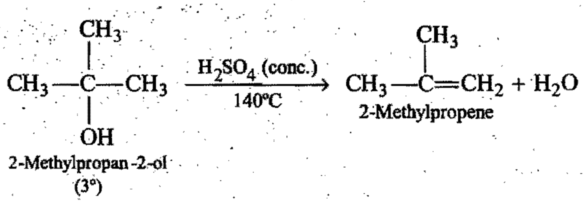
$$\underset{\text{Protonated ethoxyethane}}{CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{\ddot{O}}}-CH_2CH_3} \xrightarrow{\text{Fast}} \underset{\text{Ethoxyethane}}{CH_3-CH_2-O-CH_2CH_3} + H^+$$

The formation of ether (substitution product) is also accompanied by the formation of small amount of alkenes. (elimination product).

Note: This reaction is mainly applicable for the dehydration of primary alcohols and the alcohol is taken in excess. However, temperature 140°C must be controlled properly. Secondary and tertiary alcohols (S_N1 mechanism) form alkenes mainly due to steric hindrance, as the nucleophilic attack by the alcohol on the protonated alcohol molecule does not occur.



$$\underset{\substack{\text{Propan-2-ol}\\(2°)}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow[140°C]{H_2SO_4(\text{conc.})} \underset{\substack{\text{Propene}\\\text{(Major product)}}}{CH_3-CH=CH_2} + \underset{\substack{\text{Di-isopropyl ether}\\\text{(Minor product)}}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-O-\underset{\underset{CH_3}{|}}{CH}-CH_3}$$



$$\underset{\substack{\text{2-Methylpropan-2-ol}\\(3°)}}{CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3} \xrightarrow[140°C]{H_2SO_4(\text{conc.})} \underset{\text{2-Methylpropene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} + H_2O$$

Thus, in the formation of ethers, the dehydration of alcohols is in the order:

Primary > Secondary > Tertiary

(b) Catalytic dehydration

Dehydration of a primary alcohol is also affected by passing vapours over alumina or thoria at 250°C under pressure.

$$\underset{\substack{\text{Alcohol}\\\text{(Excess)}}}{2ROH} \xrightarrow[250°C]{Al_2O_3} \underset{\text{Dialkylether}}{R-O-R} + H_2O$$

$$\underset{\text{Ethanol}}{2C_2H_5OH} \xrightarrow[250°C]{Al_2O_3} \underset{\text{Diethylether}}{C_2H_5OC_2H_5} + H_2O$$

Note: If mixture of two alcohols is subjected to dehydration with Al_2O_3 at 250° or conc. H_2SO_4 at 140°C, then unsymmetrical ethers can not be obtained but we get mixture of three ethers.

$$R_1-OH + R_2-OH \xrightarrow[250°C]{Al_2O_3} R_1-O-R_1 + R_1-O-R_2 + R_2-O-R_2$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + \underset{n\text{-Propyl ether}}{CH_3CH_2CH_2OH} \xrightarrow[250°C]{Al_2O_3} \underset{\text{Diethyl ether}}{CH_3CH_2OCH_2CH_3} + \underset{\text{Ethyl-}n\text{-propyl ether}}{CH_3CH_2CH_2O-CH_2CH_3} + \underset{\text{Di-}n\text{-propyl ether}}{(CH_3CH_2CH_2)_2O}$$

2. Williamson's synthesis : It involves the heating of alkyl halides with sodium or potassium alkoxides. This is a very good method for the preparation of simple and mixed ethers.

$$RONa + X-R' \xrightarrow{\text{Heat}} ROR' + NaX$$

$$\underset{\text{Sodium ethoxide}}{C_2H_5ONa} + \underset{\text{Ethyl iodide}}{C_2H_5I} \xrightarrow{55°C} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + NaI$$

$$C_2H_5\overset{-}{O}\overset{+}{Na} + \underset{\text{Methyl bromide}}{\overset{\delta^-}{Br}-\overset{\delta^+}{CH_3}} \xrightarrow{\text{Heat}} \underset{\text{Ethyl methyl ether}}{C_2H_5-O-CH_3} + NaBr$$

The reaction is based on nucleophilic substitution (S_N2) of alkyl halides in which the halogen atom is replaced by alkoxy group.

Mechanism : It is a nucleophilic substitution reaction and proceeds *via* S_N2 mechanism.

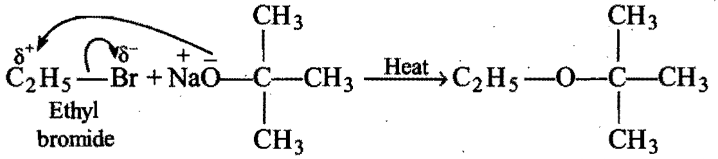
$$C_2H_5ONa \rightleftharpoons C_2H_5O^- + Na^+$$

$$C_2H_5O^- + C_2H_5I \xrightarrow{\text{Slow}} C_2H_5\overset{\delta^-}{O}---C_2H_5---\overset{\delta^-}{I} \xrightarrow{\text{Fast}} C_2H_5OC_2H_5 + I^-$$

$$Na^+ + I^- \rightleftharpoons NaI$$

Since, alkoxides and alkyl halides are both prepared from alcohols, the Williamson method ultimately involves the synthesis of an ether from two alcohols.

Limitations : The reactivity of primary (1°) alkyl halides is in the order, $CH_3 > CH_3CH_2 > CH_3CH_2CH_2$ and the tendency of alkyl halides to undergo elimination is 3° > 2° > 1°. Hence, for better yield, the **alkyl halide should be primary and alkoxide should be secondary or tertiary.**



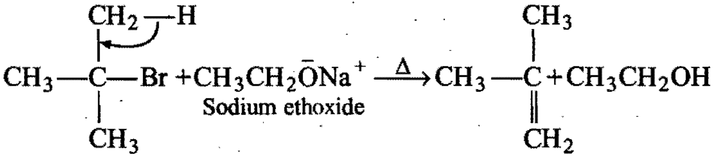
$$\overset{\delta+}{C_2H_5}-\overset{\delta-}{Br} + \overset{+}{Na}\overset{-}{O}-C(CH_3)_3 \xrightarrow{Heat} C_2H_5-O-C(CH_3)_3$$

Ethyl bromide

Sodium salt of *tert.* butyl alcohol (3° Alkoxide)

Ethyl *tert.* butyl ether

So, this method is not applicable to tert. alkyl halides, because the alkoxide ions being both powerful nucleophiles and bases would bring dehydrohalogenation of the tert. alkyl halides to form alkenes preferentially.



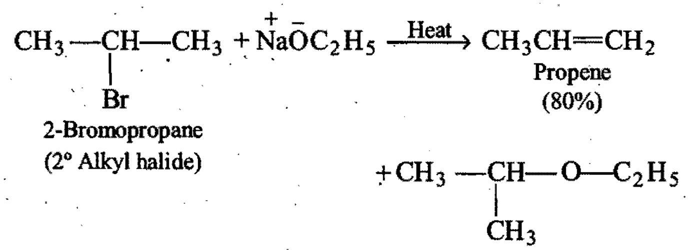
$$CH_3-C(CH_3)(CH_2-H)-Br + CH_3CH_2\overset{-}{O}Na^+ \xrightarrow{\Delta} CH_3-C(CH_3)=CH_2 + CH_3CH_2OH + NaBr$$

Sodium ethoxide

Tert. butyl bromide (3° Alkyl halide)

2-Methyl propene

Due to steric hindrance, secondary alkyl halides also prefer to undergo elimination rather than substitution. For example,



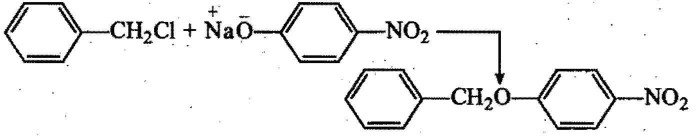
$$CH_3-CH(Br)-CH_3 + \overset{+}{Na}\overset{-}{O}C_2H_5 \xrightarrow{Heat} CH_3CH=CH_2 + CH_3-CH(CH_3)-O-C_2H_5$$

2-Bromopropane (2° Alkyl halide)

Propene (80%)

2-Ethoxypropane (20%)

Note : (i) Aromatic halides cannot be used in Williamson ether synthesis. However, if strong electron withdrawing group at *ortho* and *para*-positions are present then reaction takes place, *e.g.*,



(ii) Dimethyl sulphate or diethyl sulphate can be used at the place of a halide in Williamson's synthesis.

$$C_2H_5\overset{-}{O}Na^+ \longrightarrow C_2H_5\overset{-}{O} + Na^+$$

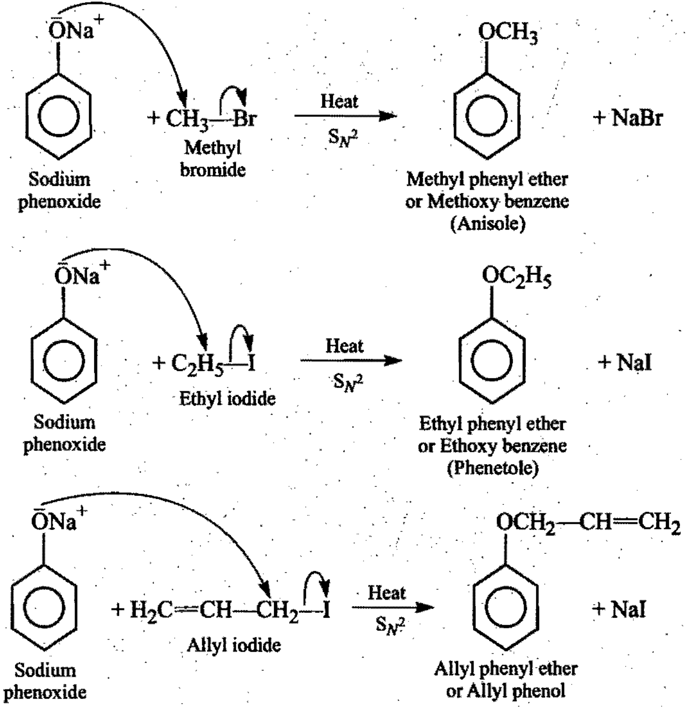
$$C_2H_5\overset{-}{O} + CH_3-O-SO_3CH_3 \longrightarrow C_2H_5-O-CH_3 + CH_3OSO_3^-$$

Dimethyl sulphate　Ethyl methyl ether

$$C_2H_5ONa + (C_2H_5)_2SO_4 \longrightarrow C_2H_5OC_2H_5 + C_2H_5SO_4^-Na^+$$

Diethyl sulphate　Diethyl ether

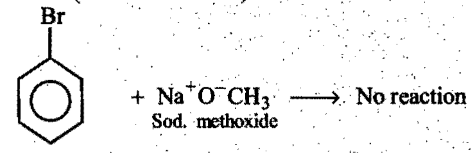
(iii) **Phenolic ethers** (alkyl aryl ethers) can also be prepared in a similar way by treating sodium phenoxide with alkyl halides. For example,



$$2C_6H_5OH + (C_2H_5)_2SO_4 \xrightarrow[\Delta]{2NaOH\ (aq.)} 2C_6H_5OC_2H_5 + Na_2SO_4 + 2H_2O$$

Phenol　Diethyl sulphate　Phenetole

However, aryl halide and sodium alkoxide cannot be used for preparing phenolic ethers because of the reason that aryl halides are much less reactive towards nucleophilic substitution reactions than alkyl halides. The C—Br bond acquires a double bond character (due to resonance).



Bromobenzene

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3. Heating alkyl halides with dry silver oxide : Symmetrical ethers can be prepared by heating alkyl halides with dry silver oxide.

$$2RX + \underset{(Dry)}{Ag_2O} \xrightarrow{Heat} R-O-R + 2AgX$$

$$2C_2H_5I + \underset{(Dry)}{Ag_2O} \xrightarrow{Heat} C_2H_5OC_2H_5 + 2AgI$$

4. Action of diazomethane on alcohols : Methyl ethers can be formed by heating diazomethane with alcohols in presence of a catalyst, boron trifluoride or HBF_4 (tetra fluoroboric acid).

$$ROH + CH_2N_2 \xrightarrow[\Delta]{BF_3} R-O-CH_3 + N_2$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow[\Delta]{HBF_4} \underset{\text{Ethyl methyl ether}}{C_2H_5OCH_3} + N_2$$

$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} + CH_2N_2 \xrightarrow[\Delta]{HBF_4} \underset{\text{2-Methoxy propane}}{(CH_3)_2CH{-}O{-}CH_3} + N_2$$

Mechanism : In this reaction, HBF_4 acts as a strong acid and protonates to diazomethane.

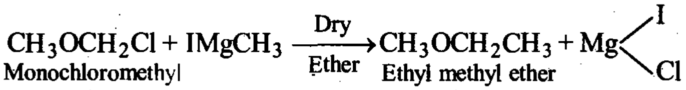
$$CH_2N_2 + HBF_4 \longrightarrow \overset{+}{C}H_3N_2 + BF_4^-$$

$$\overset{+}{C}H_3N_2 \longrightarrow \overset{+}{C}H_3 + N_2$$

$$R{-}O{-}H + \overset{+}{C}H_3 \xrightarrow{S_N2} R{-}O{-}CH_3 + H^+$$

5. Reaction of lower halogenated ethers with Grignard reagents : Higher members can be prepared by the action of Grignard reagents on lower halogenated ethers.

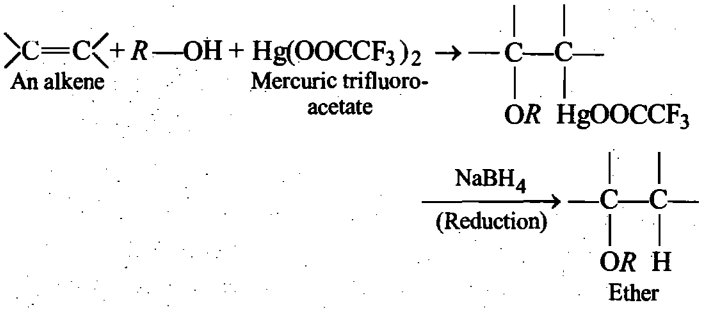
$$\underset{\substack{\text{Halogenated}\\ \text{ether}}}{ROCH_2X} + \underset{\substack{\text{Grignard}\\ \text{reagents}}}{XMgR'} \longrightarrow \underset{\substack{\text{Higher}\\ \text{ether}}}{ROCH_2R'} + MgX_2$$



$$CH_3OCH_2Cl + IMgCH_3 \xrightarrow[\text{Ether}]{\text{Dry}} CH_3OCH_2CH_3 + Mg\begin{matrix} I \\ Cl \end{matrix}$$

Monochloromethyl ether   Ethyl methyl ether

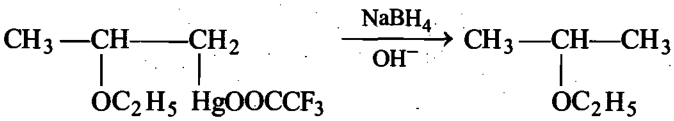
6. Alkoxy mercuration-demercuration :



$$\underset{\text{An alkene}}{\gt C{=}C\lt} + R{-}OH + \underset{\substack{\text{Mercuric trifluoro-}\\ \text{acetate}}}{Hg(OOCCF_3)_2} \rightarrow \underset{OR\quad HgOOCCF_3}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-} \xrightarrow[\text{(Reduction)}]{NaBH_4} \underset{\substack{OR\quad H\\ \text{Ether}}}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-}$$

Alkenes readily react with mercuric trifluoroacetate in presence of an alcohol to give alkoxy mercuric compounds which on reduction with $NaBH_4$ in alkaline medium yield ethers and it is in accordance with Markownikoff's (indirect) addition of alcohols to alkenes.

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + C_2H_5OH + \underset{\substack{\text{Mercuric}\\ \text{trifluoroacetate}}}{Hg(OOCCF_3)_2} \longrightarrow$$

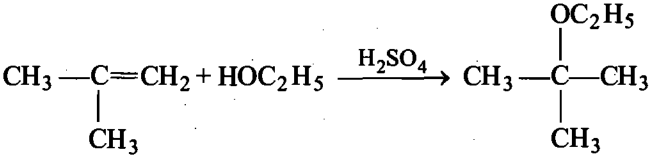


$$CH_3{-}\underset{OC_2H_5}{\underset{|}{C}H}{-}\underset{HgOOCCF_3}{\underset{|}{C}H_2} \xrightarrow[OH^-]{NaBH_4} CH_3{-}\underset{OC_2H_5}{\underset{|}{C}H}{-}CH_3$$

2-Ethoxy propane

7. Addition of alcohols to alkenes : Ethers may be prepared by the direct addition of alcohols to alkenes in the presence of acid, *e.g.*,

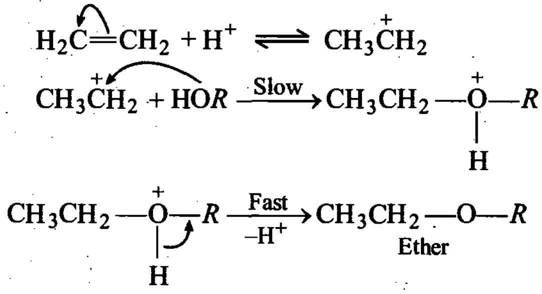
$$H_2C{=}CH_2 + \underset{\text{Alcohol}}{HOR} \xrightarrow{H_2SO_4} \underset{\text{Ether}}{CH_3{-}CH_2{-}OR}$$



$$CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2 + HOC_2H_5 \xrightarrow{H_2SO_4} CH_3{-}\overset{OC_2H_5}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}CH_3$$

2-Methyl propene   2-Ethoxy-2-methyl propane (*Tert.* butyl ethyl ether)

The intermediate is carbocation.

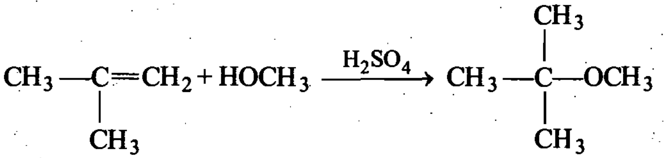


$$H_2C{=}CH_2 + H^+ \rightleftharpoons CH_3\overset{+}{C}H_2$$

$$CH_3\overset{+}{C}H_2 + HOR \xrightarrow{\text{Slow}} CH_3CH_2{-}\underset{H}{\underset{|}{\overset{+}{O}}}{-}R$$

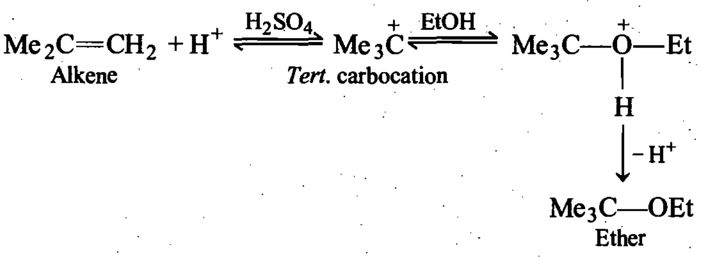
$$CH_3CH_2{-}\underset{H}{\underset{|}{\overset{+}{O}}}{-}R \xrightarrow[-H^+]{\text{Fast}} \underset{\text{Ether}}{CH_3CH_2{-}O{-}R}$$

This method is very useful for preparing mixed ethers.



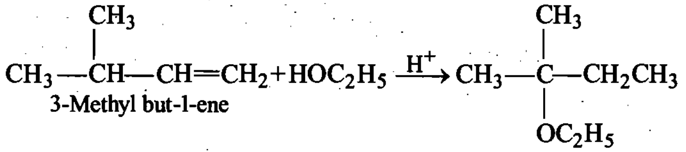
$$CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2 + HOCH_3 \xrightarrow{H_2SO_4} CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}OCH_3$$

2-Methyl propene   2-Methoxy-2-methyl propane



$$\underset{\text{Alkene}}{Me_2C{=}CH_2} + H^+ \overset{H_2SO_4}{\rightleftharpoons} \underset{\textit{Tert.}\text{ carbocation}}{Me_3\overset{+}{C}} \overset{EtOH}{\rightleftharpoons} Me_3C{-}\underset{H}{\underset{|}{\overset{+}{O}}}{-}Et \xrightarrow{-H^+} \underset{\text{Ether}}{Me_3C{-}OEt}$$

In higher cases, there can be 1,2 hydride or 1,2-methyl shift to form more stable carbocation.



$$CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}CH{=}CH_2 + HOC_2H_5 \xrightarrow{H^+} CH_3{-}\overset{CH_3}{\overset{|}{\underset{OC_2H_5}{\underset{|}{C}}}}{-}CH_2CH_3$$

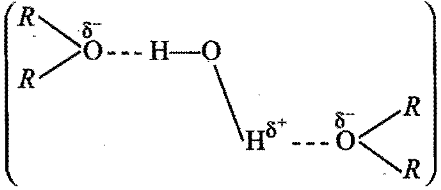
3-Methyl but-1-ene   2-Ethoxy-2-methyl butane

10.5 GENERAL CHARACTERISTICS OF ETHERS

Physical properties : (i) Dimethyl ether and ethyl methyl ether are gases. All ethers are colourless liquids with characteristic ether smell. Diethyl ether has boiling point 34.5°C.

(ii) They are lighter than water. Lower ethers are highly volatile and very inflammable.

(iii) They are sparingly soluble in water but readily soluble in organic solvents. Solubility of ethers in water in presence of small amount of alcohols perhaps due to hydrogen bonding between ether and water molecules.



Ethers themselves are very good solvents.

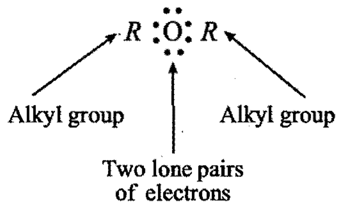
(iv) Boiling points of ethers show a gradual increase with increase in molecular mass. Ethers have much lower boiling points than isomeric alcohols as there is no association between the molecules as in alcohols due to hydrogen bonding. The boiling points of ethers are close to the boiling points of alkanes.

(v) On account of bond angle ($\gt C—O—C\lt$) 110°, the two dipoles do not cancel each other and molecules have small net dipole moment making the ethers somewhat polar. For example, the net dipole moment of dimethyl ether is 1.30 D and that of diethyl ether is 1.18D. The C—O bond length in methoxy methane (141 pm) is almost the same as in methanol (142 pm).

(vi) Ethers have a **bent structure** and are **dipolar in nature.**

(vii) Lower ethers act as anaesthetics.

Chemical properties : Ethers are chemically less reactive as they do not have any active functional group. They do not react with bases, reducing agents, oxidising agents and active metals, etc., under ordinary conditions. The electronic formula of an ether can be represented as:



Thus, the properties of ethers are due to alkyl groups, lone pair of electrons on etheral oxygen atom and cleavage of C—O bond.

1. Alkyl groups show substitution reactions like alkanes.
2. Due to the presence of two lone pairs of electrons, ethers form oxonium salts with mineral acids.
3. The C—O bond is not so stable as C—C bond. The C—O bond is ruptured in the presence of a number of reagents.

1. Reactions Due to Alkyl Groups

(i) Halogenation : Ethers undergo substitution at alkyl radicals when reacted with chlorine or bromine, in the absence of sunlight to form halogenated substituted ethers. Usually the hydrogen at the α-carbon is displaced most readily. However, in the presence of sunlight all the hydrogens of the ethers are substituted.

$$\underset{\text{Diethyl ether}}{CH_3CH_2OCH_2CH_3} \xrightarrow[\text{Dark}]{Cl_2} \underset{(\alpha\text{-Monochlorodiethyl ether})}{CH_3\overset{\alpha}{C}HClOCH_2CH_3} + HCl$$

$$\underset{\text{Diethyl ether}}{CH_3CH_2OCH_2CH_3} \xrightarrow[\text{Dark}]{2Cl_2} \underset{(\alpha,\alpha'\text{-Dichlorodiethyl ether})}{CH_3\overset{\alpha}{C}HClO\overset{\alpha'}{C}HClCH_3} + 2HCl$$

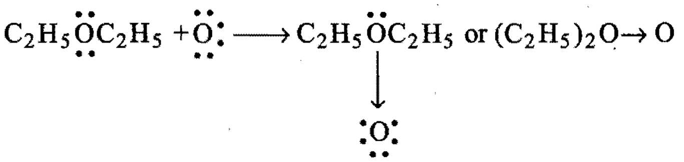
$$C_2H_5OC_2H_5 + \underset{(\text{Excess})}{10Cl_2} \xrightarrow[\text{Light}]{h\nu} \underset{(\text{Perchlorodiethyl ether})}{C_2Cl_5OC_2Cl_5} + 10HCl$$

(ii) Burning (Combustion) : Ethers are highly inflammable. They form explosive mixtures with air. They burn, like alkanes to produce carbon dioxide and water.

$$C_2H_5OC_2H_5 + 6O_2 \longrightarrow 4CO_2 + 5H_2O$$

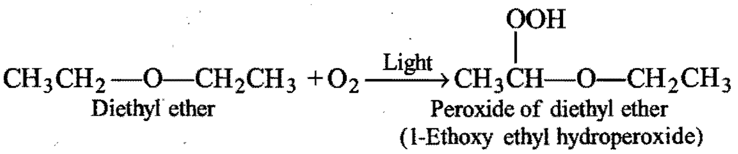
2. Reactions Due to Etheral Oxygen

(i) Oxidation and Peroxide formation : Ethers add up atmospheric oxygen or ozonised oxygen through coordination of one of the lone pair of etheral oxygen to form peroxides in presence of sunlight or ultraviolet light.



$$C_2H_5\ddot{\underset{\cdot\cdot}{O}}C_2H_5 + \ddot{\underset{\cdot\cdot}{O}}\colon \longrightarrow C_2H_5\overset{\cdot\cdot}{O}C_2H_5 \text{ or } (C_2H_5)_2O \rightarrow O$$

- The peroxide of diethyl ether is heavy, pungent oily liquid unstable compound and decomposes violently on heating. There is another concept of formation of a peroxide in long contact with air and light according to the following reaction.



$$\underset{\text{Diethyl ether}}{CH_3CH_2—O—CH_2CH_3} + O_2 \xrightarrow{\text{Light}} \underset{\substack{\text{Peroxide of diethyl ether}\\(\text{1-Ethoxy ethyl hydroperoxide})}}{CH_3\overset{OOH}{\overset{|}{C}}H—O—CH_2CH_3}$$

All ethers that have been exposed to atmosphere for any length of time invariably contain peroxides. The boiling point of peroxides is higher than that of ethers. It is left as a residue in the distillation of ether and may cause explosion. For this reason, **ethers should never be evaporated to dryness.** It is always essential to remove the peroxide before distilling the ether. Ether can be freed from peroxide by shaking with ferrous salt solution or distilling with conc. H_2SO_4.

The diethyl ether used in the preparation of Grignard reagents, must be free from the traces of water and alcohol. This is called **Absolute ether** and can be prepared by distillation of ordinary ether from concentrated H_2SO_4 and subsequent storing over metallic sodium.

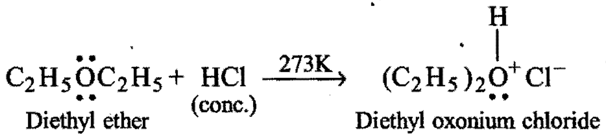
Note: 1. Formation of peroxide can be prevented by adding small amount of Cu_2O to ether.

2. With strong oxidising agents like acid **dichromate**, ethers are oxidised to aldehydes and then to acetic acid.

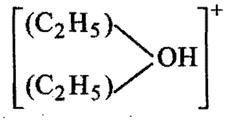
$$\underset{\text{Diethyl ether}}{CH_3CH_2OCH_2CH_3} \xrightarrow{2[O]} \underset{\text{Acetaldehyde}}{2CH_3CHO} + H_2O$$

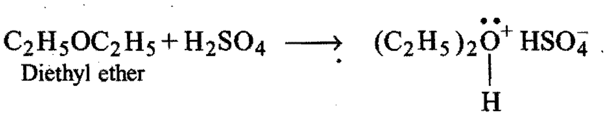
$$\xrightarrow{2[O]} 2CH_3COOH$$

(ii) Salt formation : Due to the presence of lone pair of electrons on oxygen atom, ether behaves as **Bronsted-Lowry base** or **Lewis base** and forms stable **oxonium salts** with concentrated mineral acids at low temperature.



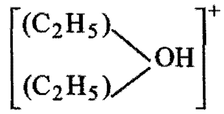
$$\underset{\text{Diethyl ether}}{C_2H_5\ddot{\underset{\cdot\cdot}{O}}C_2H_5} + \underset{\text{(conc.)}}{HCl} \xrightarrow{273K} \underset{\text{Diethyl oxonium chloride}}{(C_2H_5)_2\overset{H}{\ddot{O}}{}^+Cl^-}$$

or  Cl^- or $[(C_2H_5)_2O\cdot H]^+Cl^-$

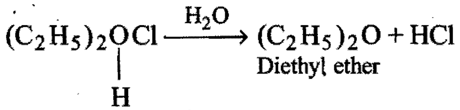


$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5 + H_2SO_4} \longrightarrow (C_2H_5)_2\underset{H}{\ddot{O}}{}^+HSO_4^-$$

Diethyl oxonium hydrogen sulphate

or  HSO_4^- or $[(C_2H_5)_2O\cdot H]^+HSO_4^-$

The oxonium salts are soluble in acid solution and ethers can be recovered from the oxonium salts by treatment with water.



$$\underset{\text{Oxonium salt}}{(C_2H_5)_2\underset{H}{O}Cl} \xrightarrow{H_2O} \underset{\text{Diethyl ether}}{(C_2H_5)_2O} + HCl$$

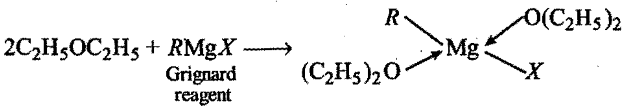
Note : 1. The formation of oxonium salts is similar to the formation of ammonium salts from ammonia and acids.

2. Ether is removed from alkyl halides by shaking with conc. H_2SO_4.

3. Ethers can be distinguished from alkanes with the help of this reaction.

4. Ethers can form coordination complexes with Lewis acids like BF_3, $AlCl_3$, $RMgX$, etc. As the ether (having lone pair of electrons) are **Lewis bases,** they easily coordinate to form complexes known as **etherates.**

$$C_2H_5\ddot{\underset{\cdot\cdot}{O}}C_2H_5 + \underset{\text{Lewis acid}}{BF_3} \longrightarrow \underset{\text{Boron trifluoride etherate}}{(C_2H_5)_2\ddot{O} \longrightarrow BF_3}$$



It is for this reason that ethers are used as solvents for Grignard reagents. That is why Grignard reagents are usually prepared in ethers.

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3. Reactions Involving Cleavage of Carbon-Oxygen Bond

(i) Hydrolysis : When heated with dilute sulphuric acid under pressure ethers are hydrolysed to the corresponding alcohols.

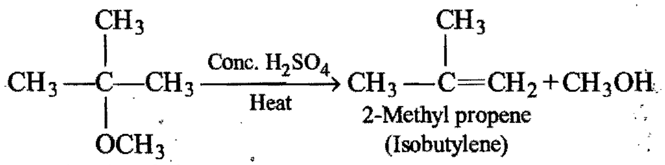
$$ROR + H_2O \xrightarrow[\text{Heat}]{\text{Dil. } H_2SO_4} 2ROH$$

$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2O \xrightarrow[\text{Heat}]{\text{Dil. } H_2SO_4} \underset{\text{Ethanol}}{2C_2H_5OH}$$

(ii) Action of conc. H_2SO_4 : When warmed with concentrated sulphuric acid, ethers form alcohol and alkyl hydrogen sulphate. The final product is alkyl hydrogen sulphate.

$$C_2H_5OC_2H_5 + H_2SO_4 \xrightarrow{\text{Heat}} C_2H_5OH + C_2H_5HSO_4$$
$$C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5HSO_4 + H_2O$$
$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + 2H_2SO_4 \xrightarrow{\text{Heat}} \underset{\text{Ethyl hydrogen sulphate}}{2C_2H_5HSO_4} + H_2O$$

The secondary and tertiary ethers, however, form alkenes with conc. H_2SO_4.



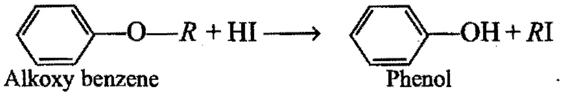
Tert. butyl methyl ether

(iii) Action of hydroiodic acid : Ethers are readily attacked by conc. HI and decomposed into RI. The etheral linkage is broken and the products formed depend on the temperature of the reaction.

(a) With cold HI a mixture of alkyl iodide and alcohol are formed. In the case of mixed ethers, the halogen atom attaches to a smaller and less complex alkyl group.

$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + HI \xrightarrow{\text{Cold}} \underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

$$\underset{\text{Ethyl methyl ether}}{CH_3OC_2H_5} + HI \xrightarrow{\text{Cold}} \underset{\text{Methyl iodide}}{CH_3I} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$



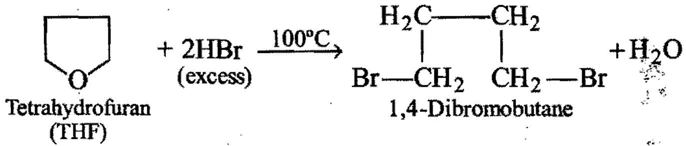
Note : The same reactions are observed with HBr and HCl. The order of reactivity of halogen acids is HI > HBr > HCl.

(b) When heated with excess of HI, only alkyl iodides are formed.

$$C_2H_5OC_2H_5 + \underset{\text{Excess}}{2HI} \xrightarrow[100°C]{\text{Heat}} \underset{\text{Ethyl iodide}}{2C_2H_5I} + H_2O$$

$$R—O—R' + 2HI \xrightarrow{\text{Heat}} RI + R'I + H_2O$$

Similarly, cyclic ethers are readily cleaved by HBr or HI to form dihaloalkanes.

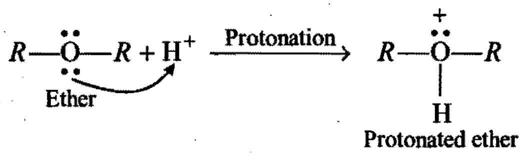


Mechanism : The mechanism of fission of ethers by halogen acids occur through:

(a) S_N2 mechanism:

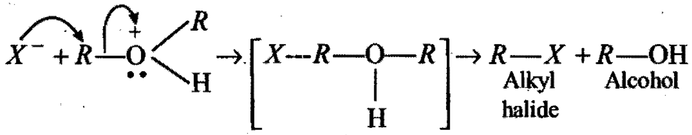
(i) The ether molecule gets protonated by the hydrogen of the acid to form protonated ether or oxonium salt.

$$HX \rightleftharpoons H^+ + X^-$$



$$\underset{\text{Ether}}{R-\ddot{O}-R}+H^+\xrightarrow{\text{Protonation}}\underset{\text{Protonated ether}}{R-\underset{\underset{H}{|}}{\overset{+}{\ddot{O}}}-R}$$

(ii) The protonated ether undergoes nucleophilic attack by halide ion (X^-) and forms alkyl alcohol and alkyl halide.

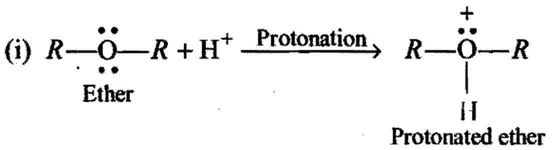


$$X^-+R-\overset{+}{\ddot{O}}\langle^{R}_{H}\rightarrow\left[X\cdots R-\underset{\underset{H}{|}}{O}-R\right]\rightarrow\underset{\text{Alkyl halide}}{R-X}+\underset{\text{Alcohol}}{R-OH}$$

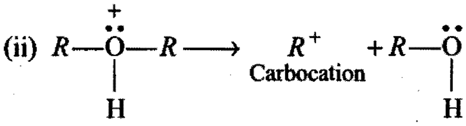
Transition stage

The reactivity through this mechanism is controlled by *steric factors.*

(b) S_N1 mechanism:



$$\text{(i) }\underset{\text{Ether}}{R-\ddot{O}-R}+H^+\xrightarrow{\text{Protonation}}\underset{\text{Protonated ether}}{R-\underset{\underset{H}{|}}{\overset{+}{\ddot{O}}}-R}$$



$$\text{(ii) }R-\underset{\underset{H}{|}}{\overset{+}{\ddot{O}}}-R\longrightarrow\underset{\text{Carbocation}}{R^+}+R-\underset{\underset{H}{|}}{\ddot{O}}:$$

(iii) $R^+ + X^- \longrightarrow R-X$

The reactivity through this mechanism is controlled by the *stability of intermediate carbocation.*

Site of cleavage : In case of **unsymmetrical ethers,** the site of cleavage depends on the nature of alkyl groups. For example,

$$\text{(a) }\underset{\text{Ethyl methyl ether}}{C_2H_5-O-CH_3}+HI\xrightarrow{373K}\underset{\text{Methyl iodide}}{CH_3I}+\underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

The alkyl halide is always formed from the smaller alkyl group (primary or secondary).

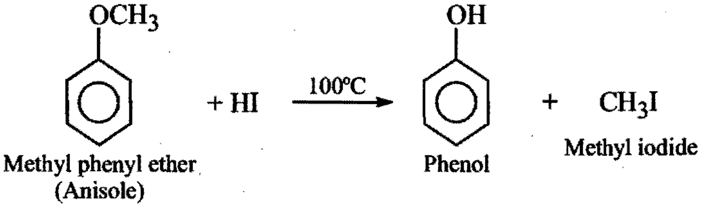
$$\underset{\text{Methyl isopropyl ether}}{CH_3-O-CH(CH_3)_2}+HI\xrightarrow{373K}\underset{\text{Methyl iodide}}{CH_3I}+\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH}$$

The cleavage of such ethers occurs by S_N2 mechanism and the formation of the product is controlled by **steric factors.**

$$\text{(b) }\underset{\textit{Tert.}\text{ butyl methyl ether}}{CH_3-O-C(CH_3)_3}+HI\xrightarrow{373K}\underset{\textit{Tert.}\text{ butyl iodide}}{(CH_3)_3C-I}+\underset{\text{Methyl alcohol}}{CH_3OH}$$

The alkyl halide is formed from the tertiary alkyl group and the cleavage of such ethers occurs by S_N1 mechanism as the product is controlled by the formation of more stable intermediate tertiary carbocation from the protonated ether.

(c) In case of alkyl aryl ethers (phenolic ethers), the products formed are always phenol and an alkyl halide and not the aryl halide and an alcohol.



Methyl phenyl ether (Anisole) Phenol Methyl iodide

This is due to the steric hindrance of larger alkyl group, the halide ion attacks the smaller alkyl group.

Diphenyl ethers are not cleaved by HI even at high temperature.

The importance of this reaction (action of HI with ethers) forms the basis of **Zeisel method** for the estimation of alkoxy groups (—OR) such as methoxy (—OCH_3) and ethoxy (—OC_2H_5) groups in ethers.

$$R-O-R+2HI\longrightarrow 2RI+H_2O$$

The alkyl iodide so formed is absorbed in ethanolic silver nitrate solution to form silver iodide. From the weight of silver iodide formed, the number of alkoxy groups can be determined.

(iv) Action of PCl_5 : On heating with PCl_5, alkyl chlorides are formed. There is no reaction in cold.

$$R-O-R+PCl_5\xrightarrow{\text{Heat}}2RCl+POCl_3$$

$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5}+PCl_5\xrightarrow{\text{Heat}}\underset{\text{Ethyl chloride}}{2C_2H_5Cl}+POCl_3$$

(v) Reaction with acetyl chloride : Ethers when heated with acetyl chloride in the presence of anhydrous zinc chloride or $AlCl_3$ to form alkyl halide and ester.

$$CH_3CO\boxed{Cl+C_2H_5}OC_2H_5\xrightarrow[\text{Heat}]{ZnCl_2}C_2H_5Cl+CH_3COOC_2H_5$$

Acetyl chloride Diethyl ether Ethyl chloride Ethyl acetate

With **acid anhydride,** esters are formed in presence of $ZnCl_2$.

$$CH_3CO\cdot\boxed{OOCCH_3+C_2H_5\cdot}OC_2H_5\xrightarrow[\text{Heat}]{ZnCl_2}2CH_3COOC_2H_5$$

Acetic anhydride Diethyl ether Ethyl acetate

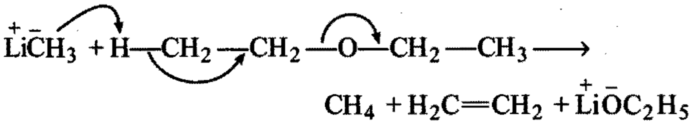
(vi) Dehydration : When ether vapours are passed over heated alumina, dehydration of ethers occur to form alkenes.

$$C_2H_5OC_2H_5\xrightarrow[300°C]{Al_2O_3}2H_2C=CH_2+H_2O$$

(vii) Reaction with carbon monoxide : Under suitable conditions ethers react with carbon monoxide to form esters.

$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + CO \xrightarrow[500\text{ atm}]{BF_3/150°C} \underset{\text{Ethyl propionate}}{C_2H_5COOC_2H_5}$$

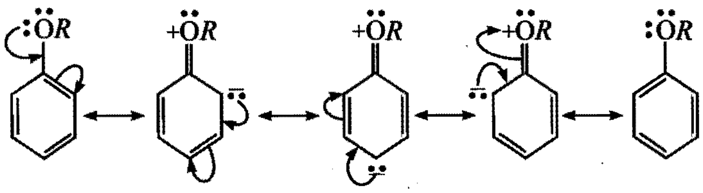
(viii) Action of bases : Unlike alcohols, the ethers are not acidic under ordinary conditions. However, they undergo some unusual cleavage reactions with strong bases such as methyl lithium.



$$\overset{+}{Li}\overset{-}{C}H_3 + H—CH_2—CH_2—O—CH_2—CH_3 \longrightarrow CH_4 + H_2C{=}CH_2 + \overset{+}{Li}\overset{-}{O}C_2H_5$$

Ring substitution in aromatic ethers

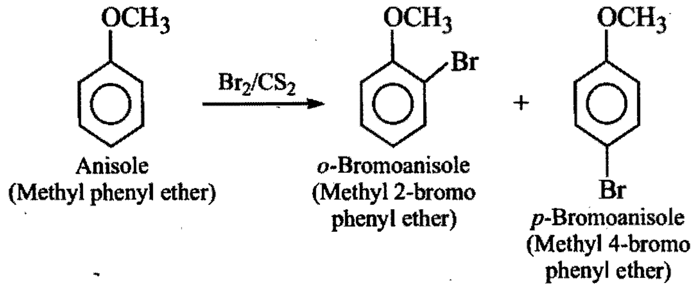
Like phenols, the alkoxy group (—O*R*) in aromatic ethers is *ortho* and *para* directing and activates the ring towards electrophilic substitution reactions.

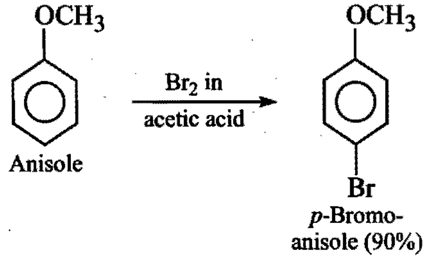


Resonating structures of alkoxybenzene

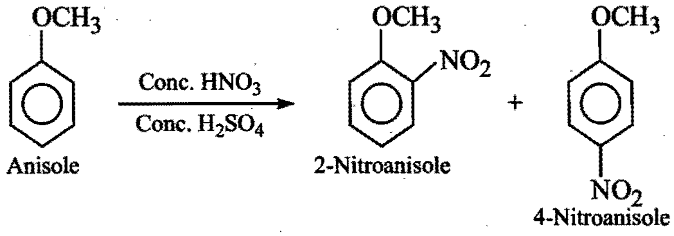
Examples are:

(i) Halogenation:

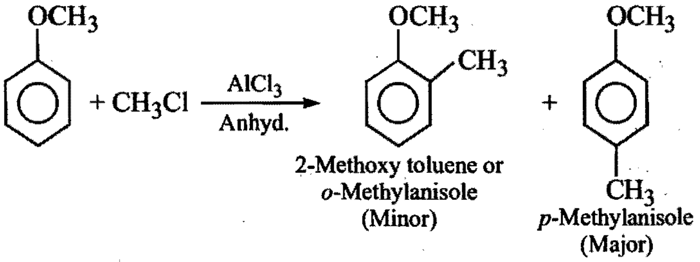


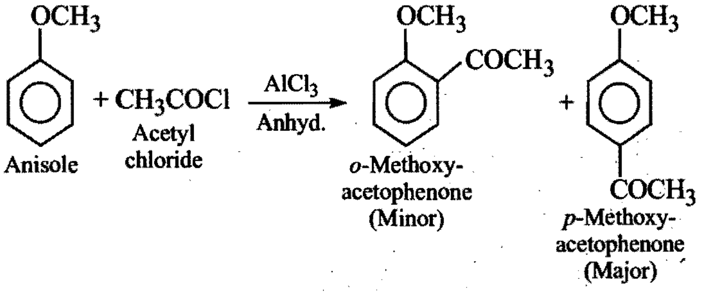


(ii) Nitration:



(iii) Friedel-Crafts reaction:





It may, however, be noted that aromatic ethers are relatively less reactive towards electrophilic ring substitution than phenols.

10.6 DIETHYL ETHER OR ETHOXY ETHANE ($C_2H_5OC_2H_5$)

Diethyl ether is the most important and useful member of ether series. It is simply known as ether. It is technically called as sulphuric ether. It can be prepared by the application of first three general methods of preparation of ethers.

Laboratory preparation : The ether is prepared in the laboratory by heating excess of ethanol with concentrated sulphuric acid at 140°C. The reaction proceeds in two steps.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{(conc.)}}{H_2SO_4} \xrightarrow{110°C} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 + C_2H_5OH \xrightarrow{140°C} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2SO_4$$

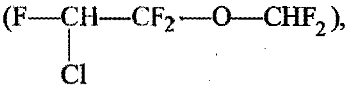
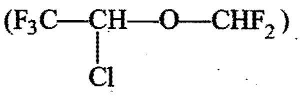
The sulphuric acid acts as a catalyst and is not used up in the reaction. Thus, theoretically a small amount of sulphuric acid should be sufficient for the conversion of large amounts of alcohol to ether.

This method is termed as **continuous etherification process** and the pure ether collected at 34-35°C is called **absolute ether.**

Uses : (i) Diethyl ether is used as an excellent solvent in laboratory and industry. It acts as a solvent for oils, fats, waxes, plastics and lacquers.

(ii) Since, water is immiscible with ether, the ether is used as a solvent for the extraction of various organic compounds.

(iii) Diethyl ether provides an inert medium for various organic reactions such as Wurtz reaction or preparation of Grignard reagents.

(iv) It is used as an inhalation anaesthetic because it produces unconsciousness without affecting lungs and heart. More recently, **Ethrane**  $\mathrm{(F{-}\underset{\substack{|\\Cl}}{CH}{-}CF_2{-}O{-}CHF_2)}$, **isoflurane**  $\mathrm{(F_3C{-}\underset{\substack{|\\Cl}}{CH}{-}O{-}CHF_2)}$ and **halothane** ($CF_3CHClBr$) has largely replaced ether as they are less hazardous and more rapid in action.

(v) The mixture of alcohol and ether is used as a substitute of petrol under the trade name **natalite.**

(vi) It is used as a refrigerant as on evaporation it produces cooling. A mixture of ether and dry ice (solid CO_2) gives a temperature as low as −110°C.

(vii) It is used in the production of smokeless powders. It is also used in perfumery.

Note: The ether containing the impurity of ether peroxide cannot be used as an anaesthetic. The presence of ether peroxide can be tested with the help of potassium iodide. Iodine is liberated when potassium iodide is added to ether containing peroxide impurity. Pure ether does not liberate iodine from potassium iodide.
The presence of peroxide in ether can also be detected by the development of red colour when ether is shaken with a mixture of ferrous ammonium sulphate and potassium thiocyanate (KCNS).

$$\begin{tikzcd}
Fe^{2+} + \text{Ether peroxide} \arrow[r] & Fe^{3+} + \text{ether} \arrow[d, "SCN^-"] \\
 & Fe(SCN)_3 \text{ red colour}
\end{tikzcd}$$

Comparison of Ethyl Alcohol and Diethyl Ether

Both ethyl alcohol and diethyl ether are typical members of their series. Ethyl alcohol has —OH group which is reactive while the oxygen ($>C-O-C<$) in ether is comparatively inert. Both may be compared as follows:

Test	Ethyl alcohol	Diethyl ether
1. Physical state	Volatile liquid, boiling point 78.3°C. It is an associated liquid due to hydrogen bonding.	Volatile liquid, boiling point 34.5°C. No hydrogen bonding is present.
2. Odour	Sweet, alcoholic vapours do not bring unconsciousness.	Pleasant, etheral vapours bring unconsciousness.
3. Solubility	Miscible with water.	Immiscible with water.
4. Action of sodium	Hydrogen is evolved.	No reaction.
5. Action of water (hot)	No action.	Hydrolysed to ethyl alcohol.
6. Action of PCl_5	Ethyl chloride is formed.	No action in cold. When heated with PCl_5, it forms ethyl chloride.
7. Action of CH_3COCl	Forms ethyl acetate (Sweet fruity smelling liquid).	No action in cold. On heating forms a mixture of ethyl acetate and ethyl chloride.
8. Action of air	No action.	Forms peroxide.
9. Oxidation	Forms acetaldehyde and acetic acid.	Not easily oxidised. It can also form acetaldehyde and acetic acid with strong oxidising agents.
10. Action of strong acids	Ethyl salts are formed.	Oxonium salts are formed.
11. Action of HI	Forms ethyl iodide in cold.	Forms ethyl iodide and ethyl alcohol in cold. On heating forms only ethyl iodide.
12. Iodine + NaOH (Iodoform test)	Forms yellow crystals of iodoform (CHI_3).	Does not respond to iodoform test.

Note : 1. The above tests (except test No. 12) can also be used to compare alcohols with ethers.
2. Test No. 3, 4, 5, 6 and 12 may be used for distinguishing ethyl alcohol from diethyl ether.

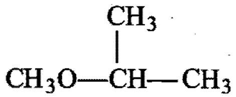
SOME SOLVED PROBLEMS

Problem 1. *Write the structural formulae of all possible ethers having the molecular formula,* $C_4H_{10}O$ *and name them.*

Solution : There are three isomeric ethers of molecular formula, $C_4H_{10}O$.

$CH_3CH_2OCH_2CH_3$,
Diethyl ether
(Ethoxy ethane)

$CH_3OCH_2CH_2CH_3$
Methyl propyl ether
(1-Methoxy propane)



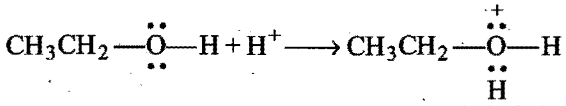
$\mathrm{CH_3O{-}\overset{\substack{CH_3\\|}}{CH}{-}CH_3}$

(2-Methoxy propane)
Methyl isopropyl ether

Problem 2. *Give a mechanism for the acid-catalysed dehydration of ethyl alcohol to form diethyl ether.*

Solution : The following four steps are involved:

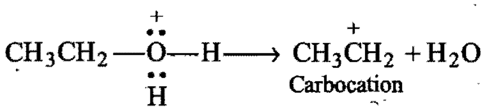
1. Protonation of ethyl alcohol.



$$\mathrm{CH_3CH_2{-}\ddot{\underset{\cdot\cdot}{O}}{-}H + H^+ \longrightarrow CH_3CH_2{-}\overset{+}{\ddot{\underset{\substack{\cdot\cdot\\H}}{O}}}{-}H}$$

Protonated alcohol

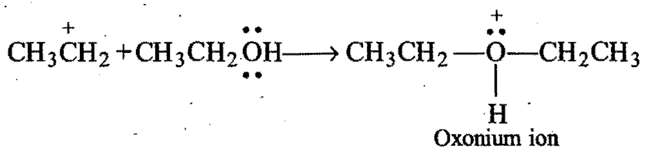
2. Elimination of water molecule to form carbocation.



$$\mathrm{CH_3CH_2{-}\overset{+}{\ddot{\underset{\substack{\cdot\cdot\\H}}{O}}}{-}H \longrightarrow \overset{+}{CH_3CH_2} + H_2O}$$

Carbocation

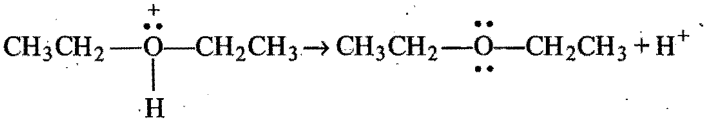
3. Carbocation combines with a molecule of alcohol to form oxonium ion.



$$CH_3\overset{+}{C}H_2 + CH_3CH_2\ddot{O}H \longrightarrow CH_3CH_2-\overset{+}{\ddot{O}}(H)-CH_2CH_3$$

Oxonium ion

4. Oxonium ion loses a proton to yield diethyl ether.



$$CH_3CH_2-\overset{+}{\ddot{O}}(H)-CH_2CH_3 \rightarrow CH_3CH_2-\ddot{O}-CH_2CH_3 + H^+$$

Problem 3. *How will you synthesise an ether from a primary alcohol?*

Solution : (i) $ROH + Na \longrightarrow \underset{\text{Alkoxide}}{RONa}$

(ii) $R'OH + HBr \longrightarrow \underset{\text{Alkyl bromide}}{R'Br} + H_2O$

(iii) $RONa + BrR' \longrightarrow \underset{\text{Ether}}{ROR'} + NaBr$

Problem 4. *How will you synthesise?*

(*a*) *Divinyl ether from ethylene.*
(*b*) *n-Butyl alcohol from ethylene.*
(*c*) *Diethyl ether from ethyl iodide.*
(*d*) *Ethyl methyl ether from methyl iodide.*
(*e*) *Diethyl ether from dimethyl ether.*
(*f*) *Ethyl methyl ether from ethyl alcohol.*

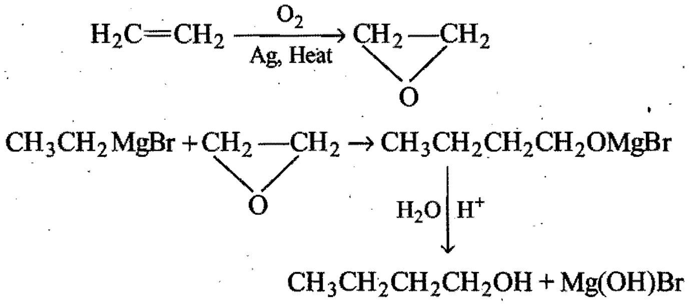
Solution :

(a) $\underset{\text{Ethylene}}{H_2C{=}CH_2} \xrightarrow{HOCl} ClCH_2 \cdot CH_2OH$

$$2ClCH_2CH_2OH \xrightarrow[140°C]{H_2SO_4} ClCH_2CH_2OCH_2CH_2Cl$$

$$\xrightarrow[\text{Heat}]{\text{Alc. KOH}} \underset{\text{Divinyl ether}}{H_2C{=}CH{-}O{-}CH{=}CH_2}$$

(b) $H_2C{=}CH_2 \xrightarrow[\text{(ii) Mg}]{\text{(i) HBr}} CH_3CH_2MgBr$



(c) $CH_3CH_2I \xrightarrow{NaOH(aq.)} CH_3CH_2OH \xrightarrow{Na} CH_3CH_2ONa$

$$CH_3CH_2ONa + ICH_2CH_3 \longrightarrow CH_3CH_2OCH_2CH_3 + NaI$$

(d) $CH_3I \xrightarrow{NaOH(aq.)} CH_3OH \xrightarrow{Na}$

$$CH_3ONa \xrightarrow{ClC_2H_5} CH_3OC_2H_5$$

(e) $CH_3OCH_3 \xrightarrow{HI} CH_3I \xrightarrow[\text{(Wurtz reaction)}]{\text{Na/ether}} CH_3CH_3 \xrightarrow[h\nu]{Cl_2}$

$$CH_3CH_2Cl \xrightarrow[\text{(Dry)}]{Ag_2O} CH_3CH_2-O-CH_2CH_3$$

(f) $CH_3CH_2OH \xrightarrow{Na} CH_3CH_2ONa \xrightarrow{ICH_3} CH_3CH_2OCH_3$

Problem 5. *Explain the following:*

(a) Dimethyl ether has a lower boiling point (–24°C) than ethyl alcohol (78°C) although both have same molecular masses.

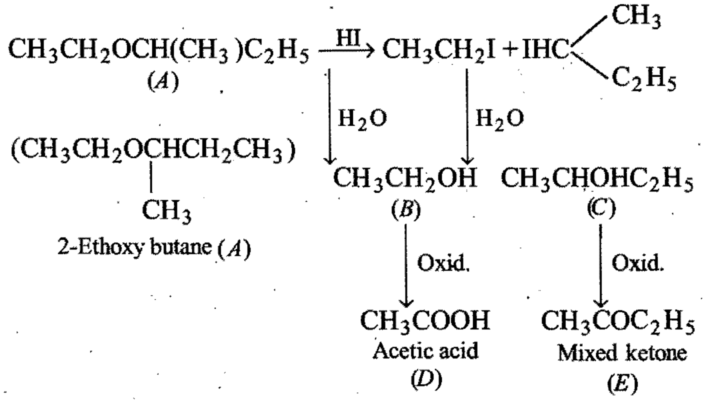
(b) Ethers have low solubility in water but high solubility in conc. H_2SO_4.

Solution : (a) Ethyl alcohol has intermolecular hydrogen bonding whereas no hydrogen bonding is present in dimethyl ether.

(b) The oxygen atom in ethers has two unshared electron pairs and therefore, the oxonium salts are formed with acids. This behaviour is not observed in the case of water. Ethers, therefore, have high solubility in conc. H_2SO_4 and low solubility in water.

Problem 6. *An ether, (A) having molecular formula,* $C_6H_{14}O$, *when treated with excess of HI produced two alkyl iodides which on hydrolysis yield compounds (B) and (C). Oxidation of (B) gives an acid (D), whereas oxidation of (C) results in the formation of a mixed ketone, (E). Give graphic representation of (A) to (E).*

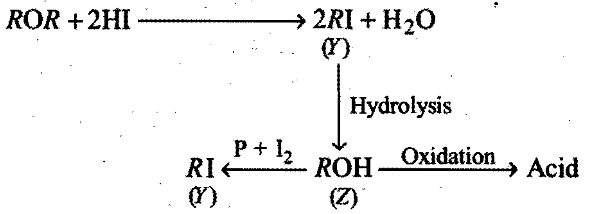
Solution : Both the alkyl halides on hydrolysis form alcohols. The alcohol (*B*) is a primary alcohol as it gives an acid on oxidation while alcohol (*C*) is a secondary alcohol as it gives mixed ketone on oxidation. The ether can be thus formulated as $CH_3CH_2OCH(CH_3)C_2H_5$.



Problem 7. *A compound (X) containing* C, H *and* O *is unreactive towards sodium. It does not add up bromine. It does also not react with Schiff's reagent. On refluxing with excess of* HI, *(X) gives only (Y). (Y) on hydrolysis gives (Z) which can be converted to (Y) by the action of* P *and* I_2. *Compound (Z) on oxidation gives an acid of equivalent mass* 60. *What are (X), (Y) and (Z)?*

Solution : The compound does not react with sodium, thus it is not an alcohol. The compound is saturated as it does not add bromine. It does not react with Schiff's reagent, thus it is not an aldehyde.

The compound with excess of HI forms only iodide. Thus, the compound is symmetrical ether.



$$\begin{tikzcd} ROR + 2HI \arrow[r] & \underset{(Y)}{2RI} + H_2O \arrow[d, "\text{Hydrolysis}"] & \\ \underset{(Y)}{RI} & \underset{(Z)}{ROH} \arrow[l, "P + I_2"'] \arrow[r, "\text{Oxidation}"] & \text{Acid} \end{tikzcd}$$

The acid formed is a monobasic acid. Hence, its molecular mass is 60, *i.e.*,

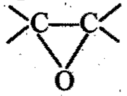
$$R'COOH = R' + 12 + 32 + 1 = 60; \quad R' = 15 = CH_3$$

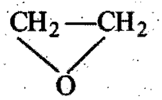
The acid is acetic acid. It is obtained by oxidation of (*Z*), thus (*Z*) is C_2H_5OH (ethyl alcohol) and (*Y*) is C_2H_5I (ethyl iodide). The compound (*X*) is, therefore, $C_2H_5OC_2H_5$ (diethyl ether).

$$C_2H_5OC_2H_5 \xrightarrow{HI} C_2H_5I \xrightarrow{\text{Hydrolysis}} C_2H_5OH \xrightarrow{\text{Oxid.}} CH_3COOH$$

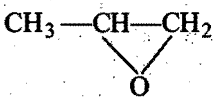
SUPPLEMENTARY READING

10.7 EPOXIDES (OXIRANES)

Epoxides are cyclic ethers in which a three membered,  , ring is present.



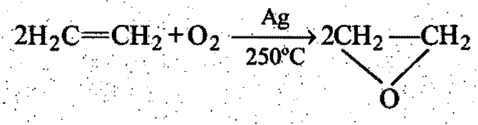
1,2-Epoxy ethane
(Ethylene oxide)



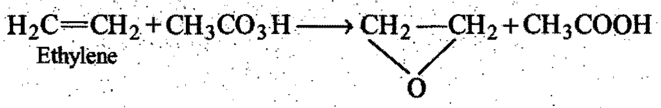
1,2-Epoxy propane
(Propylene oxide)

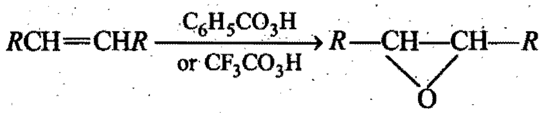
Ethylene oxide (oxirane) is the most important member of this class. It may be prepared,

(i) By oxidation of ethylene with oxygen in presence of silver catalyst.

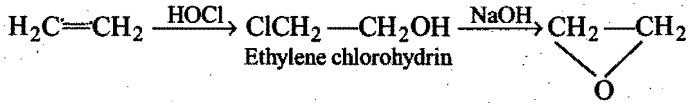


(ii) By oxidation of ethylene with peroxy acid like $CH_3CO_3H, C_6H_5CO_3H$ or CF_3CO_3H.

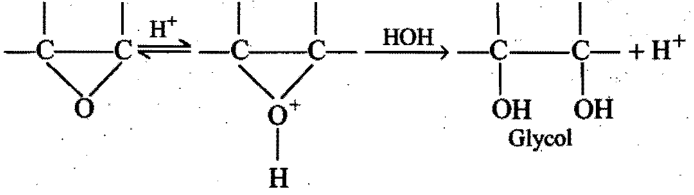




(iii) By treatment of ethylene chlorohydrin with NaOH.

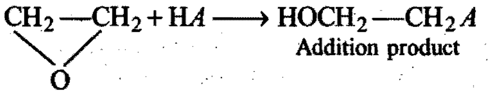


Properties : It is a poisonous, flammable gas. It boils at 14°C. It is a very reactive compound because of its strained configuration. Like other ethers, an epoxide is converted by an acid into protonated epoxide which can then undergo attack by any nucleophilic reagent.

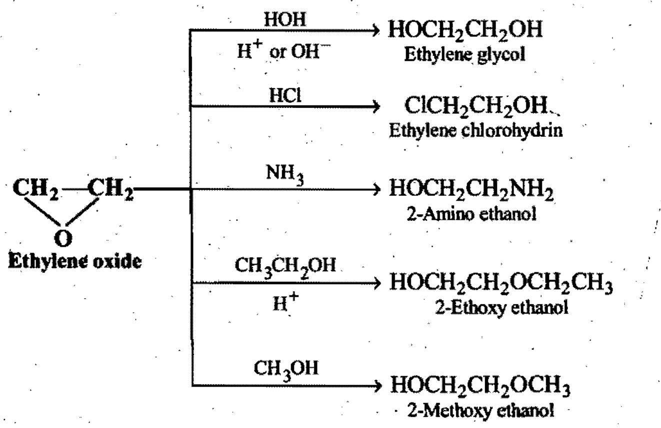


(Protonated epoxide)

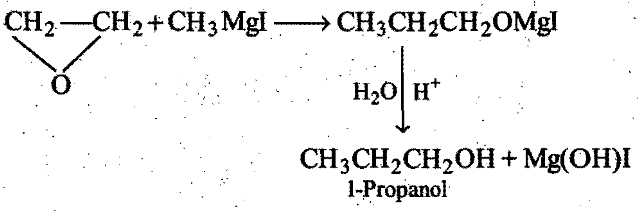
So, it has the tendency to open up the ring, the oxygen combines with the reactive hydrogen of various compounds forming a hydroxy compound.



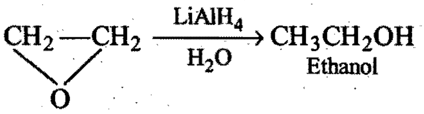
Some of the important reactions are listed below:



Grignard reagents form an addition product which on acid hydrolysis forms a primary alcohol.



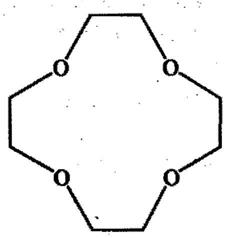
It is reduced by lithium aluminium hydride into ethyl alcohol.



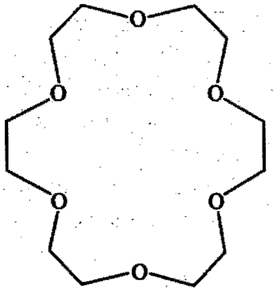
It is used (a) in the manufacture of ethylene glycol, (b) in the manufacture of **Dacron**, (c) in the manufacture of a solvent, ethoxy ethanol used in varnishes and enamels for quick drying.

10.8 CROWN ETHERS

The crown ethers are heterocyclic polyethers usually with at least four oxygen atoms. These are called crown ethers because they have a crown-like shape. Their names consist of two numbers, the first of the two numbers is the total number of atoms in the ring and the second is number of oxygen atoms.



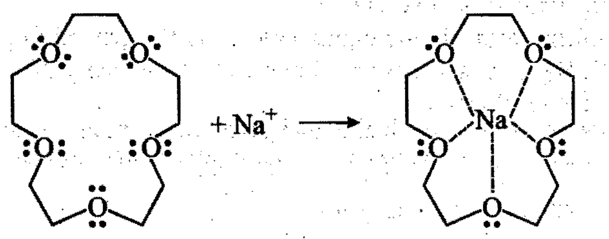
12-Crown-4
(12 atoms including 4 oxygen)



18-Crown-6
(18 atoms including 6 oxygen)

Crown ethers have the ability of forming complexes with positive ions like Na^+, K^+ and Li^+. By this property, ionic compounds can be made to dissolve in non-polar organic solvents having some crown ether.

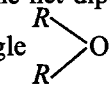
In this reaction, the crown ether is the 'host' and the species it binds is the 'guest' complex (known as **Inclusion compound**).



15-Crown-5
Crown ether
(Host)

Crown ether-sodium
metal ion complex
(Inclusion compound)

IMPORTANT POINTS TO REMEMBER (SUMMARY)

- Ethers are organic compounds which contain one divalent oxygen atom attached to two alkyl groups (same or different), *i.e.*, $R—O—R'$. When both the alkyl groups are same, they are designated as **simple** or **symmetrical ethers** and when both are different, they are called **mixed** or **unsymmetrical ethers.**
- Ethers form a homologous series with the general formula $C_nH_{2n+2}O$ (same as monohydric alcohols), hence both are functional isomers.
- Ethers are alkoxy alkanes and have a bent structure, dipolar in nature. For example, the net dipole moment of diethyl ether is 1.18 and bond angle  $\begin{matrix}R\diagdown\\ \\ R\diagup\end{matrix}\!O$ is 110°.
- Ethers exhibit chain isomerism, functional isomerism and metamerism.

Methods of Preparation

- **By dehydration of alcohols :** When an excess of alcohol is heated at 140°C with conc. H_2SO_4, symmetrical ether is formed **(acid catalysed dehydration).** It is known as Williamson's continuous etherification method. This method is only applicable for dehydration of primary alcohols.
- Dehydration of 1° alcohol is also affected by passing vapours over Al_2O_3 or thoria at 250°C **(catalytic dehydration).**
- If two molecules of different alcohols are used, then a mixture of three ethers is formed.
- **Williamson's synthesis :** It involves the heating of alkyl halides with sodium or potassium alkoxides. This is the best method for preparing simple and mixed ethers.
- For better yield of ethers, the $R—X$ should be 1° ($CH_3 > CH_3CH_2 > CH_3CH_2CH_2$) and $R—O\,Na$ should be 2° or 3°. So, this method is not applicable to 3° RX. 2° and 3° RX readily undergo E_2 elimination in presence of a strong base to form alkenes.
- Aromatic halides cannot be used in Williamson's synthesis because of their low reactivity towards S_N reaction. However, the presence of —I group in *ortho* and *para* positions increases the reactivity.
- **From alkyl halides :** By heating with dry Ag_2O.
- **From alcohols :** By the action of diazomethane (CH_2N_2) on alcohols in presence of catalyst BF_3 or HBF_4, methyl ethers are formed.
- **From Grignard reagents :** By heating with lower halogenated ethers.
- **From alkenes :** By addition of alcohol in presence of acid (H^+). Intermediate is carbocation and in higher cases, there can be 1, 2-hydride or 1, 2-methyl shift to form more stable carbocation.
- **Alkoxy mercuration-demercuration method :** Alkenes readily react with mercuric trifluoroacetate, $Hg(OOCCF_3)_2$ in presence of alcohol followed by reduction with $NaBH_4$ in alkaline medium to yield ethers.
- **Properties :** Dimethyl ether and ethyl methyl ether are gases. Diethyl ether is a volatile liquid, b.pt. is 34.5°C. Ether vapours are highly inflammable and have lower boiling points than the isomeric alcohols because they cannot form hydrogen bonds due to absence of —OH groups. Ethers are sparingly soluble in water (but less than isomeric alcohols) due to the formation of H-bond between water and ethereal oxygen.
- Ethers are relatively inert substances as they do not have any active functional group. They give properties due to alkyl groups, lone pair of electrons on etheral oxygen atom and cleavage of C—O bond.

Reactions due to alkyl groups

- **Halogenation :** On treatment with Cl_2 (or Br_2), in absence of sunlight **(in dark),** the α-hydrogen are initially substituted to give **α-monochloro** or **α, α′-dichloroether.** However, in presence of **sunlight** all the H-atoms of ether (diethyl ether) are substituted to form **perchlorodiethyl ether.**
- **Burning (Combustion) :** Ethers are highly inflammable and form an explosive mixture with air to give CO_2 and H_2O.

Reactions due to etheral oxygen

- **Oxidation and peroxide formation :** Ethers add up atmospheric oxygen or ozonised oxygen to form peroxide in presence of sunlight or in long contact with air and light, peroxide formation takes place.
- The peroxide of diethyl ether is heavy, pungent, oily liquid and decomposes violently on heating. So, ethers are never be distilled (evaporated) to dryness (due to explosive nature).
- Formation of peroxide can be **prevented** by adding small amount of Cu_2O to ether.
- To test the **presence of peroxide** in ether, the sample is treated with $FeSO_4$ as the peroxide oxidises Fe^{2+} to Fe^{3+}, which subsequently gives blood red colour with KCNS due to the formation of $Fe(CNS)_3$.

$$\text{Ether peroxide} \xrightarrow{FeSO_4} \text{Ether} + H_2O_2 \xrightarrow[{[O]}]{Fe^{2+}} Fe^{3+} \xrightarrow{KCNS} \text{Red colour of } Fe(CNS)_3$$

$$\text{or Ether peroxide} \xrightarrow{H_2SO_4} \text{Ether} + H_2O_2 \xrightarrow{KI/Starch} \text{Blue colour}$$

- With **strong oxidising agents** like $K_2Cr_2O_7/H_2SO_4$, ether is oxidised to acetaldehyde and then to acetic acid.

☐ **Action with strong acid (Salt formation) :** Due to the presence of lone pair of electrons on oxygen atom (basic nature of etheral oxygen), ether behaves as **Lewis base** and form stable **oxonium salts** with cold conc. HCl and conc. H_2SO_4.

☐ Ether also forms coordination complexes with BF_3 **(Lewis acid),** Grignard reagent and $AlCl_3$ etc.

Reactions due to cleavage of C—O bond

☐ **Hydrolysis :** Ethers are hydrolysed to alcohols when heated with dil. H_2SO_4 under pressure.

☐ **Action of conc. H_2SO_4 :** On heating with conc. H_2SO_4, ethers form alcohol and finally alkyl hydrogen sulphate.

☐ **Action of HI (or HBr) :** Etheral linkage is broken by HI (or HBr) in cold to give *R*I and *R*—OH. In case of mixed ethers, the halogen atom attaches to a smaller and less complex alkyl group. When heated with excess of HI, only alkyl iodides are formed. Similarly, cyclic ethers are readily cleaved by HBr or HI to form dihaloalkanes.

☐ **Action of PCl_5 :** On heating ethers with PCl_5, alkyl chlorides are formed.

☐ **Dehydration :** On heating ether vapours over Al_2O_3 at 300°C, dehydration occurs to form alkenes.

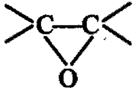
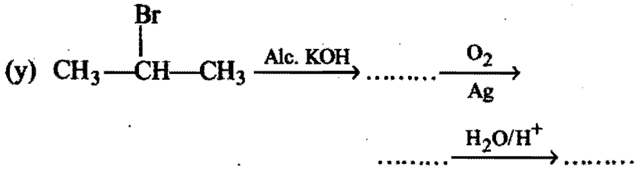
☐ **Reaction with CH_3COCl or $(CH_3CO)_2O$:** On heating ethers with CH_3COCl or $(CH_3CO)_2O$ in presence of anhyd. $ZnCl_2$, esters are formed.

☐ **Reaction with carbon monoxide :** Ethers react with CO in presence of catalyst BF_3 at 150°C under pressure forms ester.

☐ **Uses :** Diethyl ether is used as an excellent solvent for oils, fats, resins and plastic etc. It is also used as an anaesthetic. The mixture of alcohol and ether is used as a substitute of petrol under the name natalite.

QUESTIONS

◆ Very Short Answer Type

1. Fill in the blanks:
   - (a) Aliphatic saturated ethers are regarded as........... derivatives of water.
   - (b) The most common method for preparing ethers is .... synthesis.
   - (c) Sodium metal can be used for...........diethyl ether but not ethyl alcohol.
   - (d) $C_4H_{10}O$ exhibits...........metamers. One of them is diethyl ether, the other two are...........and...........
   - (e) Methyl ethers can be formed by the action of diazomethane on .... in presence of a catalyst boron trifluoride.
   - (f) Ethyl alcohol is isomeric to...........
   - (g) Aliphatic ethers are purified by shaking with a solution of ferrous salt to remove...........which are formed on prolonged standing in contact with air.
   - (h) Ethers form...........salts with concentrated acids at low temperature.
   - (i) Diethyl ether when refluxed with excess of HI gives two molecules of...........
   - (j) Ethers act as Lewis bases due to the presence of .... on oxygen atom.
   - (k) Ether on treatment with excess of chlorine in presence of sunlight forms...........
   - (l) The mixture of alcohol and ether is used as a substitute of petrol under the trade name...........
   - (m) Ethers should never be evaporated to...........because it may cause explosion.
   - (n) Ethers can form...........compounds with Lewis acids like BF_3, $AlCl_3$, $RMgX$, etc.
   - (o) Ethylene oxide on reduction with $LiAlH_4$ forms.........
   - (p) The derivatives having three membered cyclic ring,  , are called...........
   - (q) With PCl_5, ethers form...........
   - (r) When mixed ethers are treated with HI, the iodine atom goes to...........alkyl group.
   - (s) Ethers on hydrolysis with dilute sulphuric acid give ....
   - (t) The IUPAC name of diethyl ether is...........
   - (u) The reactivity of halogen acids with ethers follow the order HI...........HBr...........HCl.
   - (v) Ethers when treated with strong oxidising agents are converted into...........
   - (w) Williamson's synthesis is a........... substitution reaction.
   - (x) .... is used as inert medium in the preparation of Grignard reagents.
   - (y) 

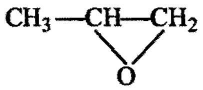
$$CH_3-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_3 \xrightarrow{\text{Alc. KOH}} \ldots\ldots \xrightarrow[\text{Ag}]{O_2} \ldots\ldots \xrightarrow{H_2O/H^+} \ldots\ldots$$

   - (z) Williamson's synthesis involves sodium alkoxide and ....

2. State, whether the following statements are **True** or **False:**
   - (a) Aliphatic saturated ethers have $C_nH_{2n+2}O$ as general formula.
   - (b) Ether is soluble in water.
   - (c) Ethers are not affected by atmosphere.
   - (d) Metamerism is shown by ethers.
   - (e) Ethyl alcohol and dimethyl ether are functional isomers.
   - (f) Diethyl ether gives iodoform test.
   - (g) Dimethyl ether and ethyl alcohol have same boiling points as both have same molecular masses.
   - (h) Ethers can be obtained by dehydration of alcohols.
   - (i) The presence of peroxide in ether can be tested by development of red colour when ether is shaken by a mixture of ferrous ammonium sulphate and KCNS.
   - (j) Pure ether liberates iodine from potassium iodide.
   - (k) Diethyl ether in presence of BF_3 combines with CO at 150°C and 500 atmospheric pressure and forms ethyl propionate.
   - (l) $C_2H_5OC_2H_5$ is a linear molecule having zero dipole moment.
   - (m) Diethyl ether and 1-butanol have the same solubility in water.
   - (n) Ethers form oxonium salts when treated with acids.
   - (o) Dioxane is an example of cyclic ethers.
   - (p) Ethers are less volatile than alcohols.
   - (q) Ethylene oxide is highly reactive because of its strained configuration.
   - (r) 2-Aminoethanol is formed when ethylene oxide combines with ammonia.
   - (s) Ethers are insoluble in conc. H_2SO_4 while alkanes are soluble.
   - (t) Williamson's synthesis of ethers is an example of nucleophilic substitution reaction.
   - (u) Coordination complexes of ethers with Lewis acids are called etherates.
   - (v) Ethers are more polar than the isomeric alcohols.

3. Match the following:

(1) Diethyl ether	(A) Epoxide
(2) Williamson's synthesis	(B) Unsymmetrical ether
(3) Zeisel's method	(C) Anaesthetic
(4) ROR'	(D) Mixture of alcohol and ether

(5) 	(E) Ether + solid CO_2
(6) Natalite	(F) Ethoxy ethane
(7) Halothane	(G) Estimation of alkoxy group
(8) Cooling material	(H) $C_2H_5ONa + C_2H_5Br$
(9) Phenetole	(I) Coordinate complexes
(10) Etherates	(J) Ethoxy benzene

4. Give the common and IUPAC names of the following ethers:
   - (i) $(CH_3)_2CHOCH(CH_3)CH_2CH_3$
   - (ii) $ClCH_2CH_2OCH_3$
   - (iii) $CH_3OCH{=}CH_2$
   - (iv) $p\text{-}NO_2C_6H_5OC_2H_5$
5. What happens when?
   - (a) Ethyl bromide reacts with sodium ethoxide.
   - (b) Ethyl alcohol is heated with conc. H_2SO_4 at 140°C.
   - (c) The vapours of ethyl alcohol are passed over anhydrous alumina at 250°C.
   - (d) Diethyl ether is heated with phosphorus pentachloride.
   - (e) Ethyl iodide is heated with dry silver oxide.
   - (f) Ether is heated with hydroiodic acid.
   - (g) Ether is heated with conc. H_2SO_4.

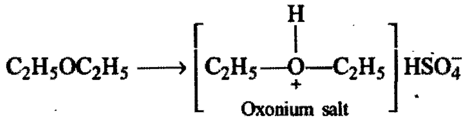
   [See the preparation and properties of diethyl ether.]

❖ Short Answer Type

6. How will you distinguish between?

(i) Diethyl ether and *n*-butane (alkane).

[**Hint:** Diethyl ether dissolves in concentrated H_2SO_4 forming oxonium salt,



$$C_2H_5OC_2H_5 \longrightarrow \left[C_2H_5-\overset{H}{\underset{+}{O}}-C_2H_5\right]HSO_4^- \quad \text{Oxonium salt}$$

n-Butane does not react with H_2SO_4 and thus, two distinct layers are formed when H_2SO_4 is added to *n*-butane.]

(ii) Diethyl ether and but-1-ene (an alkene).

[**Hint:** But-l-ene decolourises alkaline potassium permanganate solution,

$$\underset{\text{But-1-ene}}{CH_3CH_2CH{=}CH_2} + H_2O + [O] \longrightarrow \underset{\text{Butane-1,2-diol}}{CH_3CH_2CHOHCH_2OH}$$

Diethyl ether does not decolourise $KMnO_4$ solution.]

(iii) Diethyl ether and alcohol (primary).

[**Hint:** Ethyl alcohol produces hydrogen (bubbles) when reacted with sodium. Ether does not react with sodium.]

(iv) An ether and alkyl bromide.

[**Hint:** The ether dissolves in conc. H_2SO_4, the halide does not. Alkyl bromide forms a light yellow precipitate of AgBr when treated with alcoholic $AgNO_3$. This test is not given by ether.]

7. Supply structural formulae for missing compounds.

(i) $H_2C{=}CH_2 + (A) \longrightarrow ClCH_2{-}CH_2OH \xrightarrow[140°C]{H_2SO_4} (B) \xrightarrow[\text{Heat}]{\text{Alc. KOH}} (C)$

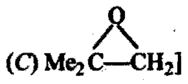
[Ans. (*A*) HOCl; (*B*) $ClCH_2CH_2OCH_2CH_2Cl$; (*C*) $H_2C{=}CHOCH{=}CH_2$]

(ii) $CH_3CHBrCH_3 \xrightarrow{\text{Alc. KOH}} (A) \xrightarrow[\text{Peroxide}]{HBr} (B) \xrightarrow{CH_3ONa} (C)$

[Ans. (*A*) $CH_3CH{=}CH_2$; (*B*) $CH_3CH_2CH_2Br$; (*C*) $CH_3CH_2CH_2OCH_3$]

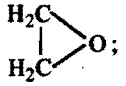
(iii) $Me_3CBr \xrightarrow{\text{Alc. KOH}} (A) \xrightarrow{HOCl} (B) \xrightarrow{NaOH} (C)$

[Ans. (*A*) $Me_2C{=}CH_2$; (*B*) $Me_2C(OH){-}CH_2Cl$;



(vi) $H_2C{=}CH_2 \xrightarrow[\text{(ii) Mg}]{\text{(i) HBr}} (A) \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) }(B)} CH_3CH_2CH_2CH_2OH \xrightarrow{HBr} (C)$

[Ans. (*A*) CH_3CH_2MgBr; (*B*)



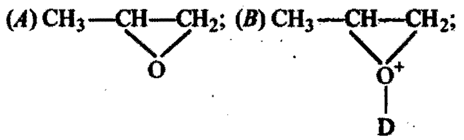
(*C*) $CH_3CH_2CH_2CH_2Br$]

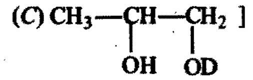
(v) $CH_3CH{=}CH_2 \xrightarrow[H_2SO_4]{H_2O} (A) \xrightarrow{(B)} (C) \xrightarrow{CH_3(CH_2)_3Br} CH_3CH_2CH_2CH_2OCH(CH_3)_2$

[Ans. (*A*) $CH_3CHOHCH_3$; (*B*) Na; (*C*) $(CH_3)_2CHONa$]

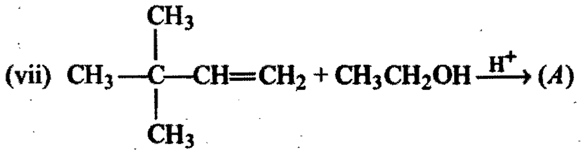
(vi) $CH_3CH{=}CH_2 \xrightarrow{C_6H_5CO_3H} (A) \xrightarrow{D^+} (B) \xrightarrow{H_2O} (C)$

[Ans.

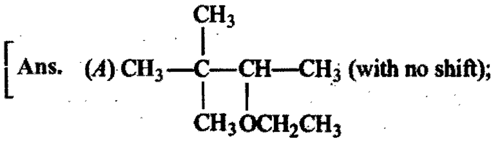




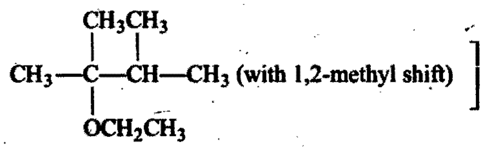
(*C*) $CH_3{-}\underset{OH}{CH}{-}\underset{OD}{CH_2}$]



(vii) $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH{=}CH_2 + CH_3CH_2OH \xrightarrow{H^+} (A)$

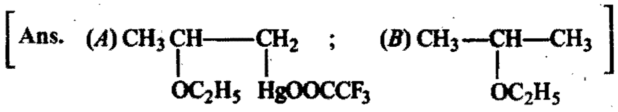


[Ans. (*A*) $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\underset{OCH_2CH_3}{CH}{-}CH_3$ (with no shift);



$CH_3{-}\overset{CH_3}{\underset{OCH_2CH_3}{C}}{-}\overset{CH_3}{CH}{-}CH_3$ (with 1,2-methyl shift)]

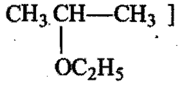
(viii) $CH_3CH{=}CH_2 + C_2H_5OH + Hg(OOCCF_3)_2 \longrightarrow (A) \xrightarrow[OH^-]{NaBH_4} (B)$



[Ans. (*A*) $CH_3\underset{OC_2H_5}{CH}{-}\underset{HgOOCCF_3}{CH_2}$; (*B*) $CH_3{-}\underset{OC_2H_5}{CH}{-}CH_3$]

(ix) $CH_3CH{=}CH_2 + HOC_2H_5 \xrightarrow{H_2SO_4} (A)$

[Ans. (*A*)



$CH_3\underset{\displaystyle OC_2H_5}{\underset{|}{C}H}—CH_3$]

(x) $(CH_3)_2CHOH + CH_2N_2 \xrightarrow{HBF_4} (A)$

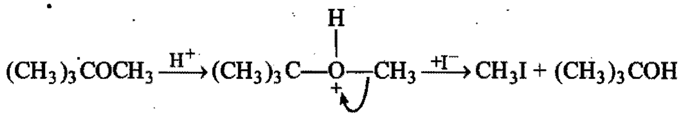
[Ans. (*A*) $(CH_3)_2CH—O—CH_3$]

8. Give reasons for the following:

(i) $(CH_3)_3C—O—CH_3 \xrightarrow[\text{ether}]{\text{Anhydrous HI}} CH_3I + (CH_3)_3COH$

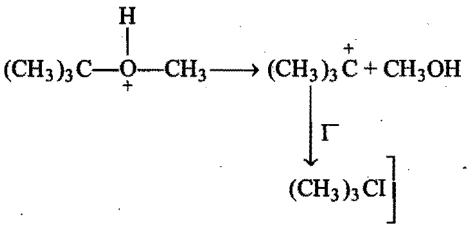
(ii) $(CH_3)_3C—O—CH_3 \xrightarrow{HI\ (aq.)} (CH_3)_3CI + CH_3OH$

[Hint: The products differ on account of solvent. In first case, the solvent (ether) is almost inert and it favours S_N2 route. The nucleophile, I^-, attacks 1° of CH_3.



$$(CH_3)_3COCH_3 \xrightarrow{H^+} (CH_3)_3C—\overset{\displaystyle H}{\underset{+}{\overset{|}{O}}}—CH_3 \xrightarrow{I^-} CH_3I + (CH_3)_3COH$$

In second case, the solvent (water) is highly polar and it favours S_N1 route. I^-, the nucleophile attacks the *tert.* carbocation.



$$(CH_3)_3C—\overset{\displaystyle H}{\underset{+}{\overset{|}{O}}}—CH_3 \longrightarrow (CH_3)_3\overset{+}{C} + CH_3OH$$
$$\downarrow I^-$$
$$(CH_3)_3CI$$]

(iii) Ethers possess a net dipole moment even if they are symmetrical in structure.

(iv) Dimethyl ether is completely miscible with water but diethyl ether is soluble in water to a small extent.

(v) The C—O—C bond angle in ether is higher than H—O—H angle in water though oxygen is sp^3-hybridized in both these cases.

(vi) Why are ethers relatively inert compounds?

9. (a) Discuss the structural relationship of water, alcohol and ethers.

[Hint: Alcohols and ethers may be regarded as derivatives of H—O—H. The replacement of one H atom affords alcohols, *R*OH. In ethers both hydrogen atoms are replaced.]

(b) Compare the bond angles of H—O—H, C—O—H of alcohols and C—O—C of ethers.

[Hint: In all the three cases, oxygen undergoes sp^3-hybridization. When hydrogen is bonded to hybridized orbitals of oxygen, there is contraction in the bond angle, which is 105°. The bond angle is very close to 109° in alcohols. The C—O—C bond angle in ethers is about 110° on account of repulsive van der Waals' forces between groups of larger size.]

(c) What is crown ether? How is it named?

[Hint: The heterocyclic polyether is called crown ether. It is named on the basis of total number of atoms in the ring and number of oxygen atoms. [15] crown-5 means 15 atoms in the ring including 5 oxygen atoms.]

(d) What is absolute ether?

[Hint: Absolute ether means diethyl ether absolutely free from water.]

(e) Compare the following alkyl halides in decreasing order of reactivity in the Williamson's reaction:

$ClCH_2CH_2CH_3 (A)$, $BrCH_2CH_2CH_3 (B)$,
$(CH_3)_3CCH_2Br (C)$, $ClCH_2CH{=}CH_2 (D)$

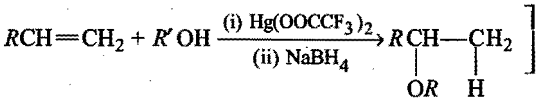
[Hint: $\underset{\text{(Allylic)}}{D} > \underset{\text{(Bromide)}}{B} > \underset{\text{(Chloride)}}{A} > \underset{\text{(Neopentyl)}}{C}$]

(f) Give six types of ethers that cannot be synthesised by the typical Williamson's reaction.

[Hint: (i) $R_3C—O—CR_3$
(ii) $R_2CH—O—CHR_2$
(iii) $R_3C—O—CHR_2$
(iv) Ar—O—Ar
(v) $RCH{=}CH—O—CH{=}CHR'$
(vi) $R_3CCH_2—O—CH_2CR_3$]

(g) Give the general equation for the alkoxy mercuration demercuration reaction of $RCH{=}CH_2$ with $R'OH$.

[Hint:



$$RCH{=}CH_2 + R'OH \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OOCCF}_3)_2} R\underset{\displaystyle OR}{\underset{|}{C}H}—\underset{\displaystyle H}{\underset{|}{C}H_2}$$]

10. Account for the following:

(i) Ethers have significant dipole moments.

[Hint: Ethers are weakly polar. The C—O—C bond angle is about 110° and the two C—O moments do not cancel each other.]

(ii) Ethers have lower boiling points then the corresponding isomeric alcohols but approximately equal to a paraffin with similar molecular mass and structure.

[Hint: *R*OH molecules have strong intermolecular attractive forces because of hydrogen bonding that is absent in ethers having low polarity. Hence, the boiling points of ethers are low.]

(iii) HI is better reagent than HBr for cleavage of ethers.

[Hint: HI is a stronger acid than HBr and thus, oxonium salt is readily formed with greater yields. I^- is also a better nucleophile than Br^- in S_N2 reaction.]

(iv) Why a non-symmetrical ether is not prepared by heating a mixture of *R*OH and *R*′OH in acid?

[Hint: A mixture of three ethers, *R*—O—*R*, *R*′—O—*R*′ and *R*—O—*R*′ is obtained.]

(v) Why is it possible to prepare tertiary butyl ethyl ether in good yield by heating tertiary butanol and ethanol?

[Hint: When one alcohol is 3°, the oxonium ion easily loses water to form carbocation, which is solvated by 2° or 1° alcohol to form mixed ether.

$$Me_3CO\overset{+}{H}_2 \xrightarrow{-H_2O} Me_3\overset{+}{C} \xrightarrow[-H^+]{HOCH_2CH_3} Me_3C—O—CH_2CH_3$$]

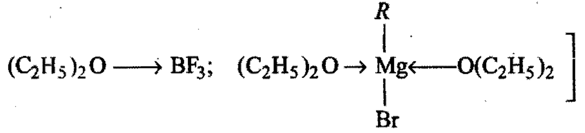
(vi) Ethers are soluble in conc. H_2SO_4 but ethers separate out from the solution on addition of water.

[Hint: Water is a stronger base than ether and removes the proton from R_2OH^+

$$R_2OH^+ + H_2O \longrightarrow R_2O + H_3\overset{+}{O}\ ]$$

(vii) Why is diethyl ether used as a solvent for (i) BF_3 and (ii) RMgBr?

[Hint: Diethyl ether acts as a Lewis base due to presence of lone pairs of electrons on oxygen atom and combines with Lewis acids such as BF_3 and RMgBr through coordination.



$$(C_2H_5)_2O \longrightarrow BF_3;\quad (C_2H_5)_2O \rightarrow \underset{\displaystyle Br}{\overset{\displaystyle R}{Mg}} \leftarrow O(C_2H_5)_2\ ]$$

(viii) Sometimes explosion occurs during distillation of an ether sample.

[Hint: Ethers form peroxide with oxygen. The boiling point of peroxide is higher than that of ether. It is, thus, left as residue in the distillation of ether which is very unstable and decomposes violently on heating.]

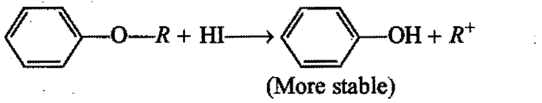
(ix) Why $[(CH_3)_3C]_2O$ cannot be prepared either by Williamson's reaction or by dehydration of tertiary butylalcohol?

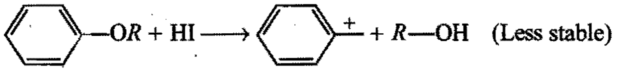
[Hint: The product in both the cases is isobutylene as the *tert.* butyl carbocation eliminates an H^+. The reaction between $(CH_3)_3\overset{+}{C}$ on $(CH_3)_3COH$ to give an ether is sterically hindered.

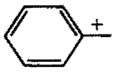
The instability of di-, *tert.*-butyl ether in sulphuric acid may also be due to steric crowding of CH_3 groups.]

(x) Why ArO—R ethers are cleaved with HI to give RI and ArOH rather than ArI and R—OH?

[Hint:





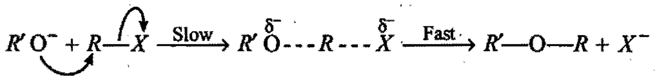
S_N2 attack on a carbon of benzene ring does not occur, nor does the high energy  (phenyl) form by S_N1 reaction. Hence, ArI cannot be formed.]

(xi) Which of the following is the correct method for synthesising methyl *tert.* butyl ether and why?

(a) $(CH_3)_3C—Br + NaOMe \longrightarrow$

(b) $CH_3Br + NaO\text{-}t\text{-}Bu \longrightarrow$

[Hint: The ether formation involves nucleophilic substitution of alkoxide ion for halide ion.



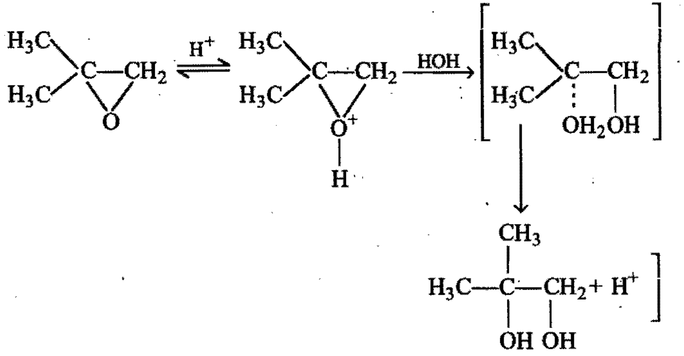
$$R'O^- + R—X \xrightarrow{\text{Slow}} R'\overset{\delta-}{O}\text{---}R\text{---}\overset{\delta-}{X} \xrightarrow{\text{Fast}} R'—O—R + X^-$$

3° alkyl halide can also involve elimination of HX to give alkene in the presence of a base. So, it is better to start with 3° alkoxide and 1° alkyl halide, *i.e.*, equation (b)]

$$\underset{\text{Sodium } tert. \text{ butoxide}}{CH_3Br + NaOC(CH_3)_3} \longrightarrow \underset{\text{Methyl } tert. \text{ butyl ether}}{CH_3—O—C(CH_3)_3} + NaBr$$

(xii) 2,2-Dimethyl oxirane can be cleaved by acid (H^+). Write mechanism. [IIT 1997]

[Hint: The oxirane ring is cleaved *via* S_N2 mechanism.



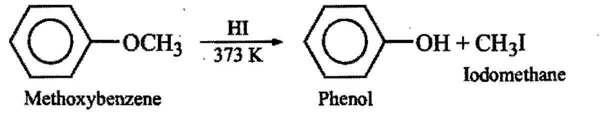
(xiii) Write the equations of the reaction of hydrogen iodide with:

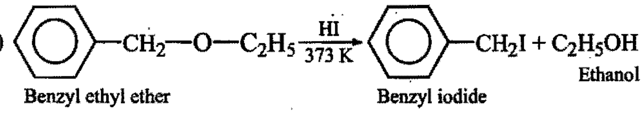
(i) 1-Propoxypropane (ii) Methoxybenzene

(iii) Benzyl ethyl ether

[Hint: (i) $\underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2—O—CH_2CH_2CH_3} \xrightarrow[373K]{HI}$

$$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + \underset{\text{1-Iodopropane}}{CH_3CH_2CH_2I}$$

(ii) 

(iii) 

11. Answer the following:

(i) What is the synthetic utility of the reaction RMgX or RLi with ethylene oxide?

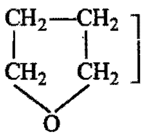
[Hint: It is a good method for extending R group of organometallic by —CH_2CH_2OH in one step.]

(ii) How is di-, *tert.*-butyl ether synthesised?

[Hint: $2Me_3C—Cl \xrightarrow{Ag_2CO_3} Me_3C—O—CMe_3$

However, yield is poor due to steric hindrance.]

(iii) What product is formed when, $HOCH_2CH_2CH_2{\cdot}CH_2OH$ is heated with conc. H_2SO_4?

[Hint: Tetrahydrofuran is formed. ]

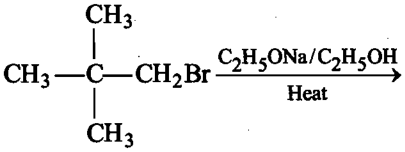
(iv) The following reaction gives two products. Write the structures of the products.

$$(CH_3)_2CH—O—CH_3 \xrightarrow[\text{Heat}]{\text{HI (excess)}}$$

[Hint: The two products obtained are $(CH_3)_2CH—I$ and CH_3I.

In the presence of excess of HI, the initially formed alcohol is also converted to iodide.]

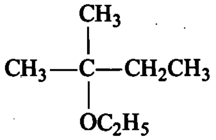
(v) What would be the major product in the following reaction?



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Br \xrightarrow[\text{Heat}]{C_2H_5ONa/C_2H_5OH}$$

[IIT 2000]

[Hint: The product is



$$CH_3-\underset{OC_2H_5}{\overset{CH_3}{C}}-CH_2CH_3$$

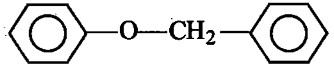
(Ethyl *tert.* pentyl ether)

as the reaction proceeds *via* S_{N^1} mechanism with rearrangement of neopentyl carbocation to *tert.* pentyl carbocation.]

(vi) Sodium metal can be used for drying diethyl ether but not ethanol.

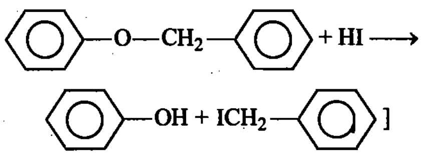
[Hint: Sodium metal reacts with ethanol to form sodium ethoxide. On the contrary, ethers do not have replaceable hydrogen atom and therefore, do not react with sodium.]

(vii) What products are obtained when:



is treated with HI?

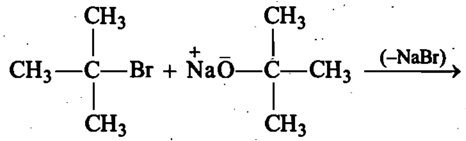
[Hint:



Phenol Benzyl iodide

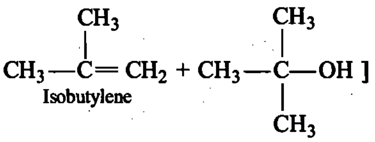
(viii) Di-, *tert.*butyl ether cannot be obtained by Williamson's synthesis.

[Hint: To prepare di-*tert.*butyl ether, the reagents to be used are *tert.*butyl bromide and sodium *tert.*butoxide. Since, the tertiary bromide (3°) prefers to undergo elimination (rather than substitution), therefore, the major product obtained is isobutylene and not di-, *tert.*butyl ether.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + \overset{+}{Na}\bar{O}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{(-NaBr)}$$

Tert. butyl bromide (3°) Sodium *tert.* butoxide



$$CH_3-\overset{CH_3}{C}{=}CH_2 + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH\,]$$

Isobutylene

(ix) A mixture of ethyl alcohol and *n*-propyl alcohol on treatment with conc. H_2SO_4 gives a mixture of three ethers.

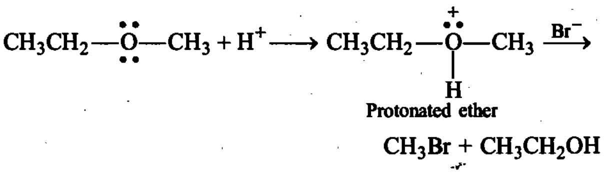
[Hint: The 1° alcohols, *i.e.*, ethyl alcohol and *n*-propyl alcohol (both) yields equally stable carbocations and each one of which can be attacked either by ethyl or *n*-propyl alcohol to give a mixture of three ethers.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + \underset{n\text{-propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow[\text{(Conc.)}]{H_2SO_4} \underset{\text{Diethyl ether}}{(CH_3CH_2)_2O}$$

$$+ \underset{\text{Ethyl-}n\text{-propyl ether}}{CH_3CH_2O-CH_2CH_2CH_3} + \underset{\text{Di-}n\text{-propyl ether}}{(CH_3CH_2CH_2)_2O]}$$

(x) Ethers can be cleaved only by acids and not by bases.

[Hint: The C—$\ddot{O}$—C bond in ethers is very strong. The addition of acid forms protonated ether which is attacked by nucleophiles (Br^- or I^-) on the less hindered alkyl groups to bring the cleavage of ethers to form alkyl halide and an alcohol.

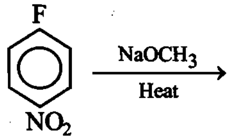


$$CH_3CH_2-\ddot{O}-CH_3 + H^+ \longrightarrow CH_3CH_2-\underset{H}{\overset{+}{O}}-CH_3 \xrightarrow{Br^-} CH_3Br + CH_3CH_2OH$$

Protonated ether

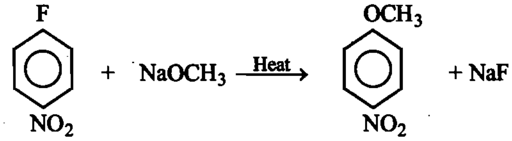
Ethers themselves are Lewis bases and are not attacked by strong bases.]

(xi) Predict the product of the following reaction:



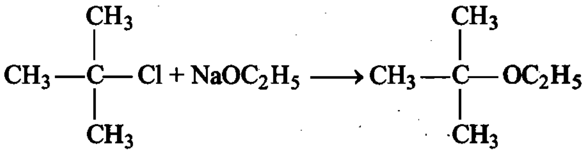
[IIT 2000]

[Hint: As the nitro group is highly deactivating in nature, it will make the cleavage of C—F bond very easy, *i.e.*, F^- ions can be replaced by $-\bar{O}CH_3$ ion.



4-Nitrofluorobenzene 4-Nitroanisole

(xii) The following is not an appropriate reaction for the preparation of *tert.* butyl ethyl ether.



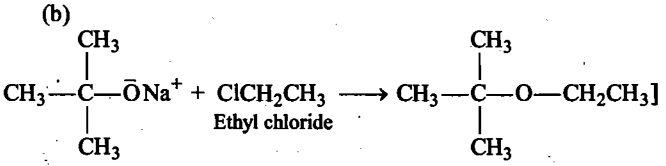
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl + NaOC_2H_5 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OC_2H_5$$

(a) What would be the major product of this reaction?

(b) Write a suitable reaction for the preparation of *tert.* butyl ethyl ether.

[Hint: (a) The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus, elimination reaction predominates over substitution reaction.

(b)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\bar{O}Na^+ + \underset{\text{Ethyl chloride}}{ClCH_2CH_3} \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_2CH_3]$$

Sod. *tert.* butoxide *Tert.* butyl ethyl ether

(xiii) How is 1-propoxypropane synthesized from propan-1-ol? Write mechanism of this reaction.

[**Hint :** The following two methods can be used:

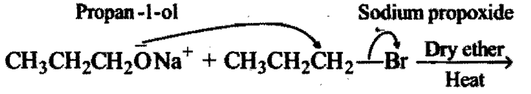
(a) Williamson's synthesis

(i) $3CH_3CH_2CH_2OH + PBr_3 \longrightarrow 3CH_3CH_2CH_2Br + H_3PO_3$

Propan-1-ol → 1-Bromopropane

(ii) $2CH_3CH_2CH_2OH + 2Na \longrightarrow 2CH_3CH_2CH_2ONa + H_2$

Propan-1-ol → Sodium propoxide

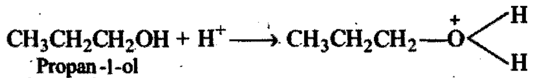


$CH_3CH_2CH_2\bar{O}Na^+ + CH_3CH_2CH_2—Br \xrightarrow[\text{Heat}]{\text{Dry ether}}$

$CH_3CH_2CH_2—O—CH_2CH_2CH_3 + NaBr$

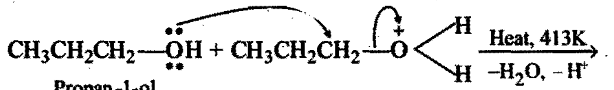
1-Propoxy propane

(b) By dehydration of propan-1-ol with conc. H_2SO_4 at 413 K.



$CH_3CH_2CH_2OH + H^+ \longrightarrow CH_3CH_2CH_2—\overset{+}{O}H_2$

Propan-1-ol; Protonated propan-1-ol



$CH_3CH_2CH_2—\ddot{O}H + CH_3CH_2CH_2—\overset{+}{O}H_2 \xrightarrow[-H_2O,\ -H^+]{\text{Heat, 413K}}$

Propan-1-ol; Protonated propan-1-ol

$CH_3CH_2CH_2—O—CH_2CH_2CH_3$

1-Propoxy propane

12. How would you bring the following conversions?

(i) Ethyl alcohol to diethyl ether.

[**Hint :** Heat ethyl alcohol and conc. H_2SO_4 at 140°C,

or $C_2H_5OH \xrightarrow{Na} C_2H_5ONa$
$C_2H_5OH \xrightarrow{HBr} C_2H_5Br$ $\Big] \longrightarrow C_2H_5OC_2H_5$]

(ii) Diethyl ether to ethyl alcohol.

[**Hint :** $C_2H_5OC_2H_5 \xrightarrow[\text{Heat}]{HI} 2C_2H_5I \xrightarrow{NaOH(aq.)} 2C_2H_5OH$]

(iii) Ethyl iodide to diethyl ether.

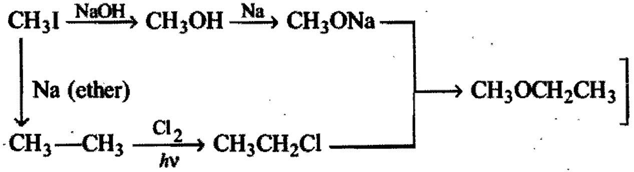
[**Hint :** $C_2H_5I \xrightarrow{NaOH(aq.)} C_2H_5OH \xrightarrow{Na} C_2H_5ONa \xrightarrow{C_2H_5I} C_2H_5OC_2H_5$]

(iv) Diethyl ether to ethyl iodide.

[**Hint :** $C_2H_5OC_2H_5 \xrightarrow[\text{Heat}]{HI} 2C_2H_5I$]

(v) Methyl iodide to methyl ethyl ether.

[**Hint :**



$CH_3I \xrightarrow{NaOH} CH_3OH \xrightarrow{Na} CH_3ONa$

$CH_3I \xrightarrow{\text{Na (ether)}} CH_3—CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2Cl$

$CH_3ONa + CH_3CH_2Cl \longrightarrow CH_3OCH_2CH_3$]

13. Two compounds (*A*) and (*B*) have molecular formula C_2H_6O. On reacting with HI, (*A*) gives alkyl iodide and water while (*B*) gives alkyl iodide and alcohol. What are (*A*) and (*B*)? Write their structures.

[**Ans.** (*A*) C_2H_5OH; (*B*) CH_3OCH_3]

14. Compound (*A*), $C_4H_{10}O$, is found to be soluble in sulphuric acid. (*A*) does not react with sodium or potassium permanganate. When (*A*) is heated with excess of HI, it is converted into a single alkyl halide. What is (*A*)?

[**Ans.** $C_2H_5OC_2H_5$]

15. A neutral compound (*A*) having C, H and O, on refluxing with HI yields methyl iodide and an alkyl iodide (*B*), which contains 74.6 per cent iodine. (*B*) when treated with moist Ag_2O produces a product which undergoes the haloform reaction. Characterize (*A*), what would have been produced if (*B*) were treated with dry Ag_2O?

[**Hint :** (*A*) is neutral and produces alkyl halides on refluxing with HI, hence, it should be an ether.

$$\text{Molecular mass of } (B) = \frac{127 \times 100}{74.6} = 170$$

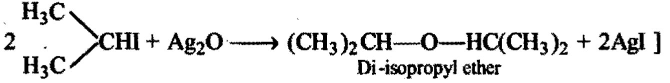
$$RI = 170$$

$$R + 127 = 170$$

$$R = 170 - 127 = 43 = C_3H_7$$

Thus, the alkyl iodide, (*B*), should be isopropyl iodide as the hydrolysis product, (*i.e.*, isopropyl alcohol) undergoes the haloform reaction. (*A*) is methyl isopropyl ether.

The reaction of (*B*) with Ag_2O is,

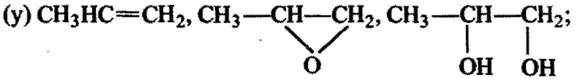


$2(CH_3)_2CHI + Ag_2O \longrightarrow (CH_3)_2CH—O—HC(CH_3)_2 + 2AgI$]

Di-isopropyl ether

ANSWERS

1. (a) Dialkyl; (b) Williamson's; (c) drying; (d) three; methyl propyl ether, methyl isopropyl ether; (e) alcohol; (f) dimethyl ether; (g) peroxide; (h) oxonium; (i) ethyl iodide; (j) lone pairs of electron; (k) $C_2Cl_5OCl_5C_2$, perchlorodiethyl ether; (l) natalite; (m) dryness; (n) coordination; (o) ethyl alcohol; (p) epoxides; (q) alkyl chloride; (r) smaller; (s) alcohols; (t) ethoxy ethane; (u) >, >; (v) aldehydes; (w) nucleophilic; (x) diethyl ether;



(y) $CH_3HC{=}CH_2$, $CH_3—\underset{\diagdown O \diagup}{CH—CH_2}$, $CH_3—\underset{OH}{CH}—\underset{OH}{CH_2}$;

(z) alkyl halide.

2. (a) True; (b) False—insoluble in water; (c) False—all ethers that have been exposed to atmosphere for any length of time invariably contain peroxides; (d) True; (e) True; (f) False—it does not give iodoform test; (g) False—both have different boiling points; (h) True; (i) True; (j) False—does not liberate iodine; (k) True; (l) False—the molecule is not linear, bond angle about 110°. It has dipole moment; (m) False—Butanol-1 has higher solubility as it can form hydrogen bonds with water; (n) True; (o) True; (p) False—more volatile than alcohols; (q) True; (r) True; (s) False—ethers are soluble in conc. H_2SO_4 while alkanes are insoluble; (t) True; (u) True; (v) True.

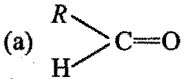
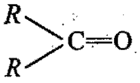
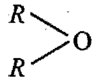
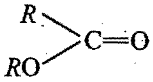
3. (1—F); (2—H); (3—G); (4—B); (5—A); (6—D); (7—C); (8—E); (9—J); (10—I).

4.

	Common names	IUPAC names
(i)	*Sec.* butyl isopropyl ether	2-Isopropoxy butane
(ii)	β-Chloroethyl methyl ether	2-Chloro-1-methoxy ethane
(iii)	Methyl vinyl ether	Methoxy ethene
(iv)	Ethyl *p*-nitrophenyl ether	4-Ethoxy nitrobenzene

OBJECTIVE QUESTIONS

Set I : This set contains questions with single correct answer:

1. Ethers are isomeric with monohydric alcohols. Both have the general formula:
   (a) $C_nH_{2n+2}O$ ☐ (b) $C_nH_{2n}O$ ☐
   (c) $C_nH_{2n+4}O$ ☐ (d) $C_nH_{2n-2}O$ ☐
2. Ether is:
   (a)  ☐ (b)  ☐
   (c)  ☐ (d)  ☐
3. The IUPAC name of $CH_3OC_2H_5$ is:
   (a) ethoxy methane ☐ (b) methoxy ethane ☐
   (c) ethyl methyl ether ☐ (d) methyl ethyl ether ☐
4. An isomer of ethanol is:
   (a) methanol ☐ (b) diethyl ether ☐
   (c) acetone ☐ (d) dimethyl ether ☐
5. $C_4H_{10}O$ is the molecular formula of diethyl ether. The metamers represented by this formula is/are:
   (a) 1 ☐ (b) 2 ☐
   (c) 3 ☐ (d) 4 ☐
6. Diethyl ether may be regarded as an anhydride of:
   (a) C_2H_5OH ☐ (b) C_2H_5COOH ☐
   (c) C_2H_5CHO ☐ (d) $C_2H_5COOC_2H_5$ ☐
7. Heating together sodium ethoxide and ethyl chloride will give:
   (a) ether ☐ (b) ethyl alcohol ☐
   (c) acetaldehyde ☐ (d) acetic acid ☐
8. The reaction,
   $$C_2H_5ONa + C_2H_5I \longrightarrow C_2H_5OC_2H_5 + NaI$$
   is called: **[KCET 2006; CET (Pb) Engg. 2007]**
   (a) Wurtz reaction ☐
   (b) Kolbe's reaction ☐
   (c) Williamson's synthesis ☐
   (d) Grignard synthesis ☐
9. Diethyl ether can be decomposed by heating with:
   (a) water ☐ (b) HI ☐
   (c) NaOH ☐ (d) $KMnO_4$ ☐
10. Diethyl ether on heating with conc. HI gives two moles of:
   (a) ethanol ☐ (b) iodoform ☐
   (c) ethyl iodide ☐ (d) methyl iodide ☐
11. The compound which has the lowest boiling point is:
   (a) H_2O ☐ (b) C_2H_5OH ☐
   (c) CH_3OH ☐ (d) $C_2H_5OC_2H_5$ ☐
12. The product (*D*) in the following sequence of reactions is:
   $$C_2H_4 \xrightarrow{HBr} (A) \xrightarrow{NaOH(aq.)} (B) \xrightarrow{Na} (C) \xrightarrow{CH_3I} (D)$$
   (a) butane ☐ (b) ethane ☐
   (c) propane ☐ (d) ethyl methyl ether ☐
13. Ethers are obtained by reacting alkyl halides with:
   (a) dry Ag_2O ☐ (b) moist Ag_2O ☐
   (c) dry ZnO ☐ (d) moist ZnO ☐
14. Indicate the incorrect statement:
   (a) Diethyl ether is used as anaesthetic ☐
   (b) Diethyl ether is used as a fuel ☐
   (c) Diethyl ether is an inert compound ☐
   (d) Diethyl ether is insoluble in water ☐
15. Ethers are not distilled to dryness for fear of explosion. This is due to formation of:
   (a) oxides ☐ (b) peroxides ☐
   (c) alcohols ☐ (d) ketones ☐
16. Diethyl ether combines with CO under specific conditions to form:
   (a) ethyl propanoate ☐ (b) acetic acid ☐
   (c) carbon dioxide ☐ (d) acetone ☐
17. According to Lewis concept of acids and bases, ethers are:
   (a) neutral ☐ (b) acidic ☐
   (c) basic ☐ (d) amphoteric ☐
18. The mixture of ethanol and sulphuric acid is heated in a closed flask at 140°C. The flask would then contain:
   (a) H_2SO_4 and $C_2H_5OC_2H_5$ only ☐
   (b) H_2O, H_2SO_4 and $C_2H_5HSO_4$ only ☐
   (c) H_2O, $C_2H_5HSO_4$, $C_2H_5OC_2H_5$ and H_2SO_4 only ☐
   (d) H_2O, $C_2H_5OC_2H_5$, $C_2H_5HSO_4$, H_2SO_4 and C_2H_5OH ☐
19. Diethyl ether does not react with:
   (a) sulphuric acid ☐ (b) hydrochloric acid ☐
   (c) hydroiodic acid ☐ (d) acetic acid ☐
20. Oxygen atom of ether is:
   (a) very active ☐ (b) replaceable ☐
   (c) active ☐ (d) comparatively inert ☐
21. The compound which has lowest boiling point among the following is:
   (a) diethyl ether ☐ (b) ethanol ☐
   (c) methanol ☐ (d) water ☐
22. Ethers in contact with air for a long time form peroxides. The presence of peroxide can be tested by adding Fe^{2+} ions, followed by the addition of:
   (a) KCNS ☐ (b) $SnCl_2$ ☐
   (c) $HgCl_2$ ☐ (d) KI ☐
23. When diethyl ether is treated with chlorine in presence of sunlight, it forms:
   (a) C_2H_5Cl ☐ (b) C_2H_6 ☐
   (c) CH_3COCl ☐ (d) $(C_2Cl_5)_2O$ ☐
24. When diethyl ether is heated with excess of sulphuric acid, it forms:
   (a) propionic acid ☐
   (b) acetic acid ☐
   (c) ethyl hydrogen sulphate ☐
   (d) ethyl alcohol ☐

25. The hybrid state of central oxygen atom in diethyl ether is: **[EAMCET (Engg.) 2007]**
(a) sp^2 ☐ (b) sp^3 ☐
(c) sp ☐ (d) sp^3d ☐

26. In ethers, the C—O—C bond angle is:
(a) 110° ☐ (b) 105° ☐
(c) 180° ☐ (d) 120°. ☐

27. Complete combustion of ether gives:
(a) C_2H_5OH ☐ (b) CO_2 and H_2O ☐
(c) C_2H_4 ☐ (d) C_2H_2 ☐

28. Intermolecular hydrogen bonding is not present in:
(a) CH_3COOH ☐ (b) C_2H_5OH ☐
(c) CH_3OCH_3 ☐ (d) $C_2H_5NH_2$ ☐

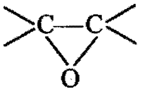
29. Ethoxy ethane does not react with:
(a) HI ☐ (b) conc. H_2SO_4 ☐
(c) PCl_5 ☐ (d) Na ☐

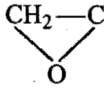
30. Which of the following pairs of reagents will not form ether?
(a) $C_2H_5Br + CH_3COONa$ ☐
(b) $C_2H_5Br + C_2H_5ONa$ ☐
(c) $C_2H_5Br + (CH_3)_2CHONa$ ☐
(d) $(CH_3)_2CHBr + CH_3ONa$ ☐

31. An equimolar quantities of ethanol and propanol are heated with conc. H_2SO_4. The product/s formed is/are:
(a) $C_2H_5OC_2H_5$ ☐ (b) $C_3H_7OC_3H_7$ ☐
(c) $C_2H_5OC_3H_7$ ☐ (d) all of these ☐

32. Crown ethers are:
(a) cyclic ethers ☐
(b) ethers with several other functional groups ☐
(c) mixed ethers ☐
(d) not ethers ☐

33. In [18]-crown-6, the number of oxygen atoms is:
(a) 18 ☐ (b) 6 ☐
(c) 12 ☐ (d) 24 ☐

34. Epoxides are:
(a) unsaturated ethers ☐
(b) mixed ethers ☐
(c) cyclic ethers with  ring ☐
(d) not ethers ☐

35.  $+ LiAlH_4 \longrightarrow (A)$, (A) is:
(a) CH_3CHO ☐ (b) CH_3CH_2OH ☐
(c) $H_2C{=}CH_2$ ☐ (d) $CH_2OH—CH_2OH$ ☐

36. $CH_3MgI + \ldots\ldots\ldots \xrightarrow[H^+]{H_2O}$ 1-Propanol,
the missing reagent is:
(a) HCHO ☐ (b) C_2H_5OH ☐
(c) C_2H_5Cl ☐ (d) ethylene oxide ☐

37. When vapours of alcohol are passed under pressure over heated Al_2O_3 at 250°C, the product obtained is:
(a) dimethyl ether ☐ (b) ethyl methyl ether ☐
(c) diethyl ether ☐ (d) none of these ☐

38. When diethyl ether is treated with chlorine in dark, it forms:
(a) perchloro diethyl ether ☐
(b) ethyl chloride ☐
(c) acetyl chloride ☐
(d) 1,1-dichloro ether ☐

39. Ether form peroxide in contact with air and light and it may cause explosion, since the boiling point of peroxide is:
(a) equal to ether ☐ (b) lower than ether ☐
(c) higher than ether ☐ (d) none of these ☐

40. Formation of peroxide in ether can be prevented by:
(a) adding small amount of Cu_2O ☐
(b) shaking with ferrous salt solution ☐
(c) distilling with conc. H_2SO_4 ☐
(d) all of the above ☐

41. When an ether is treated with P_2S_5, it gives:
(a) thioalcohol ☐ (b) thioether ☐
(c) thioester ☐ (d) thioacetal ☐

42. The boiling point of thioether are.........than those of ethers.
(a) higher ☐ (b) lower ☐
(c) equal ☐ (d) nearly same ☐

43. Sulphuric ether is:
(a) $C_2H_5—O—C_2H_5$ ☐ (b) $CH_3—O—CH_3$ ☐
(c) $C_2H_5—S—C_2H_5$ ☐ (d) $CH_3—S—CH_3$ ☐

44. Ethanol reacts with diazomethane to produce:
(a) $CH_3—O—CH_3$ ☐ (b) $C_2H_5—O—CH_3$ ☐
(c) $C_2H_5—O—C_2H_5$ ☐ (d) none of these ☐

45. Which is correct?
(a) $CH_3—O—C_2H_5 + HI \longrightarrow C_2H_5I + CH_3OH$ ☐
(b) $CH_3—O—C_2H_5 + HI \longrightarrow 2CH_3I + H_2O$ ☐
(c) $CH_3—O—C_2H_5 + HI \longrightarrow 2C_2H_5OH + H_2O$ ☐
(d) $CH_3—O—C_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$ ☐

46. Ether on heating with acetyl chloride in presence of anhydrous $ZnCl_2$ gives:
(a) ethyl alcohol ☐
(b) ethyl chloride ☐
(c) ethyl acetate ☐
(d) ethyl chloride and ethyl acetate ☐

47. An organic compound of molecular formula $C_4H_{10}O$ does not react with sodium. With excess of HI, it gives only one type of alkyl iodide. The compound is: **[SCRA 2001]**
(a) ethoxy ethane ☐ (b) 2-methoxy propane ☐
(c) 1-methoxy propane ☐ (d) 1-butanol ☐

48. In the following reaction, **[PMT 2002]**

$$C_2H_5—O—C_2H_5 + 4H \xrightarrow[HI]{Red\ P} 2X + H_2O,\ X \text{ is:}$$

(a) ethane ☐ (b) ethylene ☐
(c) butane ☐ (d) propane ☐

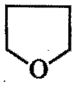
49. The reagent used for the preparation of higher ethers from halogenated ethers is: **[CET (Tamilnadu) 2001]**
(a) conc. H_2SO_4 ☐ (b) sodium alkoxide ☐
(c) dry silveroxide ☐ (d) Grignard reagent ☐

50. Ether which is liquid at room temperature is: **[BV (Pune) 2002]**
(a) $C_2H_5—O—CH_3$ ☐ (b) $CH_3—O—CH_3$ ☐
(c) $C_2H_5—O—C_2H_5$ ☐ (d) none of these ☐

51. Ethyl phenyl ether on boiling with conc. HBr gives:
(a) phenol and ethane ☐
(b) bromobenzene and ethane ☐
(c) phenol and ethyl bromide ☐
(d) bromobenzene and ethanol ☐

52. Which of the following will not give anisole?
(a) Phenol is reacted with dimethyl sulphate in presence of a base ☐
(b) Sodium phenoxide is treated with methyl iodide ☐
(c) Diazomethane is reacted with phenol ☐
(d) Methyl magnesium iodide is treated with phenol ☐

53. Anisole on treatment with Br_2/CS_2 gives:
(a) bromobenzene ☐
(b) methyl-2-bromophenyl ether ☐
(c) *o*- and *p*-bromoanisole ☐
(d) phenol ☐

54. Which of the following is not cleaved by HI even at 525K?
(a) $C_6H_5—O—CH_3$ ☐ (b) $C_6H_5—O—C_6H_5$ ☐
(c) $C_6H_5OC_3H_7$ ☐ (d)  ☐

55. Epichlorohydrin is:
(a) 3-chloropropane ☐
(b) 3-chloropropan-l-ol ☐
(c) 2-chloromethyloxirane ☐
(d) none of the above ☐

56. Which of the following compounds is resistant to nucleophilic attack by OH^- ions?
(a) Methyl acetate ☐ (b) Acetonitrile ☐
(c) Acetamide ☐ (d) Diethyl ether ☐

57. In Williamson's synthesis, ethoxy ethane is prepared by: **[BHU 2005; UGET (Med.) 2007]**
(a) passing ethanol over heated alumina ☐
(b) heating ethanol with dry Ag_2O ☐
(c) heating sodium ethoxide with ethyl bromide ☐
(d) treating ethyl alcohol with excess of H_2SO_4 at 430-440 K ☐

58. Tertiary butyl methyl ether on heating with HI of one molar concentration gives: **[UGET (Med.) 2008; BVP (Med.) 2008]**
(a) $CH_3OH + (CH_3)_3C—Cl$ ☐
(b) $CH_3I + (CH_3)_3C—OH$ ☐
(c) $CH_3I + (CH_3)_3C—Cl$ ☐
(d) none of the above ☐

59. An organic compound (*A*) reacts with sodium metal to form (*B*). On heating with conc. H_2SO_4, (*A*) and (*B*) give diethyl ether. Compounds (*A*) and (*B*) are respectively:
(a) $C_2H_5OH + C_2H_5ONa$ ☐
(b) C_3H_7OH and C_3H_7ONa ☐
(c) $CH_3OH + CH_3ONa$ ☐
(d) C_4H_9OH and C_4H_9ONa ☐

60. The products formed when diethyl ether is reacted with cold HI are: **[EAMCET 2002]**
(a) $C_2H_5I + C_2H_5OH$ ☐ (b) $2C_2H_5I + H_2O$ ☐
(c) $2C_2H_5OH$ ☐ (d) $C_2H_5—O—O—C_2H_5$ ☐

61. Excess of ethanol when heated with conc. H_2SO_4 at 140°C, the compound obtained is: **[AFMC 2002]**
(a) ethene ☐
(b) diethyl sulphate ☐
(c) ethoxy ethane ☐
(d) ethyl hydrogen sulphate ☐

62. Which of the following will be obtained by keeping ether in contact with air for a long time? **[PET (Raj) 2003]**
(a) $C_2H_5—O—CH(CH_3)—O—OH$ ☐
(b) $C_2H_5—O—CH_3OH$ ☐
(c) $C_2H_5—O—C_2H_5OH$ ☐
(d) $CH_3—O—CH(CH_3)—O—OH$ ☐

63. Anisole can be prepared by the action of methyl iodide on sodium phenolate. The reaction is called: **[CET (Karnataka) 2008]**
(a) Williamson reaction ☐ (b) Fittig reaction ☐
(c) Wurtz reaction ☐ (d) Etard reaction ☐

64. In the reaction,

$$C_2H_5—O—C_2H_5 + CO \xrightarrow[150°C,\ 500\ atm.\ press.]{BF_3} (X)$$

What is (*X*)? **[EAMCET 2003]**
(a) Diethyl carbonate ☐ (b) Ethyl carbonate ☐
(c) Diethyl peroxide ☐ (d) Ethyl propionate ☐

65. An ether is more volatile than an alcohol having the same molecular formula. This is due to: **[AIEEE 2003]**
(a) dipolar character of ethers ☐
(b) alcohols having resonance structures ☐
(c) intermolecular hydrogen bonding in ethers ☐
(d) intermolecular hydrogen bonding in alcohols ☐

66. $CH_3CH_2OCH_2CH_3$ reacts with hot and excess HI, then formed product is: **[PMT (Punjab) 2005]**
(a) CH_3CH_2I and CH_3CH_2OH ☐
(b) CH_3CH_2OH ☐
(c) CH_3CH_2I ☐
(d) none of the above ☐

67. Methyl phenyl ether can be obtained by reacting: **[CET (J & K) 2005]**
(a) phenolate ions and methyl iodide ☐
(b) methoxide ion and bromobenzene ☐
(c) methanol and phenol ☐
(d) bromobenzene and methyl bromide ☐

68. The major organic product in the reaction,

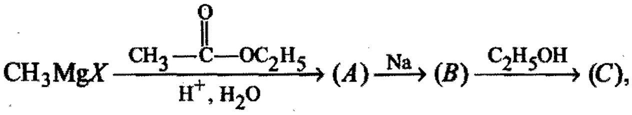
$$CH_3—O—CH(CH_3)_2 + HI \longrightarrow \text{Product, is:}$$

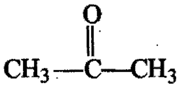
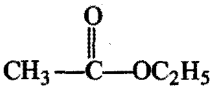
[CBSE (Med.) 2006]
(a) $CH_3OH + (CH_3)_2CHI$ ☐
(b) $CH_3I + (CH_3)_2CHOH$ ☐

(c) $ICH_2OCH(CH_3)_2$ ☐
(d) 
$CH_3O\underset{\underset{I}{|}}{C}(CH_3)_2$ ☐

69. State the product formed during the reaction between sodium phenoxide and ethyl iodide on heating: **[CET (Gujarat) 2006]**
(a) benzyl alcohol ☐ (b) phenol ☐
(c) phenetole ☐ (d) none of these ☐

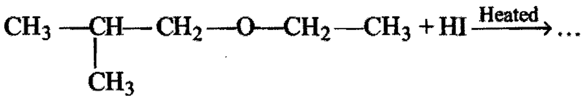
70. In which of the following reactions, ethyl chloride is not formed? **[EAMCET (Med.) 2006]**
(a) $C_2H_5OC_2H_5 + PCl_5 \xrightarrow{\Delta}$ ☐
(b) $C_2H_5OC_2H_5 + CH_3COCl \xrightarrow{AlCl_3}$ ☐
(c) $C_2H_5OC_2H_5 + Cl_2 \xrightarrow{h\nu}$ ☐
(d) $C_2H_5OH + PCl_3 \longrightarrow$ ☐

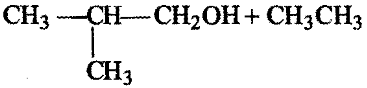
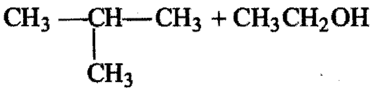
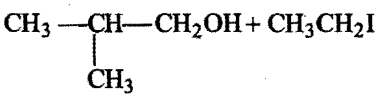
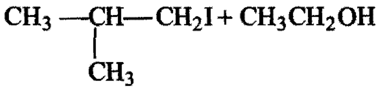
71. 
$CH_3MgX \xrightarrow[H^+,\,H_2O]{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} (A) \xrightarrow{Na} (B) \xrightarrow{C_2H_5OH} (C)$,

(*C*) is: **[DCE 2006]**
(a) 
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ ☐ (b) $(CH_3)_3C-O-C_2H_5$ ☐
(c) $C_2H_5OC_2H_5$ ☐ (d) 
$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$ ☐

72. Formation of diethyl ether from ethanol is based on a: **[BCECE (Med.) 2006]**
(a) dehydration reaction ☐
(b) dehydrogenation reaction ☐
(c) hydrogenation reaction ☐
(d) homolytic fission reaction ☐

73. In the reaction,


$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3 + HI \xrightarrow{\text{Heated}} \ldots$

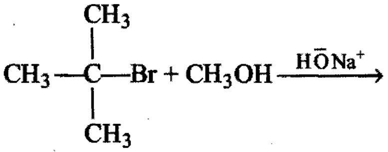
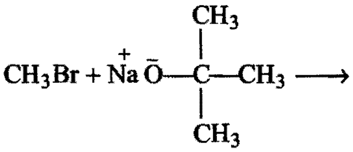
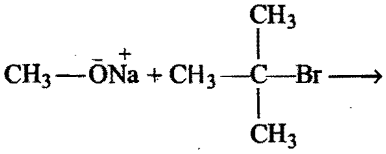
Which of the following compounds will be formed? **[CBSE (Med.) 2007]**
(a) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH + CH_3CH_3$ ☐
(b) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 + CH_3CH_2OH$ ☐
(c) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH + CH_3CH_2I$ ☐
(d) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2I + CH_3CH_2OH$ ☐

74. From Williamson's synthesis, the preparation of which of the following is possible? **[AFMC 2007; CMC (Med.) Ludhiana 2008]**
(a) Only symmetrical ethers ☐
(b) Only asymmetrical ethers ☐
(c) Both (a) and (b) ☐
(d) None of the above ☐

75. When alkyl halide is heated with dry Ag_2O, it produces: **[BVP (Med.) 2007]**
(a) ester ☐ (b) ether ☐
(c) ketone ☐ (d) alcohol ☐

76. A simple method to remove peroxides from ethers is to treat them with an aqueous solution of: **[CMC (Med.) Vellore 2007]**
(a) KI ☐ (b) KCNS ☐
(c) $Na_2S_2O_3$ ☐ (d) Br_2 ☐

77. Williamson's synthesis involves: **[MGIMS (Med.) 2007]**
(a) S_N1 mechanism ☐ (b) nucleophilic addition ☐
(c) S_N2 mechanism ☐ (d) S_E mechanism ☐

78. In which of the following reactions, the product obtained is *tert.* butyl methyl ether? **[AIIMS 2008]**
(a) $CH_3OH + HOCH_2CH_3 \xrightarrow{\text{Conc. } H_2SO_4}$ ☐
(b) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br + CH_3OH \xrightarrow{H\bar{O}Na^+}$ ☐
(c) 
$CH_3Br + \overset{+}{Na}\,\bar{O}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \longrightarrow$ ☐
(d) 
$CH_3-\bar{O}\overset{+}{Na} + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br \longrightarrow$ ☐

79. Which of the following compounds when heated with CO at 150°C and 500 atm pressure in presence of BF_3 forms ethyl propionate? **[AFMC 2008]**
(a) C_2H_5OH ☐ (b) CH_3-O-CH_3 ☐
(c) $CH_3-O-C_2H_5$ ☐ (d) $C_2H_5-O-C_2H_5$ ☐

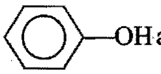
80. Wet ether is not used as a solvent in Wurtz reaction, because the water present in it: **[DCE 2008]**
(a) hydrolysis *RX* to *R*OH ☐
(b) reduces *RX* to *R*H ☐
(c) destroy the Na metal ☐
(d) reacts with *R*—*R* ☐

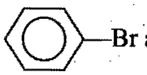
81. Which of the following does not react with sodium metal? **[UPSEE (Engg.) 2008]**
(a) $(CH_3)_2O$ ☐ (b) CH_3CH_2OH ☐
(c) CH_3COOH ☐ (d) C_6H_5OH ☐

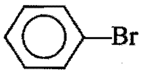
82. '*A*' reacts with C_2H_5I giving '*B*' and NaI. Here '*A*' and '*B*' respectively, are: **[Punjab PMET (Med.) 2008]**
(a) CH_3COONa, CH_3OCH_3 ☐
(b) $C_2H_5ONa, C_2H_5OC_2H_5$ ☐
(c) $C_2H_5OC_2H_5, C_2H_5COOC_2H_5$ ☐
(d) $C_2H_5OH, C_2H_5OC_2H_5$ ☐

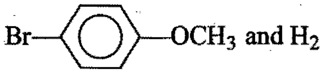
83. Decreasing order of reactivity in Williamson's ether synthesis of the following: **[DUMET 2010]**
(I) Me_3CCH_2Br (II) $CH_3CH_2CH_2Br$
(III) $H_2C{=}CHCH_2Cl$ (IV) $CH_3CH_2CH_2Cl$
(a) III > II > IV > I ☐ (b) I > II > IV > III ☐
(c) II > III > IV > I ☐ (d) I > III > II > IV ☐

84. In the reaction  the products are: **[IIT 2010]**

(a)  and CH_3Br ☐

(b)  and CH_3Br ☐

(c)  and CH_3OH ☐

(d)  and H_2 ☐

85. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene? **[AMU (Med.) 2010]**

(A)  + CH_3ONa

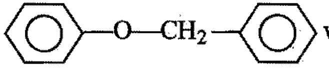
(B)  + CH_3Br

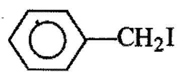
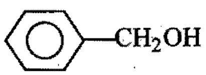
(a) both A and B ☐ (b) only A ☐
(c) only B ☐ (d) none of these ☐

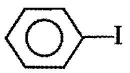
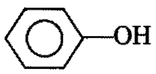
Set II: This set contains the questions with two or more correct answers:

86. Diethyl ether can be distinguished from *n*-butanol by: **[BHU (Mains) 2007]**
(a) aqueous $FeCl_3$ ☐
(b) reaction with Na metal ☐
(c) Tollens reagent ☐
(d) reaction with CrO_3 in dil H_2SO_4 ☐

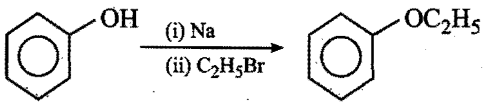
87. Select the correct statement(s) about crown ether 18-crown-6:
(a) it is a cyclic polyether ☐
(b) it has total 18 atoms ☐
(c) it has 12 carbon atoms ☐
(d) it has 6 oxygen atoms ☐

88. The ether  when treated with HI produces: **[IIT 1999]**

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

89. Which of the following reactions will give good yield of ether?

(a)  ☐

(b) $(CH_3)_3C{-}OH \xrightarrow[\text{(ii) } C_6H_5Br]{\text{(i) Na}} C_6H_5{-}O{-}C(CH_3)_3$ ☐

(c) $(CH_3)_3C{-}OH \xrightarrow[\text{(ii) } CH_3CH_2CH_2Br]{\text{(i) Na}} (CH_3)_3C{-}O{-}CH_2CH_2CH_3$ ☐

(d) $CH_3CH_2CH_2OH \xrightarrow[\text{(ii) } (CH_3)_3CBr]{\text{(i) Na}} (CH_3)_3C{-}O{-}CH_2CH_2CH_3$ ☐

90. Diethyl ether on treatment with HI in small amount, gives:
(a) C_2H_5OH ☐ (b) C_2H_5I ☐
(c) C_4H_{10} ☐ (d) C_3H_7I ☐

91. Natalite contains:
(a) C_2H_5OH ☐ (b) $C_2H_5{-}O{-}C_2H_5$ ☐
(c) CH_3OH ☐ (d) $CH_3{-}O{-}CH_3$ ☐

92. Ethyl bromide can be converted into diethyl ether by:
(a) reacting with sodium ethoxide ☐
(b) heating with moist silver oxide ☐
(c) heating with dry silver oxide ☐
(d) treating with C_2H_5MgBr ☐

93. $C_6H_5{-}O{-}CH_3$ is named as:
(a) phenoxy methane ☐ (b) methoxy benzene ☐
(c) anisole ☐ (d) methyl phenyl ether ☐

94. Indicate the correct statement for diethyl ether that it is:
(a) used as an anaesthetic ☐
(b) used as refrigerant ☐
(c) decomposed by HI ☐
(d) used as an inert solvent ☐

95. What is the function of diethyl ether in the preparation of Grignard reagent?
(a) To act as a catalyst ☐
(b) To act as a solvent ☐
(c) To provide lone pair of electrons for coordination ☐
(d) To act as an acid ☐

96. Ethers can be prepared by:
(a) boiling alkyl halide with dry silver oxide ☐
(b) boiling alkyl halide with ammoniacal KOH ☐
(c) heating alkyl halide with potassium alkoxide ☐
(d) heating an excess of alcohol with alumina under pressure ☐

97. Diethyl ether is obtained by the reaction of: **[BHU (Mains) 2008]**
(a) sodium ethoxide with methyl iodide ☐
(b) sodium ethoxide with ethyl chloride ☐
(c) ethanol with red phosphorus ☐
(d) ethanol with conc. H_2SO_4 ☐

ASSERTION-REASON TYPE QUESTIONS

These questions consist of an **Assertion (A)** and **Reason (R).** Use the following keys to choose appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. **(A)** Ether behaves as bases in the presence of mineral acids.
(R) Due to the presence of lone pair of electrons on oxygen.

2. **(A)** The boiling point of ethanol is much higher than that of dimethyl ether.
(R) In ethanol, the molecules are associated by the formation of intermolecular hydrogen bonding, whereas in diethyl ether it is absent.

3. **(A)** Phenetole on cleavage with HI yields phenol and ethyl iodide.
(R) Phenetole is a mixed aromatic ether.

4. **(A)** Anisole undergoes electrophilic substitution at *ortho* and *para* positions.
(R) Anisole is less reactive than phenol towards electrophilic substitution reactions.

5. **(A)** With HI, anisole forms iodobenzene and methyl alcohol.
(R) I^- ion will combine with smaller group to avoid steric hindrance.

6. **(A)** *Tert.* butyl methyl ether on cleavage with HI at 373 K gives *tert.*butyl iodide and methanol.
(R) The reaction occurs by S_N2 mechanism.

7. **(A)** The C—O—C bond angle in ethers is higher than H—O—H bond angle in water.
(R) Oxygen is sp^3-hybridized in both ethers and water.

8. **(A)** *Tert.* butyl alcohol on heating with conc. H_2SO_4 at 413 K gives 2-methyl propane as the main product and not di-*tert.* butyl ether.
(R) All alcohols are readily dehydrated with conc. H_2SO_4.

9. **(A)** 1-Bromo-2,2-dimethyl propane on heating with ethanol gives 2-ethoxy-2-methyl butane as the main product.
(R) The reaction occurs by S_N2 mechanism.

10. **(A)** *Tert.* butyl methyl ether is not prepared by the reaction of *tert.* butyl bromide with sodium methoxide.
(R) Sodium methoxide is a strong nucleophile.
[AIIMS 2005]

ANSWERS

OBJECTIVE QUESTIONS

1. (a)	**2.** (c)	**3.** (b)	**4.** (d)	**5.** (c)	**6.** (a)	**7.** (a)	**8.** (c)	**9.** (b)	**10.** (c)
11. (d)	**12.** (d)	**13.** (a)	**14.** (b)	**15.** (b)	**16.** (a)	**17.** (c)	**18.** (d)	**19.** (d)	**20.** (d)
21. (a)	**22.** (a)	**23.** (d)	**24.** (c)	**25.** (b)	**26.** (a)	**27.** (b)	**28.** (c)	**29.** (d)	**30.** (a)
31. (d)	**32.** (a)	**33.** (b)	**34.** (c)	**35.** (b)	**36.** (d)	**37.** (c)	**38.** (d)	**39.** (c)	**40.** (d)
41. (b)	**42.** (a)	**43.** (a)	**44.** (b)	**45.** (d)	**46.** (d)	**47.** (a)	**48.** (a)	**49.** (d)	**50.** (c)
51. (c)	**52.** (d)	**53.** (c)	**54.** (b)	**55.** (c)	**56.** (d)	**57.** (c)	**58.** (b)	**59.** (a)	**60.** (a)
61. (c)	**62.** (a)	**63.** (a)	**64.** (d)	**65.** (d)	**66.** (c)	**67.** (a)	**68.** (b)	**69.** (c)	**70.** (c)
71. (b)	**72.** (a)	**73.** (c)	**74.** (c)	**75.** (b)	**76.** (a)	**77.** (c)	**78.** (c)	**79.** (d)	**80.** (c)
81. (a)	**82.** (b)	**83.** (c)	**84.** (a)	**85.** (a)	**86.** (b,d)	**87.** (a,b,c,d)	**88.** (a,d)	**89.** (a,c)	**90.** (a,b)
91. (a,b)	**92.** (a,c)	**93.** (b,c,d)	**94.** (a,c,d)	**95.** (b,c)	**96.** (a,c,d)	**97.** (b,d)			

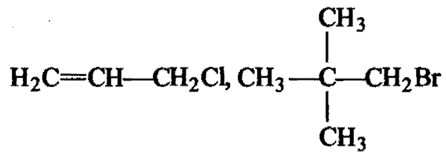
ASSERTION-REASON TYPE QUESTIONS

1. (a)	**2.** (a)	**3.** (b)	**4.** (b)	**5.** (d)	**6.** (c)	**7.** (b)	**8.** (a)	**9.** (c)	**10.** (b)

BRAIN STORMING PROBLEMS

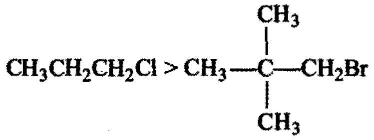
1. Arrange the following halides in decreasing order of reactivity for Williamson's synthesis:

$CH_3CH_2CH_2Br$, $CH_3CH_2CH_2Cl$,



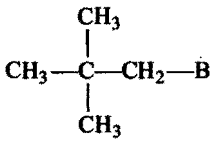
$H_2C{=}CH{-}CH_2Cl$, $CH_3{-}C(CH_3)_2{-}CH_2Br$

[Hint : $H_2C{=}CH{-}CH_2Cl > CH_3{-}CH_2{-}CH_2Br >$



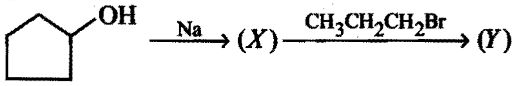
$CH_3CH_2CH_2Cl > CH_3{-}C(CH_3)_2{-}CH_2Br$

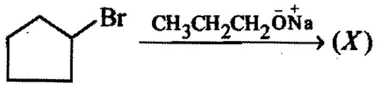
Allylic compounds will be more reactive than saturated halides. Bromides are more reactive than chlorides because C—Br bond is weaker than C—Cl bond.

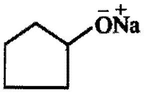


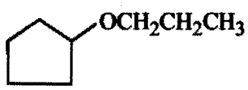
$CH_3{-}C(CH_3)_2{-}CH_2{-}Br$ is least reactive because of steric hindrance.]

2. Complete the following reactions:

(a) 

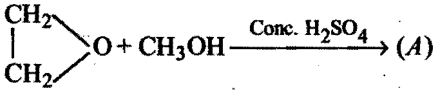
(b) 

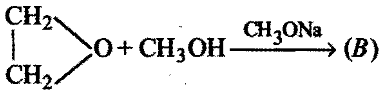
[Ans. (a) (X) = 

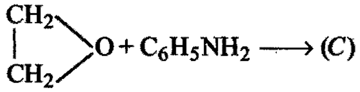
; (Y) = 

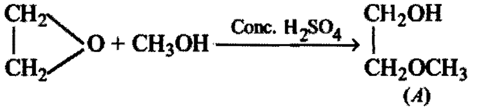
(b)  + $CH_3CH_2CH_2OH$ + NaBr]

3. What are (A), (B) and (C) in the following reactions?

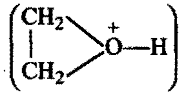
(a) 

(b) 

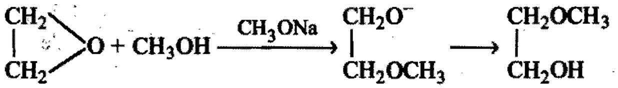
(c) 

[Hint : (a) 

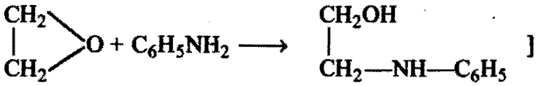
(A)



Intermediate

(b) 

Intermediate (B)

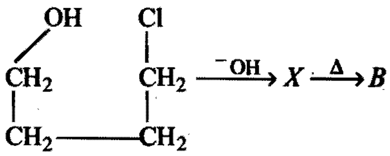
(c) 

]

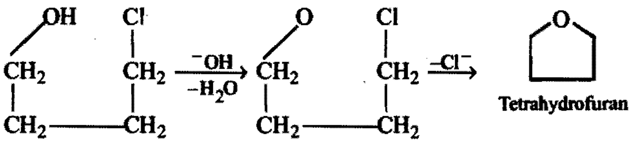
N-phenyl-2-aminoethan-1-ol

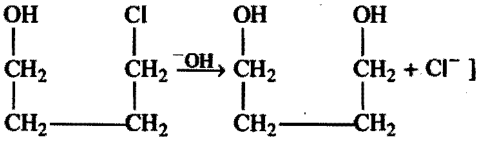
(C)

4. Complete the following reactions:



[Hint: It is cyclic Williamson's ether synthesis involving S_N2 reaction.

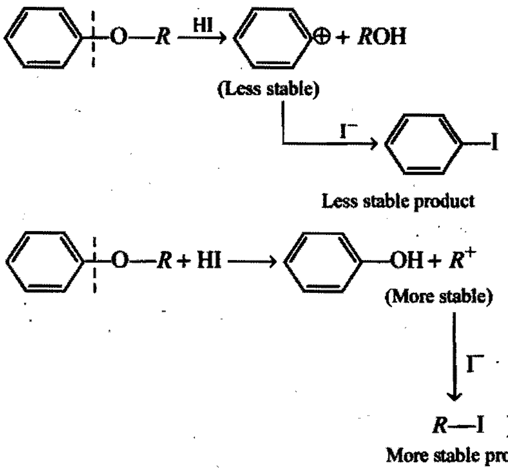


By-product : 

]

5. Alkyl aryl ethers on treatment with HI gives alkyl iodide not aryl iodide, explain why?

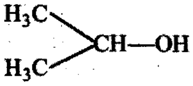
[Hint:

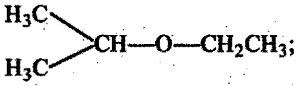


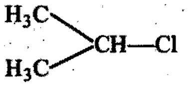
]

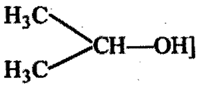
6. (A) $C_5H_{12}O$ (ether) on treatment with PCl_5 forms alkyl chlorides (B) and (C). (B) and (C) both on treatment with *aq.* NaOH give alcohols (D) and (E), both (D) and (E) give iodoform test. What are (A), (B), (C), (D) and (E) ?

[**Hint:** Alcohols giving iodoform test will be

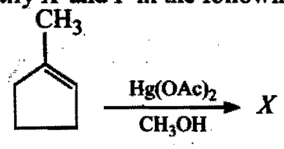
CH_3CH_2OH and 
$(H_3C)_2CH-OH$

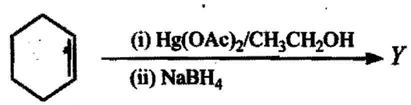
∴ (*A*) ⟶ 
$(H_3C)_2CH-O-CH_2CH_3$;

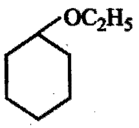
(*B*) ⟶ CH_3-CH_2Cl; (*C*) ⟶ 
$(H_3C)_2CH-Cl$

(*D*) ⟶ CH_3CH_2OH; (*E*) ⟶ 
$(H_3C)_2CH-OH$]

7. Identify *X* and *Y* in the following reactions:

(a) 

(b) 

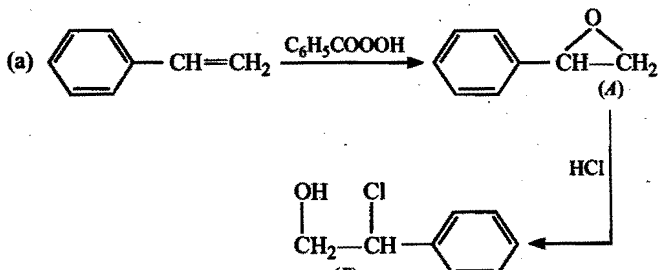
[**Ans.** (*X*) =  ; (*Y*) = ]

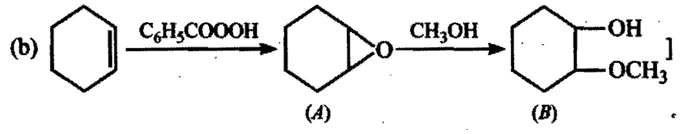
8. Identify the unknown products among the following:

(a) $-CH=CH_2 \xrightarrow{C_6H_5COOOH} (A) \xrightarrow{HCl} (B)$

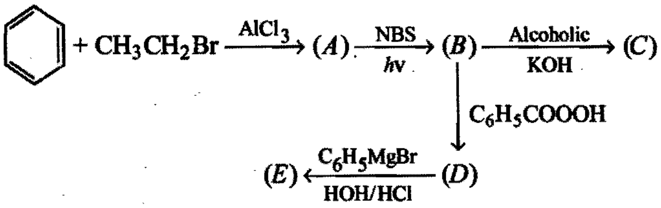
(b) $\xrightarrow{C_6H_5COOOH} (A) \xrightarrow{CH_3OH} (B)$

[**Ans.**

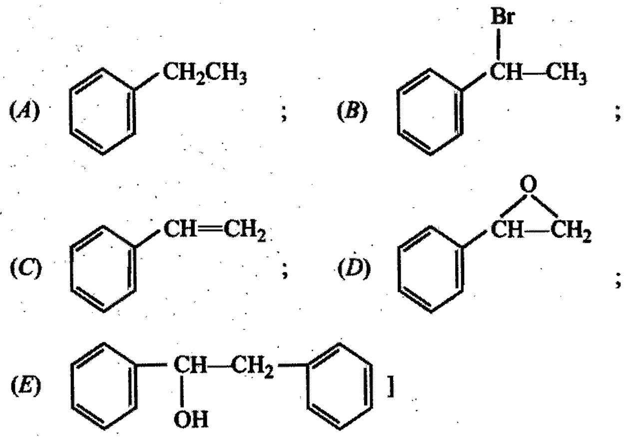
(a) 

(b) 
]

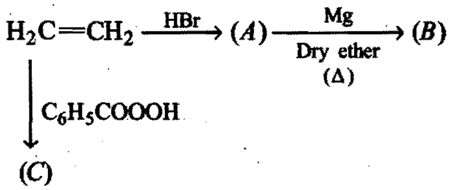
9. Complete the following chain of reactions:



[**Ans.**


(*A*) ; (*B*) ; (*C*) ; (*D*) ; (*E*)]

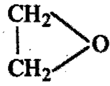
10. Complete the following reaction:



$$\begin{tikzcd} H_2C=CH_2 \arrow[r, "HBr"] \arrow[d, "C_6H_5COOOH"] & (A) \arrow[r, "Mg", "\text{Dry ether } (\Delta)"'] & (B) \\ (C) \end{tikzcd}$$

$(B) + (C) \xrightarrow[HCl]{HOH} (D)$

[**Ans.** (*A*) ⟶ CH_3-CH_2Br; (*B*) ⟶ CH_3CH_2MgBr

(*C*) ⟶  ; (*D*) ⟶ $CH_3CH_2CH_2CH_2OH$]

11. The ether having best anaesthetic properties is:
(a) diethyl ether ☐ (b) dimethyl ether ☐
(c) vinyl ether ☐ (d) allyl ether ☐

12. When ether is exposed to air for some time, an explosive substance produced is:
(a) ether peroxide ☐ (b) TNT ☐
(c) ether oxide ☐ (d) ether superoxide ☐

13. Which of the following is the best procedure to make isopropyl methyl ether using the Williamson's method?
(a) $CH_3OH + (CH_3)_2CHOH + H_2SO_4 \longrightarrow$ ☐
(b) $CH_3OH + (CH_3)_2CH-CH_2OH + H_2SO_4 \longrightarrow$ ☐
(c) $CH_3ONa + (CH_3)_2CHBr \longrightarrow$ ☐
(d) $CH_3I + (CH_3)_2CHO^-Na^+ \longrightarrow$ ☐

14. The reactivity of halogen acids with ether follows the order:
(a) HI > HBr > HCl ☐ (b) HCl > HBr > HI ☐
(c) HBr > HI > HCl ☐ (d) HCl > HI > HBr ☐

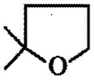
15. Phenetole reacts with HI to produce:
(a) $C_6H_5I + CH_3CH_2OH$ ☐
(b) $CH_3CH_2I + C_6H_5OH$ ☐
(c) $C_6H_5CH_2OH + CH_3CH_2I$ ☐
(d) $C_6H_5OH + CH_3CH_2OH$ ☐

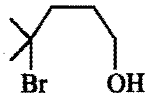
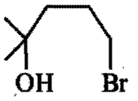
16. Select the incorrect statement among the following:
(a) The C—O—C bond angle in ether is 110° ☐
(b) Diethyl ether reacts with excess of HI to form ethyl iodide ☐

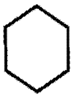
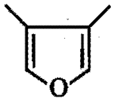
(c) Ethers and alcohols are functional isomers ☐
(d) Ethers are Lewis base hence do not react with Bronsted acid like H_2SO_4 ☐

17. Which among the following statements about ethers are correct?

(a) Peroxide is obtained in presence of air ☐
(b) Ethers are weakly acidic ☐
(c) Ethers form oxonium salt ☐
(d) Ethers form stable complexes with Lewis acids ☐

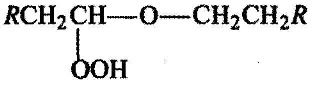
18.  on reaction with cold conc. HBr gives :

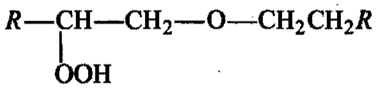
(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

19. $RCH_2CH_2—O—CH_2CH_2R$ on reaction with O_2 gives :

(a) $RCH_2COOCOCH_2R$ ☐

(b) 
$RCH_2\underset{OOH}{CH}—O—CH_2CH_2R$ ☐

(c) 
$R—\underset{OOH}{CH}—CH_2—O—CH_2CH_2R$ ☐

(d) $RCOCH_2—O—CH_2COR$ ☐

20. Tertiary butyl methyl ether on reaction with anhydrous HI gives an alcohol (*A*) and halide (*B*). Which of the following statements is correct?

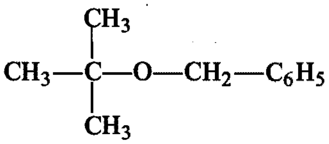
(a) Alcohol (*A*) performs Lucas test immediately at room temperature ☐
(b) Halide (*B*) undergoes S_N1 reaction most readily ☐
(c) Alcohol (*A*) on heating with copper gives formaldehyde ☐
(d) Halide (*B*) on reaction with KCN mainly gives eliminated product ☐

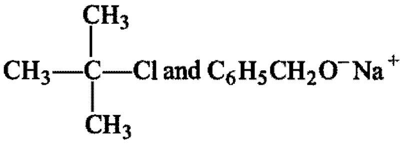
21. $CH_3—O—C(CH_3)_3$ on reaction with CH_3COCl in presence of $AlCl_3$ gives (*A*) and $C_6H_5—O—C(CH_3)_3$ on reaction with cold HI gives (*B*). The compounds (*A*) and (*B*) are :

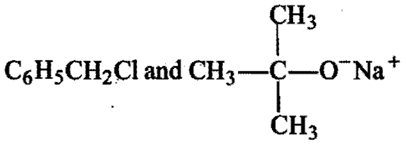
	A	*B*
(a)	$(CH_3)_3C—Cl$	$(CH_3)_3C—I$
(b)	CH_3Cl	$(CH_3)_3C—I$
(c)	CH_3OH	$C_6H_5—I$
(d)	CH_3COOCH_3	$(CH_3)_3C—OH$

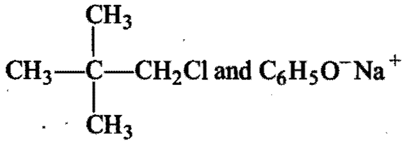
22. Conversion of alcohol into ether in the presence of conc. H_2SO_4 is an example of :

(a) S_N1 reaction ☐ (b) S_N2 reaction ☐
(c) E^1 reaction ☐ (d) addition reaction ☐

23. 
$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—O—CH_2—C_6H_5$ can be prepared from Williamson's ether synthesis using :

(a) 
$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—Cl$ and $C_6H_5CH_2O^-Na^+$ ☐

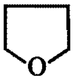
(b) 
$C_6H_5CH_2Cl$ and $CH_3—\overset{CH_3}{\underset{CH_3}{C}}—O^-Na^+$ ☐

(c) 
$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—CH_2Cl$ and $C_6H_5O^-Na^+$ ☐

(d) all of the above ☐

24. In the reaction $R—S—R \xrightarrow[KMnO_4]{[O]} X$, the product *X* is:

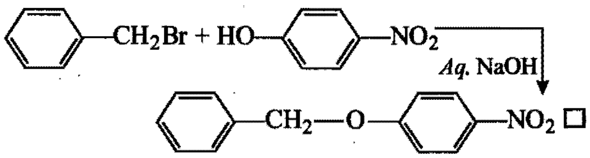
(a) a sulphoxide ☐ (b) a sulphone ☐
(c) an alkane ☐ (d) an alkene ☐

25.  $\xrightarrow[373\text{ K}]{HI}$ Product,

the product is :

(a) $ICH_2CH_2CH_2CH_2I$ ☐
(b) $ICH_2CH_2CH_2CH_2OH$ ☐
(c) both ☐
(d) none ☐

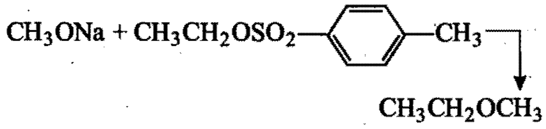
26. Which among the following is not useful for the synthesis of ether ?

(a) 

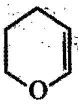
☐

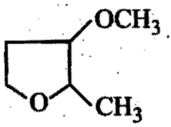
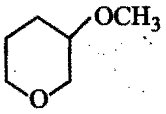
(b) $C_2H_5O^-Na^+ + (CH_3)_2SO_4 \longrightarrow C_2H_5OCH_3$ ☐

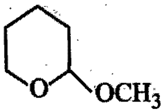
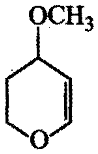
(c) $(CH_3)_3CBr + CH_3CH_2ONa \longrightarrow$
$(CH_3)_3C—O—CH_2CH_3$ ☐

(d) 

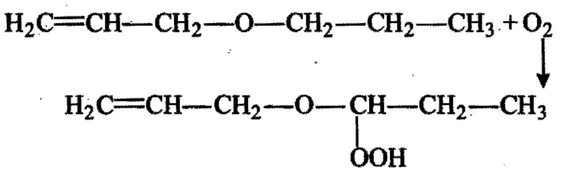
☐

27.  on reaction with CH_3OH in presence of H^+ gives :

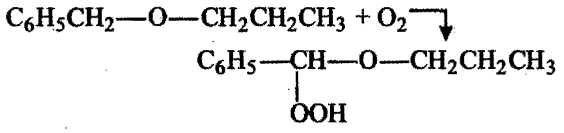
(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

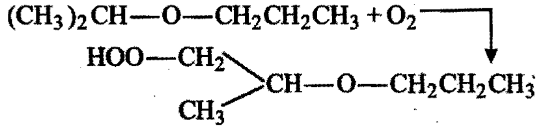
28. Select the correct reaction among the following :

(a) 

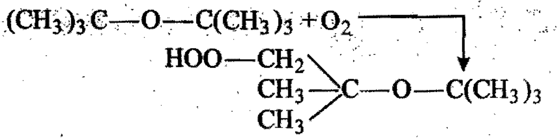
$H_2C{=}CH-CH_2-O-CH_2-CH_2-CH_3+O_2 \longrightarrow H_2C{=}CH-CH_2-O-\underset{OOH}{\underset{|}{CH}}-CH_2-CH_3$ ☐

(b) 

$C_6H_5CH_2-O-CH_2CH_2CH_3+O_2 \longrightarrow C_6H_5-\underset{OOH}{\underset{|}{CH}}-O-CH_2CH_2CH_3$ ☐

(c) 

$(CH_3)_2CH-O-CH_2CH_2CH_3+O_2 \longrightarrow \begin{matrix}HOO-CH_2\\ CH_3\end{matrix}{>}CH-O-CH_2CH_2CH_3$ ☐

(d) 

$(CH_3)_3C-O-C(CH_3)_3+O_2 \longrightarrow \begin{matrix}HOO-CH_2\\ CH_3\\ CH_3\end{matrix}{>}C-O-C(CH_3)_3$ ☐

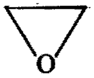
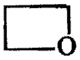
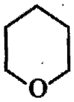
29. $C_4H_{10}O+PCl_5 \longrightarrow R_1Cl+R_2Cl+POCl_3$

R_1Cl gives haloform test but R_2Cl does not, hence, the original compound of the reaction is :

(a) ethoxy ethane ☐ (b) 1-methoxy propane ☐

(c) 2-methoxy propane ☐ (d) isobutyl alcohol ☐

30. Match the **List I** with **List II** and select the correct answer from the given codes :

List I (Cyclic ether)	**List II** (Name)
A. 	1. Oxane
B. 	2. Oxolane
C. 	3. Oxirane
D. 	4. Oxetane

Codes	A	B	C	D	
(a)	3	4	2	1	☐
(b)	1	2	3	4	☐
(c)	4	3	2	1	☐
(d)	1	4	2	3	☐

ANSWERS : BRAIN STORMING PROBLEMS

11. (c) **12.** (a) **13.** (d) **14.** (a) **15.** (b) **16.** (d) **17.** (a,c,d) **18.** (a) **19.** (b) **20.** (a)
21. (a) **22.** (b) **23.** (b) **24.** (b) **25.** (c) **26.** (c) **27.** (c) **28.** (b) **29.** (c) **30.** (a)

LINKED COMPREHENSION TYPE QUESTIONS

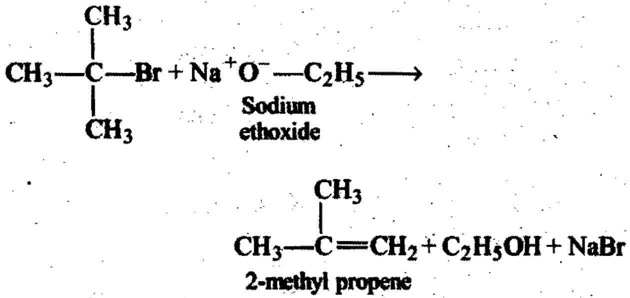
Passage 1

Alexander Williamson prepared diethyl ether by a simple method, now called as Williamson's ether synthesis. In this method, an alkyl halide is treated with sodium alkoxide prepared from sodium and alcohol.

$$R—O^- + R'—X \longrightarrow R—O—R' + X^-$$

This reaction is used in the synthesis of symmetrical and unsymmetrical ethers.

It may be noted that for preparing unsymmetrical ethers, the halide used should preferably be primary because secondary and tertiary alkyl halides may form alkenes as major product due to elimination process.



$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—Br + \underset{\text{Sodium ethoxide}}{Na^+O^-—C_2H_5} \longrightarrow \underset{\text{2-methyl propene}}{CH_3—\overset{CH_3}{C}=CH_2} + C_2H_5OH + NaBr$$

Aryl ethers or phenolic ethers can be prepared by using sodium phenoxide and alkyl halides. However, aryl halides and sodium alkoxide cannot be used for preparing phenolic ethers because aryl halides are less reactive towards nucleophilic substitution reactions.

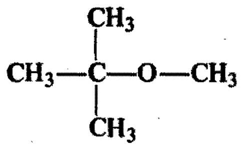
Answer the following questions :

1. Arrange the following halides in decreasing order of reactivity towards Williamson's ether synthesis :

$\underset{(u)}{CH_3CH_2CH_2Cl}$; $\underset{(v)}{CH_3CH_2CH_2Br}$;
$\underset{(w)}{(CH_3)_3C—CH_2Br}$; $\underset{(x)}{H_2C=CH—CH_2Cl}$

(a) $(x) > (v) > (u) > (w)$ (b) $(u) > (v) > (w) > (x)$
(c) $(w) > (x) > (v) > (u)$ (d) $(v) > (w) > (x) > (u)$

2. Methyl tertiary butyl ether (MTBE) is added in gasoline to improve its octane number.



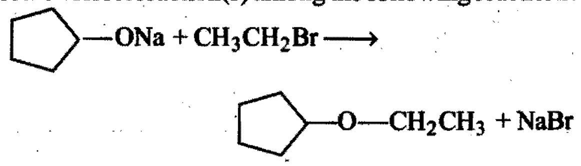
$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—O—CH_3$$

Which of the following is the best method for synthesis of the above ether ?

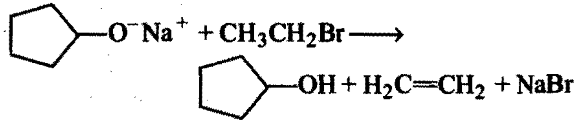
(a) $(CH_3)_2C=CH_2 + CH_3OH \xrightarrow{H_2SO_4}$
(b) $(CH_3)_3CBr + CH_3ONa \longrightarrow$
(c) $(CH_3)_3C—O^-Na^+ + CH_3I \longrightarrow$
(d) All of these reactions

3. Select the correct reaction(s) among the following reactions:

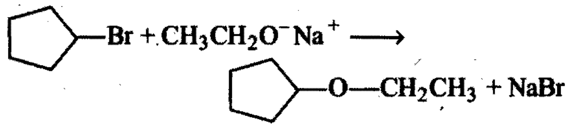
(a)



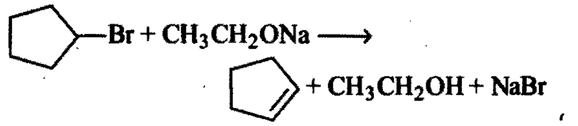
(b)



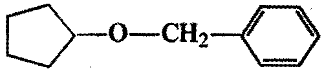
(c)



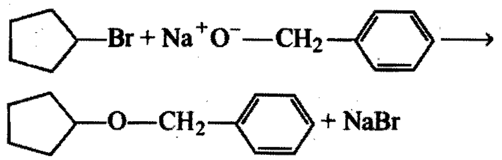
(d)



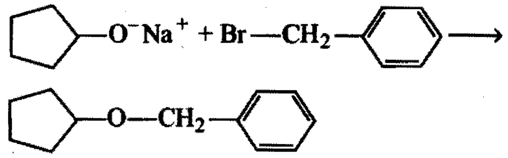
4. There are two possibilities for the synthesis of following ether:



Route 1



Route 2



Which of the following is correct ?
(a) Route 1 gives required ether
(b) Route 2 gives required ether
(c) Both route 1 and route 2 give the required ether
(d) None of the route is correct

5. To which of the following mechanisms does the reaction (Williamson's ether synthesis) belong?

(a) $S_N{}^1$ (b) $S_N{}^2$
(c) E^1 (d) E^2

Passage 2

Carbon-oxygen bond in ethers can be cleaved by halogen acids, sulphuric acid, phosphorus pentachloride, etc. The cleavage of C—O bond takes place under drastic conditions with excess of hydrogen halides.

$$R—O—R + 2HX \longrightarrow 2RX + H_2O$$

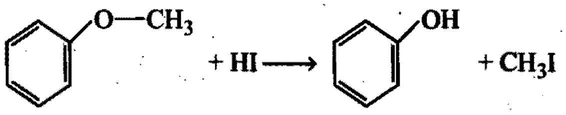
If hydrogen halide is not taken in excess then a molecule of alcohol and alkyl halide are formed.

$$R—O—R + HI \xrightarrow{373\text{ K}} R—OH + R—I$$

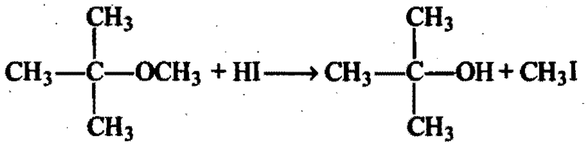
The order of reactivity of hydrogen halides towards the given reaction depends on the bond strength of halogenated acids, weaker is the H—X bond, greater is its reactivity. In case of unsymmetrical ethers, the site of cleavage is such that the halide is formed from the alkyl group which is smaller in size. However, when one of the alkyl group is tertiary, the halide formed is the tertiary halide.

Indicate whether the following statements/reactions are true or false.

1. Hydrogen fluoride (HF) is not effective in ether cleavage.
   (a) True (b) False
2. The order of hydrogen halide reactivity is, HI < HBr < HCl.
   (a) True (b) False
3. Alkyl aryl ethers react with HI to give phenol and alkyl halide.

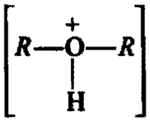


   (a) True (b) False
4. Tertiary butyl methyl ether reacts with HI according to the following reaction.



$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—OCH_3 + HI \longrightarrow CH_3—\underset{CH_3}{\overset{CH_3}{C}}—OH + CH_3I$$

   (a) True (b) False
5. In the reaction, $R—O—R + HX \longrightarrow RX + ROH$,

oxonium  $\left[R—\underset{H}{\overset{+}{O}}—R\right]$ ion is formed as intermediate.

   (a) True (b) False
6. Cyclic ethers are easily cleaved by HBr or HI to form dihaloalkanes.

 $+ \underset{\text{(Excess)}}{2HI} \xrightarrow{373\text{ K}} ICH_2CH_2CH_2CH_2I + H_2O$

   (a) True (b) False

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

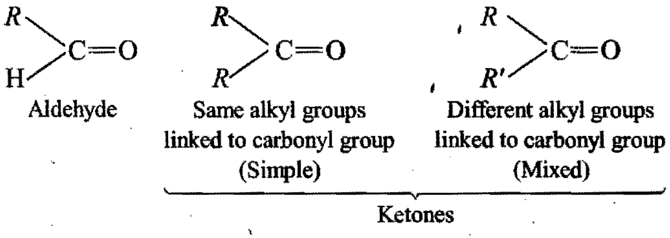
Passage 1	1. (a)	2. (c)	3. (a,d)	4. (b)	5. (b)	
Passage 2	1. (a)	2. (b)	3. (a)	4. (b)	5. (a)	6. (a)

11

ALDEHYDES AND KETONES

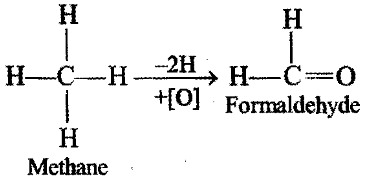
11.1 INTRODUCTION

Both aldehydes and ketones possess the same general formula $C_nH_{2n}O$ and contain a carbon-oxygen double bond ($>C=O$) known as carbonyl group. Thus, aldehydes and ketones are collectively referred to as **carbonyl compounds.** In aldehydes, the carbonyl group is linked to an alkyl group and a hydrogen atom, while in ketones it is united with two alkyl groups which may be same or different. When both the alkyl groups are the same, the ketone is called a simple or symmetrical ketone and in case both the alkyl groups are different, it is known as a mixed or an unsymmetrical ketone.

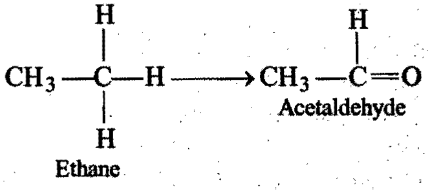


However, the first member of aldehyde series, formaldehyde ($H-\overset{H}{\overset{|}{C}}=O$) is an exception to the above definition as it does not have an alkyl group.

Aldehydes may be considered as derivatives of hydrocarbons in which two hydrogen atoms of the end carbon atom have been replaced by a bivalent oxygen atom.



$$\underset{\text{Methane}}{H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H} \xrightarrow[+[O]]{-2H} \underset{\text{Formaldehyde}}{H-\overset{H}{\overset{|}{C}}=O}$$



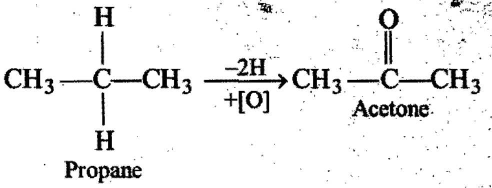
$$\underset{\text{Ethane}}{CH_3-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3-\overset{H}{\overset{|}{C}}=O}$$

Thus, aldehydes contain the monovalent group $-\overset{H}{\overset{|}{C}}=O$ (aldehydic or formyl group) linked to a hydrogen atom or an alkyl group. Hence, the general formula of the aldehydes is represented as $R-\overset{H}{\overset{|}{C}}=O$ (R may be H or alkyl group).

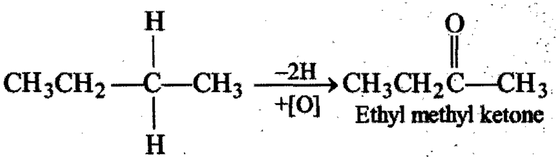
Aldehydes can also be regarded as the first oxidation products of primary alcohols.

$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow{[O]} \underset{\text{Aldehyde}}{RCHO} + H_2O$$

Ketones may be considered as derivatives of hydrocarbons in which the two hydrogen atoms of a carbon atom present in the middle of carbon chain have been replaced by a bivalent oxygen atom.

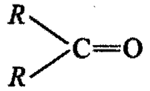


$$\underset{\text{Propane}}{CH_3-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_3} \xrightarrow[+[O]]{-2H} \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$$



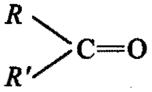
$$CH_3CH_2-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_3 \xrightarrow[+[O]]{-2H} \underset{\text{Ethyl methyl ketone}}{CH_3CH_2\overset{O}{\overset{\|}{C}}-CH_3}$$

Thus, ketones contain the divalent group $>C=O$ (ketonic or oxo group) linked to two alkyl groups, same or different. Hence, the general formula of the ketones is represented as,



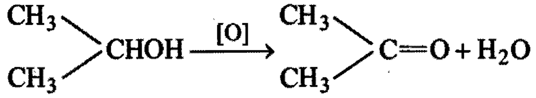
$R_2C=O$

or



$RR'C=O$

Ketones can also be regarded as the first oxidation products of secondary alcohols.

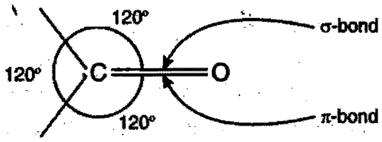


$$(CH_3)_2CHOH \xrightarrow{[O]} (CH_3)_2C=O + H_2O$$

Isopropyl alcohol Acetone

Electronic structure of carbonyl group : The carbonyl group like the carbon-carbon double bond of alkenes, is composed of one sigma (σ) bond and one pi (π) bond. Carbon atom of the carbonyl group is in a state of sp^2-hybridization, *i.e.*, giving three sp^2-hybrid orbitals. The sigma bond between carbon and oxygen is formed by overlap of an sp^2-orbital of carbon and a *p*-orbital of oxygen. The pi (π) bond is formed by the sideway overlap of an unhybridized *p*-orbital of carbon and a *p*-orbital of oxygen. Two of the hybridized orbitals of carbon form sigma bonds with two hydrogen atoms or one hydrogen atom and one alkyl group or two alkyl groups.

Carbonyl carbon atom is, thus, joined to three atoms by sigma bonds. Since, these bonds utilise sp^2-orbitals,they lie in the same plane and are 120° apart. Therefore, carbonyl group is **planar.** The carbon-oxygen double bond is different than carbon-carbon double bond. Since, oxygen is more electronegative, the electrons of the bond are attracted towards oxygen. Consequently, oxygen attains a partial negative charge and carbon a partial positive charge making the bond polar (electronegativity values, C = 2.5 and O = 3.5). The high values of dipole moment,



$$>\overset{\delta+}{C}=\overset{\delta-}{O}$$

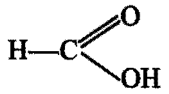
(2.3–2.8D) cannot be explained only on the basis of inductive effect and thus, it is proposed that carbonyl group due to high polar character is a resonance hybrid of the following two structures:

$$>C=O \longleftrightarrow >\overset{+}{C}-\overset{-}{O}$$

11.2 NOMENCLATURE

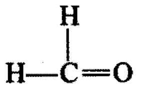
Aldehydes : There are two systems of naming aldehydes.

1. Common system : Common names of aldehydes are derived from the names of corresponding carboxylic acids to which they are oxidised. Suffix "ic acid" of the acid is replaced by "aldehyde".



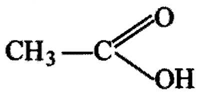
$H-C(=O)OH$

Formic acid ;



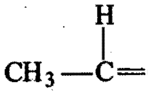
$H-\overset{H}{\overset{|}{C}}=O$

Formaldehyde



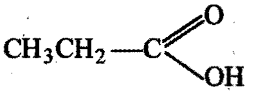
$CH_3-C(=O)OH$

Acetic acid ;



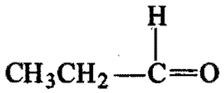
$CH_3-\overset{H}{\overset{|}{C}}=O$

Acetaldehyde



$CH_3CH_2-C(=O)OH$

Propionic acid ;

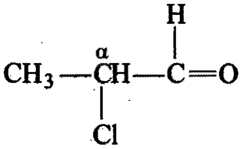


$CH_3CH_2-\overset{H}{\overset{|}{C}}=O$

Propionaldehyde

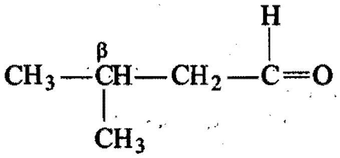
The position of the substituents on the parent chain is indicated by Greek letters α, β, γ; etc. The α-carbon is one which is directly attached to the —CHO group.

$$\overset{\delta}{C}-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-CHO$$



$CH_3-\underset{Cl}{\overset{\alpha}{C}H}-\overset{H}{\overset{|}{C}}=O$

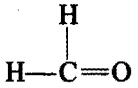
α-Chloropropionaldehyde ;



$CH_3-\underset{CH_3}{\overset{\beta}{C}H}-CH_2-\overset{H}{\overset{|}{C}}=O$

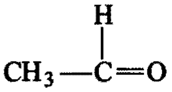
β-Methyl butyraldehyde

2. IUPAC system : In IUPAC system, aldehydes are named after the corresponding alkanes. Suffix -e of the alkane is replaced by the suffix -al. Therefore, aldehydes are called **Alkanals.** When substituents are present the carbonyl carbon is assigned no. 1.



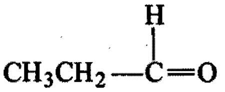
$H-\overset{H}{\overset{|}{C}}=O$

Methanal ;



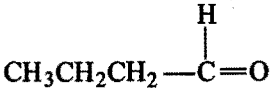
$CH_3-\overset{H}{\overset{|}{C}}=O$

Ethanal



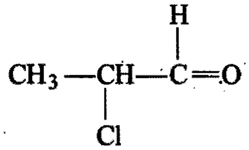
$CH_3CH_2-\overset{H}{\overset{|}{C}}=O$

Propanal ;



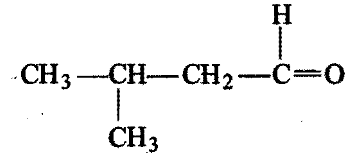
$CH_3CH_2CH_2-\overset{H}{\overset{|}{C}}=O$

Butanal



$CH_3-\underset{Cl}{CH}-\overset{H}{\overset{|}{C}}=O$

2-Chloropropanal ;



$CH_3-\underset{CH_3}{CH}-CH_2-\overset{H}{\overset{|}{C}}=O$

3-Methyl butanal

Ketones : There are two systems of naming ketones.

1. Common system : Common names of ketones are given by simply naming the alkyl groups attached to the carbonyl group and adding the word ketone. In case of simple or symmetrical ketones, they are named as dialkyl ketones. However, unsymmetrical or mixed ketones are named by naming the two alkyl groups attached to the ketonic group as separate words in alphabetical order and adding the word ketone. The common name of the first member is given acetone (as obtained by distilling calcium acetate). Examples are,

CH_3COCH_3	Dimethyl ketone (Acetone)
$CH_3COC_2H_5$	Ethyl methyl ketone
$C_2H_5COC_2H_5$	Diethyl ketone

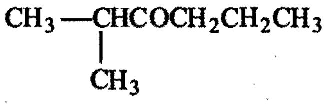
2. **IUPAC system :** In this system, longest chain containing the ketonic group is taken as the parent chain. In naming the ketone corresponding to the chain, the following procedure is adopted:

Root word + ane − e + one

i.e., Alkanone

The positions of the ketonic group and the substituents are indicated by the locants.

CH_3COCH_3	Propanone
$CH_3COCH_2CH_3$	Butan-2-one
$CH_3CH_2COCH_2CH_3$	Pentan-3-one

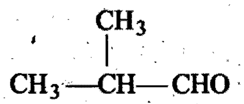

$\underset{\displaystyle CH_3}{CH_3—CH}COCH_2CH_2CH_3$ 2-Methyl hexan-3-one

11.3 ISOMERISM

Aldehydes : Aldehydes show chain isomerism amongst themselves and functional isomerism with ketones, cyclic ethers and unsaturated alcohols. Tautomerism with unsaturated alcohols is also observed.

Chain isomerism:

$CH_3CH_2CH_2CHO$; Butanal


$CH_3—\overset{CH_3}{CH}—CHO$

2-Methyl propanal

Functional isomerism :

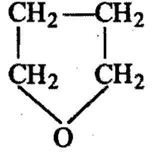
CH_3CH_2CHO ; CH_3COCH_3 ; $H_2C{=}CHCH_2OH$

Propanal; Propanone; Allyl alcohol

These are functional isomers.

$CH_3CH_2CH_2CHO$; $CH_3COCH_2CH_3$

Butanal; Butanone


Tetrahydrofuran

; $CH_3CH{=}CHCH_2OH$

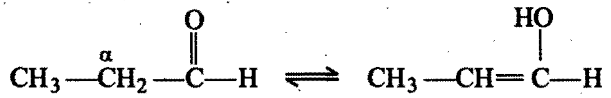
Crotyl alcohol

These are functional isomers.

Tautomerism :


$$CH_3—\overset{O}{\overset{\|}{C}}—H \rightleftharpoons H_2C{=}CHOH$$

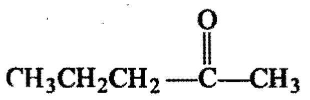
Acetaldehyde and vinyl alcohol are tautomers.


$$CH_3—\overset{\alpha}{CH_2}—\overset{O}{\overset{\|}{C}}—H \rightleftharpoons CH_3—CH{=}\overset{HO}{\overset{|}{C}}—H$$

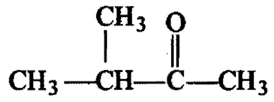
Only α- H atoms are involved in tautomerism.

Ketones : Besides chain isomerism, functional isomerism and tautomerism, ketones also show metamerism which arises due to different positions of carbonyl group in the carbon chain.

Chain isomerism :


$CH_3CH_2CH_2—\overset{O}{\overset{\|}{C}}—CH_3$;

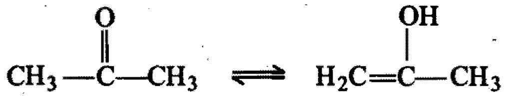
Pentan-2-one
(Methyl propyl ketone)


$CH_3—\overset{CH_3}{\overset{|}{CH}}—\overset{O}{\overset{\|}{C}}—CH_3$

3-Methyl butan-2-one
(Methyl isopropyl ketone)

Functional isomerism :
See examples in aldehydes.

Tautomerism :


$$CH_3—\overset{O}{\overset{\|}{C}}—CH_3 \rightleftharpoons H_2C{=}\overset{OH}{\overset{|}{C}}—CH_3$$

(Keto form) (Enol form)

Metamerism :


$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$;

Pentan-3-one


$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$

Pentan-2-one

SOME SOLVED PROBLEMS

Problem 1. *Give the common and* IUPAC *names for the following compounds:*

(*i*) $(CH_3)_2CHCHO$ (*ii*) $H_2C{=}CHCOCH{=}CH_2$
(*iii*) $CH_3COCH(CH_3)_2$ (*iv*) $Cl_2CHCOCH_3$
(*v*) $H_2C{=}CHCHO$ (*vi*) $CH_3CH_2CH(OH)CH_2CHO$.

Solution :

	Common name	IUPAC name
(i)	Isobutyraldehyde	2-Methyl propanal
(ii)	Divinyl ketone	Penta-1,4-dien-3-one
(iii)	Methyl isopropyl ketone	3-Methyl butan-2-one
(iv)	α, α-Dichloro acetone	1,1-Dichloropropanone
(v)	Acrolein	Prop-2-enal
(vi)	β-Hydroxyvaleraldehyde	3-Hydroxypentanal

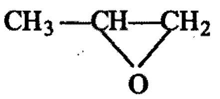
Problem 2. *Give* IUPAC *names of the functional isomers of formula* C_3H_6O.

Solution : The following are the functional isomers of formula C_3H_6O.

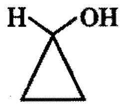
(i) C_2H_5CHO
Propanal

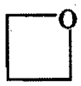
(ii) CH_3COCH_3
Propanone

(iii) $H_2C{=}CH—CH_2OH$
Prop-2-en-1-ol
or Allyl alcohol

(iv)

1,2-Epoxypropane
(2-Methyl oxirane)

(v) $H_2C{=}CH—O—CH_3$
Methyl vinyl ether

(vi)

Cyclopropanol

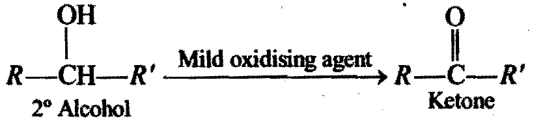
(vii)

1,3-Epoxypropane
(Oxetane)

11.4 GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

1. From Alcohols

(i) By controlled oxidation : Mild oxidising agents oxidises primary alcohols into aldehydes and secondary alcohols into ketones.

$$\underset{1^\circ\text{ Alcohol}}{R-CH_2OH} \xrightarrow{\text{Mild oxidising agent}} \underset{\text{Aldehyde}}{R-CHO}$$



$$\underset{2^\circ\text{ Alcohol}}{R-\overset{\overset{\displaystyle OH}{|}}{CH}-R'} \xrightarrow{\text{Mild oxidising agent}} \underset{\text{Ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-R'}$$

Some mild oxidising agents are:

1. $K_2Cr_2O_7/H_2SO_4$(dil.)/cold
2. Jones reagent (CrO_3, H_2SO_4 and acetone)
3. Fenton's reagent ($FeSO_4/H_2O_2$)
4. Sarret's reagent (PCC in CH_2Cl_2)
5. PDC, Pyridinium dichromate (CrO_3 with pyridine in H_2O)
6. X_2 (Cl_2)
7. DMSO/$COCl_2$ in $(C_2H_5)_3N$
8. Manganese dioxide (MnO_2 in CCl_4 or acetone).
9. Aluminium *tert.* butoxide in acetone
10. Ceric ammonium nitrate (CAN)
11. Silver carbonate (Ag_2CO_3)
12. Cu/300°C or Ag/300°C

$$\underset{\substack{\text{Ethyl alcohol}\\ \text{b.pt. 78°C}}}{CH_3CH_2OH} + [O] \xrightarrow[H_2SO_4(\text{dil.})]{K_2Cr_2O_7} \underset{\substack{\text{Acetaldehyde}\\ \text{b.pt. 20°C}}}{CH_3CHO} + H_2O$$

$$\underset{\substack{\text{1-Propanol}\\ \text{b.pt. 97°C}}}{CH_3CH_2CH_2OH} + [O] \xrightarrow[H_2SO_4(\text{dil.})]{K_2Cr_2O_7} \underset{\substack{\text{Propanal}\\ \text{b.pt. 48°C}}}{CH_3CH_2CHO}$$

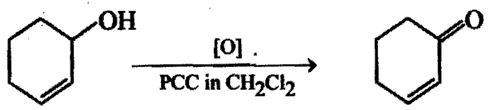
$$\underset{\text{Methyl alcohol}}{2CH_3OH} + 2[O] \xrightarrow[H_2SO_4(\text{dil.})]{K_2Cr_2O_7} \underset{\text{Formaldehyde}}{2HCHO} + 2H_2O$$

$$CH_3CH_2OH + \underset{(\text{Orange})}{Cr_2O_7^{2-}} + H^+ \longrightarrow CH_3CHO + \underset{(\text{Green})}{Cr^{3+}}$$

$$\underset{\substack{p\text{-Alcohol}\\ (1^\circ)}}{RCH_2OH} \xrightarrow[(CH_2Cl_2)]{\substack{C_5H_5N\cdot CrO_3\cdot HCl\\ \text{(Pyridinium chlorochromate or PCC)}}} \underset{\text{Aldehyde}}{RCHO}$$

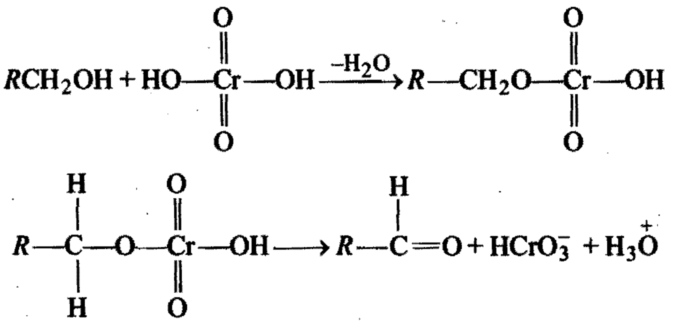
PCC is the mixture of pyridine, CrO_3 and HCl in 1 : 1 : 1 ratio. By PCC and Collin's reagent (which is CrO_3 + pyridine and is called **Sarett's reagent** or **Sarett Collin's reagent**) the oxidation stops at aldehyde.

This reagent also does not attack double bonds.



Cyclohex-2-en-1-ol Cyclohex-2-en-1-one

Mechanism of oxidation of an alcohol by Cr(vi) is believed to involve initial formation of a chromate ester which loses a proton and $HCrO_3^-$ ion to form the aldehyde.



$$RCH_2OH + HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-OH \xrightarrow{-H_2O} R-CH_2O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-OH$$

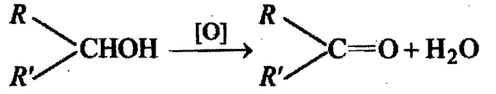
$$R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-OH \longrightarrow R-\overset{\overset{H}{|}}{C}=O + HCrO_3^- + H_3\overset{+}{O}$$

$H_2\ddot{O}:$

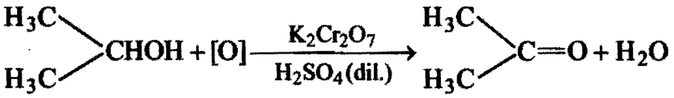
Cr(iv) is not stable and is reduced to Cr(iii) resulting in the oxidation of more alcohol.

Since, aldehydes are very susceptible to further oxidation to yield acids, the oxidation of primary alcohols is to be carried out under conditions which promote high yields of aldehydes. **Advantage is taken of the fact that aldehydes are more volatile than alcohols,** the oxidation is carried out at a temperature which is much above the boiling point of an aldehyde to be prepared but lower than the boiling point of the primary alcohol. Under such a condition **as soon as the aldehyde is formed,** it distills over and thus prevented from being oxidised. Orange ($Cr_2O_7^{2-}$) changes to green (Cr^{3+}) indicates the stage of completion.

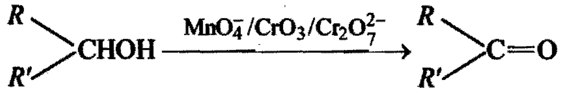
Ketones can be obtained by the oxidation of secondary alcohols. Ketones are not easily oxidised further and can be obtained in high yields by this method.

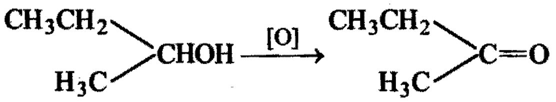


Sec. alcohol (2°) Ketone



Isopropyl alcohol Acetone





Sec. butyl alcohol Ethyl methyl ketone

(ii) Catalytic dehydrogenation : When vapours of primary or secondary alcohols are mixed with air and passed over reduced copper or silver catalyst heated to 300°C, primary alcohols are dehydrogenated to aldehydes and secondary alcohols to ketones.

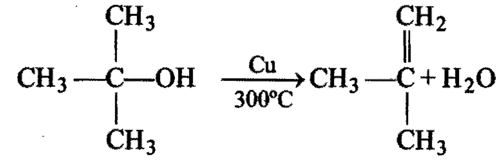
$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow[300^\circ C]{Cu} \underset{\text{Aldehyde}}{RCHO} + H_2$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[300°C]{Cu} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2$$

$$\underset{\text{Sec. alcohol}}{RCHOHR'} \xrightarrow[300°C]{Cu} \underset{\text{Ketone}}{RCOR'} + H_2$$

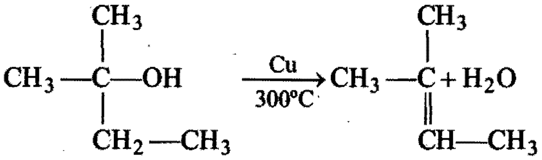
$$\underset{\text{Isopropyl alcohol}}{CH_3CHOHCH_3} \xrightarrow[300°C]{Cu} \underset{\text{Acetone}}{CH_3COCH_3} + H_2$$

3° alcohol undergo dehydration to form alkene whereas other alcohols (1° and 2°) by dehydrogenation forms carbonyl compound.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[300°C]{Cu} CH_3-\overset{\overset{CH_2}{\|}}{\underset{\underset{CH_3}{|}}{C}}+H_2O$$

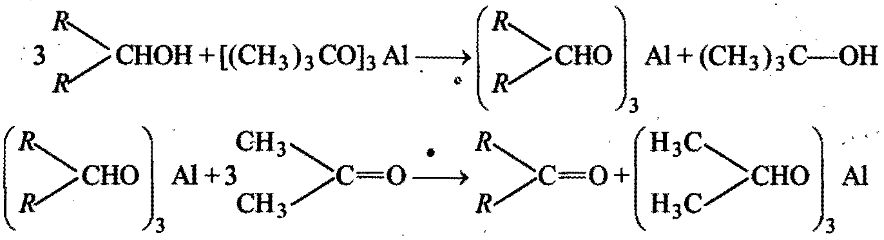
Tert. butyl alcohol (3°) 2-Methyl propene



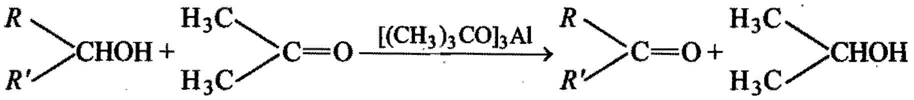
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2-CH_3}{|}}{C}}-OH \xrightarrow[300°C]{Cu} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH-CH_3}{\|}}{C}}+H_2O$$

2-Methyl butan-2-ol 2-Methyl but-2-ene

(iii) Oppenauer oxidation : Secondary alcohols can be oxidised to ketones by aluminium *tert.* butoxide, $[(CH_3)_3CO]_3\,Al$. The secondary alcohol is refluxed with the reagent and then acetone (or cyclo hexanone or *p*-benzoquinone, etc.) is added.

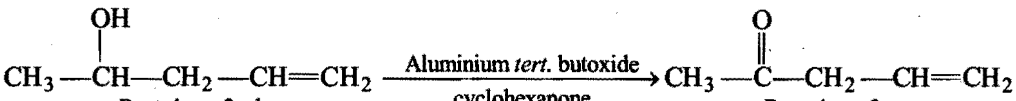


Secondary alcohol oxidises to ketone and acetone reduces to isopropyl alcohol.



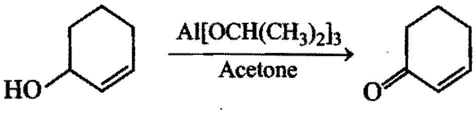
Sec. alcohol (2°) Acetone (excess) Ketone Isopropyl alcohol

Unsaturated sec. alcohols can also be oxidised to unsaturated ketones (without affecting the $>C=C<$ double bond) by this reagent.



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CH=CH_2 \xrightarrow[\text{cyclohexanone}]{\text{Aluminium } tert. \text{ butoxide}} CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH=CH_2$$

Pent-4-en-2-ol Pent-4-en-2-one



Cyclohex-2-en-1-ol Cyclohex-2-en-1-one

2. From Carboxylic Acids

(i) By dry distillation of calcium salts of fatty acids : When calcium formate is dry distilled alone formaldehyde is obtained.

$$\underset{\text{Calcium formate}}{(HCOO)_2Ca} \xrightarrow{\Delta} \underset{\text{Formaldehyde}}{HCHO} + \underset{\text{Calcium carbonate}}{CaCO_3}$$

Other aldehydes can be prepared by the dry distillation of equimolar mixture of calcium salt of a fatty acid with calcium formate.

$$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} 2RCHO + 2CaCO_3$$

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium formate}}{(HCOO)_2Ca} \xrightarrow{\Delta} \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2CaCO_3$$

The yield is generally poor due to side reactions. Thus, aldehydes are not prepared by this method.

Symmetrical ketones may be obtained when calcium salts of fatty acids (other than formic acid) are heated at 400°C.

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\Delta} \underset{\text{Acetone}}{CH_3COCH_3} + CaCO_3$$

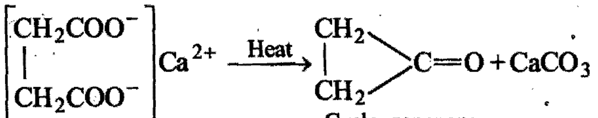
Note: The calcium salts of fatty acids are formed by heating carboxylic acids with calcium oxide.

The yield of simple ketones can be increased by using barium, thorium or manganese salts in place of calcium salts. If a mixture of calcium salts of carboxylic acid is heated, mixed ketone is obtained. The yield of a mixed ketone is generally poor.

$$(RCOO)_2Ca + (R'COO)_2Ca \xrightarrow{\Delta} \underset{\text{Mixed ketone}}{2RCOR'} + 2CaCO_3$$

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium propionate}}{(C_2H_5COO)_2Ca} \xrightarrow{\Delta} \underset{\text{Ethyl methyl ketone}}{2CH_3COC_2H_5} + 2CaCO_3$$

Cyclic ketones are formed when calcium salts of dicarboxylic acids are heated.



Calcium succinate

Cyclopropanone

(ii) Catalytic decomposition of carboxylic acids : Vapours of carboxylic acids mixed with formic acid, when passed over heated thoria (350°C), alumina (400°C) or manganous oxide (300°C), give aldehydes.

$$RCOOH + HCOOH \xrightarrow[400°C]{Al_2O_3} RCHO + H_2O + CO_2$$

$$CH_3COOH + HCOOH \xrightarrow[400°C]{Al_2O_3} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O + CO_2$$

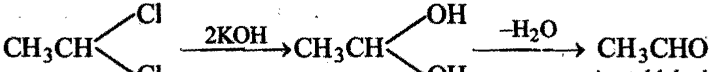
The yield is about 60%.

Symmetrical ketones are also obtained when vapours of a carboxylic acid are passed over under similar conditions.

$$\underset{\text{Acetic acid}}{2CH_3COOH} \xrightarrow[300°C]{MnO} \underset{\text{Acetone}}{CH_3COCH_3} + H_2O + CO_2$$

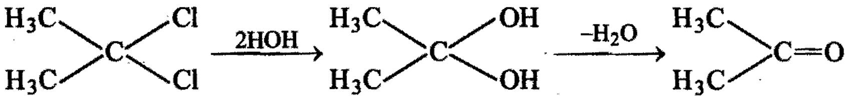
3. By Hydrolysis of Gem-dihalides

Aldehydes are obtained by alkaline hydrolysis of those gem-dihalides in which two halogen atoms are attached to the terminal carbon atom. Usually a mild alkali is used for this purpose.



Ethylidene chloride Unstable Acetaldehyde

Ketones are formed by hydrolysis of those gem-dihalides in which the two halogen atoms are attached to a non-terminal carbon atom.

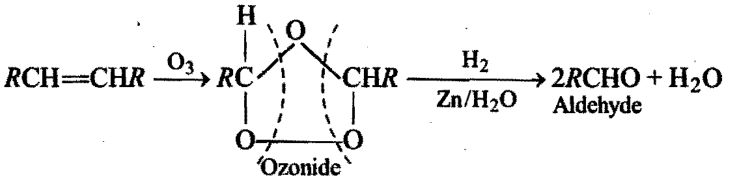


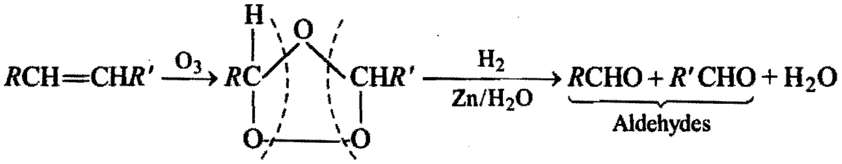
Isopropylidene chloride Unstable Acetone

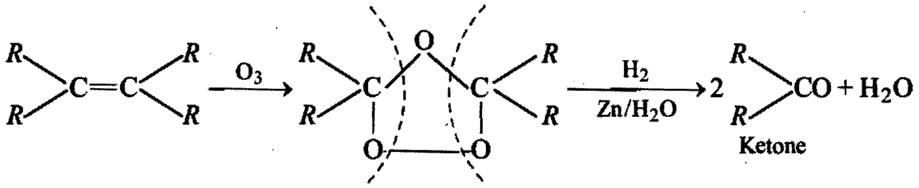
This method is not used much since aldehydes are affected by alkali and dihalides are usually prepared from the carbonyl compounds.

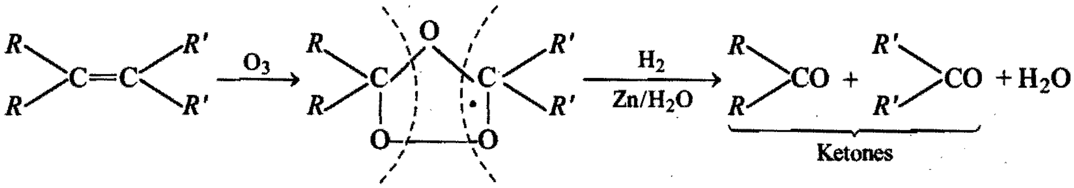
4. From Alkenes

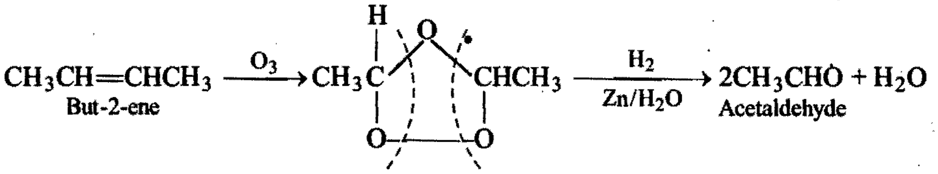
(i) By reductive ozonolysis : Alkenes are dissolved in an organic solvent such as chloroform, carbon tetrachloride or glacial acetic acid and a stream of ozonised oxygen is passed. The ozonide formed is then decomposed by passing hydrogen in presence of palladium or zinc dust and water. The product or products formed depend on the structure of alkene.

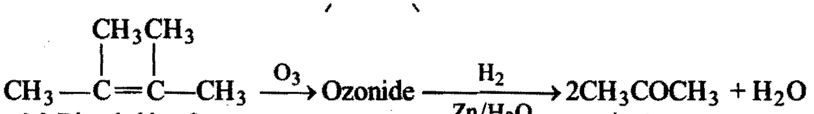








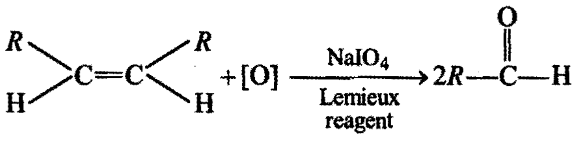




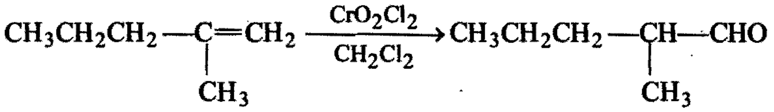
$$CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3 \xrightarrow{O_3} \text{Ozonide} \xrightarrow[Zn/H_2O]{H_2} 2CH_3COCH_3 + H_2O$$

2,3-Dimethyl but-2-ene Acetone

(ii) Alkenes can be oxidised to aldehydes by an oxidising agent called **Lemieux reagent.**

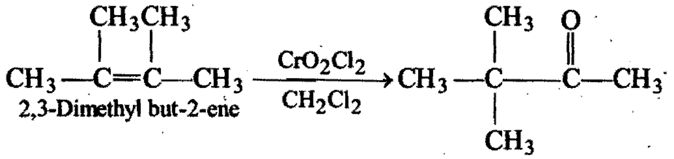


(iii) Alkenes can be oxidised to aldehydes and ketones by an oxidising agent CrO_2Cl_2 in CH_2Cl_2.



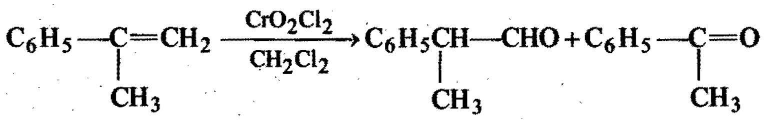
$$CH_3CH_2CH_2-\underset{CH_3}{\underset{|}{C}}=CH_2 \xrightarrow[CH_2Cl_2]{CrO_2Cl_2} CH_3CH_2CH_2-\underset{CH_3}{\underset{|}{C}H}-CHO$$

2-Methyl pent-1-ene 2-Methyl pentanal



$$CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3 \xrightarrow[CH_2Cl_2]{CrO_2Cl_2} CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-CH_3$$

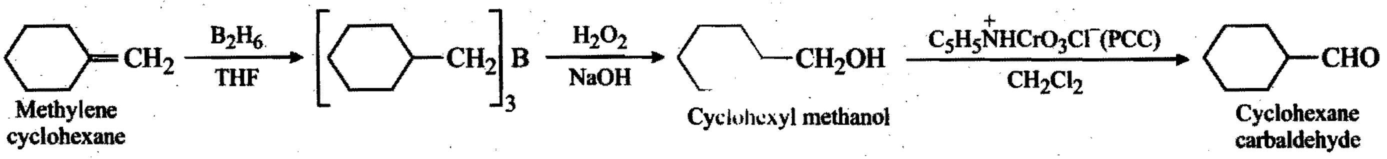
2,3-Dimethyl but-2-ene 3,3-Dimethyl butan-2-one



$$C_6H_5-\underset{CH_3}{\underset{|}{C}}=CH_2 \xrightarrow[CH_2Cl_2]{CrO_2Cl_2} C_6H_5\underset{CH_3}{\underset{|}{C}}H-CHO + C_6H_5-\underset{CH_3}{\underset{|}{C}}=O$$

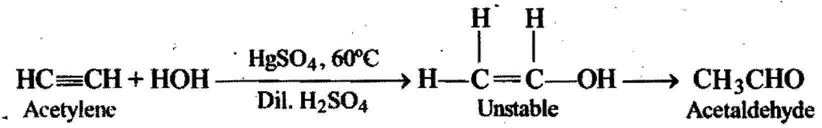
(iv) By hydroboration oxidation reaction : Alkenes can be oxidised to aldehydes.

$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\text{in THF}]{B_2H_6} \underset{\text{Tripropyl borane}}{(CH_3CH_2CH_2)_3B} \xrightarrow[NaOH]{H_2O_2} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} \xrightarrow[\text{in }CH_2Cl_2]{C_5H_5\overset{+}{N}HCrO_3Cl^-\text{ (PCC)}} \underset{\text{Propanal}}{CH_3CH_2CHO}$$



5. From Alkynes

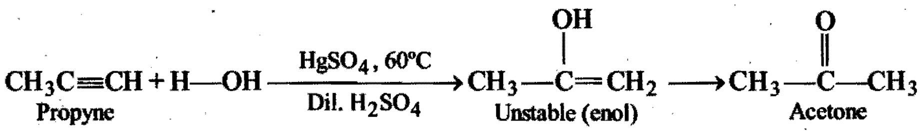
(i) By hydration : Hydration of acetylene gives acetaldehyde. Water molecule adds up to acetylene in presence of mercuric sulphate and dilute sulphuric acid at about 60°C to form an unstable enol-intermediate. It rearranges to give acetaldehyde.



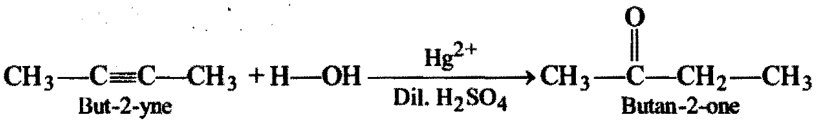
$$\underset{\text{Acetylene}}{HC\equiv CH} + HOH \xrightarrow[\text{Dil. }H_2SO_4]{HgSO_4,\ 60^\circ C} \underset{\text{Unstable}}{H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-OH} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}$$

Formaldehyde cannot be prepared by this method.

Ketones are formed on hydration of homologues of acetylene under similar conditions. Markownikoff's rule is followed in water addition.



$$\underset{\text{Propyne}}{CH_3C\equiv CH} + H-OH \xrightarrow[\text{Dil. }H_2SO_4]{HgSO_4,\ 60^\circ C} \underset{\text{Unstable (enol)}}{CH_3-\overset{OH}{\overset{|}{C}}=CH_2} \longrightarrow \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$$



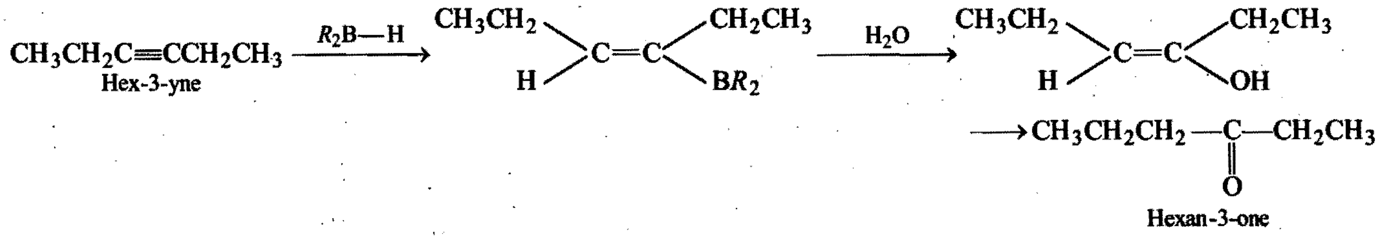
$$\underset{\text{But-2-yne}}{CH_3-C\equiv C-CH_3} + H-OH \xrightarrow[\text{Dil. }H_2SO_4]{Hg^{2+}} \underset{\text{Butan-2-one}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3}$$

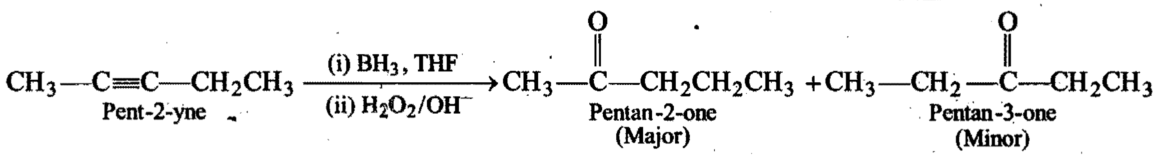
(ii) By hydroboration-oxidation : Hydroboration occurs with alkynes and the products formed are oxidised with alkaline H_2O_2. Aldehydes are formed if the triple bond is located at the end of the chain (*i.e.*, non-terminal alkynes), and in all other cases (*i.e.*, terminal alkynes) ketones are formed.

$$\underset{\text{Propyne}}{3CH_3-C\equiv CH} \xrightarrow{BH_3,\ THF} (CH_3CH=CH-)_3B \xrightarrow{H_2O_2/OH^-} \underset{\text{(Enol)}}{CH_3-CH=CHOH} \xrightarrow{\text{Tautomerises}} \underset{\text{Propanal}}{CH_3CH_2CHO}$$

$$\underset{\text{Pent-1-yne}}{CH_3CH_2CH_2C\equiv CH} \xrightarrow{R_2B-H} CH_3CH_2CH_2CH=CHBR_2 \xrightarrow{H_2O_2/OH^-} \underset{\text{(Enol)}}{CH_3CH_2CH_2CH=CHOH} \longrightarrow$$

$$\underset{\text{Pentanal}}{CH_3CH_2CH_2CH_2CHO}$$

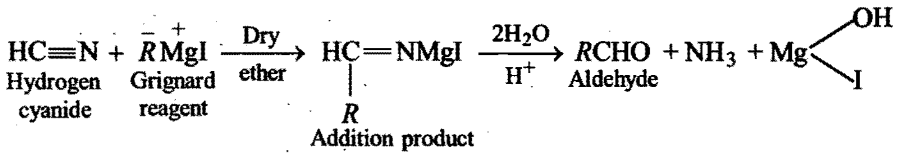




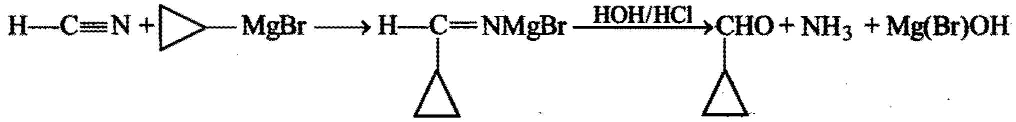
$$\underset{\text{Pent-2-yne}}{CH_3-C\equiv C-CH_2CH_3} \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } BH_3,\ THF} \underset{\substack{\text{Pentan-2-one}\\ \text{(Major)}}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3} + \underset{\substack{\text{Pentan-3-one}\\ \text{(Minor)}}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3}$$

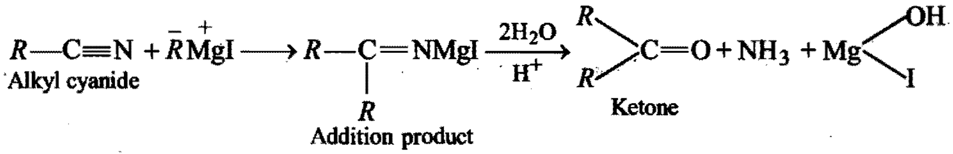
6. From Grignard Reagents

(i) On reaction with nitriles : Grignard reagents give aldehydes with hydrogen cyanide (HCN) and ketones with alkyl cyanides (*R*CN).



$$\underset{\substack{\text{Hydrogen}\\ \text{cyanide}}}{HC\equiv N} + \underset{\substack{\text{Grignard}\\ \text{reagent}}}{\overset{-}{R}\overset{+}{Mg}I} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Addition product}}{\underset{\substack{|\\ R}}{HC}=NMgI} \xrightarrow[H^+]{2H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_3 + Mg{<}^{OH}_{I}$$

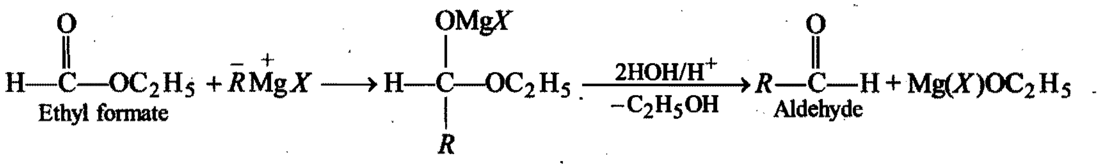




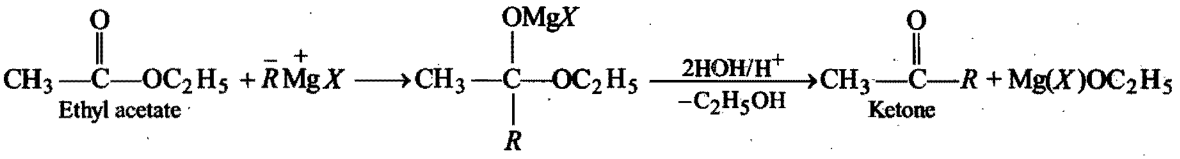
$$\underset{\text{Alkyl cyanide}}{R-C\equiv N} + \overset{-}{R}\overset{+}{Mg}I \longrightarrow \underset{\text{Addition product}}{R-\underset{\substack{|\\ R}}{C}=NMgI} \xrightarrow[H^+]{2H_2O} \underset{\text{Ketone}}{{}^{R}_{R}{>}C=O} + NH_3 + Mg{<}^{OH}_{I}$$

The alkyl radical in the aldehyde comes from the Grignard reagent and in case of ketone one of the alkyl radicals is contributed by Grignard reagent.

(ii) On reaction with esters : Formic ester is used to prepare aldehyde and all other esters give ketone on treatment with Grignard reagent.

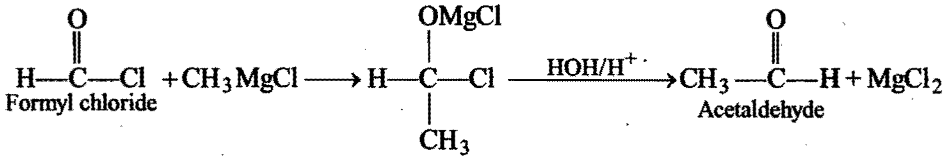


$$\underset{\text{Ethyl formate}}{H-\overset{\overset{O}{\|}}{C}-OC_2H_5} + \overset{-}{R}\overset{+}{Mg}X \longrightarrow H-\overset{\overset{OMgX}{|}}{\underset{\underset{R}{|}}{C}}-OC_2H_5 \xrightarrow[-C_2H_5OH]{2HOH/H^+} \underset{\text{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} + Mg(X)OC_2H_5$$

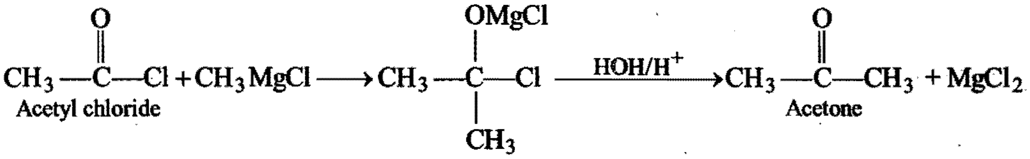


$$\underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} + \overset{-}{R}\overset{+}{Mg}X \longrightarrow CH_3-\overset{\overset{OMgX}{|}}{\underset{\underset{R}{|}}{C}}-OC_2H_5 \xrightarrow[-C_2H_5OH]{2HOH/H^+} \underset{\text{Ketone}}{CH_3-\overset{\overset{O}{\|}}{C}-R} + Mg(X)OC_2H_5$$

(iii) On reaction with acid halide and acid anhydride : Formyl chloride gives an aldehyde and all other halides give ketone.

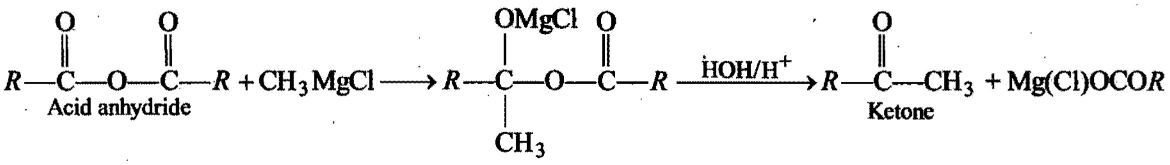


$$\underset{\text{Formyl chloride}}{H-\overset{\overset{O}{\|}}{C}-Cl} + CH_3MgCl \longrightarrow H-\overset{\overset{OMgCl}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl \xrightarrow{HOH/H^+} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + MgCl_2$$



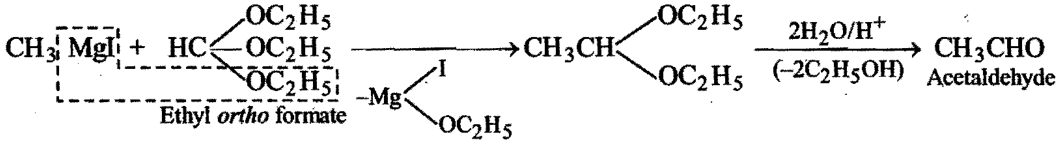
$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} + CH_3MgCl \longrightarrow CH_3-\overset{\overset{OMgCl}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl \xrightarrow{HOH/H^+} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + MgCl_2$$

But acid anhydride gives ketone only with Grignard reagent.

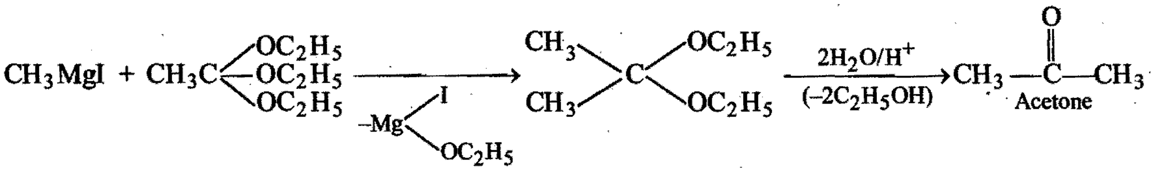


$$\underset{\text{Acid anhydride}}{R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R} + CH_3MgCl \longrightarrow R-\overset{\overset{OMgCl}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-\overset{\overset{O}{\|}}{C}-R \xrightarrow{HOH/H^+} \underset{\text{Ketone}}{R-\overset{\overset{O}{\|}}{C}-CH_3} + Mg(Cl)OCOR$$

(iv) On reaction with *ortho* ester : Ethyl *ortho* formate gives aldehyde.

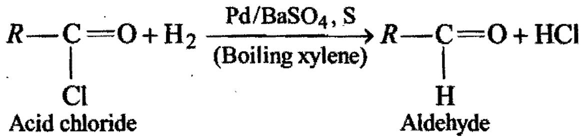


Except *ortho* formic ester, all other *ortho* esters on reaction with Grignard reagent give ketones.

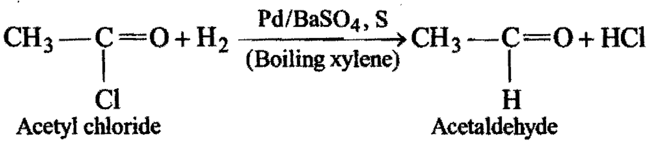


7. From acid chlorides

(i) Rosenmund's reduction (only for aldehydes) : Acid chlorides can be reduced into aldehydes with hydrogen in boiling xylene using palladium or platinum as a catalyst supported on barium sulphate. This reaction is called Rosenmund's reduction. **Ketones** cannot be prepared by this method.



$$\underset{\text{Acid chloride}}{R-\underset{\substack{|\\ Cl}}{C}=O} + H_2 \xrightarrow[\text{(Boiling xylene)}]{Pd/BaSO_4,\ S} \underset{\text{Aldehyde}}{R-\underset{\substack{|\\ H}}{C}=O} + HCl$$

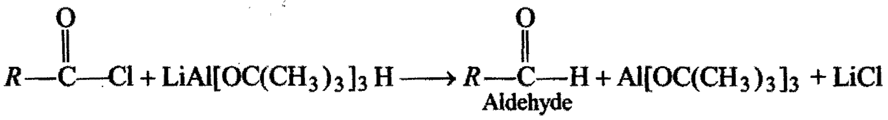


$$\underset{\text{Acetyl chloride}}{CH_3-\underset{\substack{|\\ Cl}}{C}=O} + H_2 \xrightarrow[\text{(Boiling xylene)}]{Pd/BaSO_4,\ S} \underset{\text{Acetaldehyde}}{CH_3-\underset{\substack{|\\ H}}{C}=O} + HCl$$

The function of $BaSO_4$ is to poison the catalyst at the aldehyde stage.

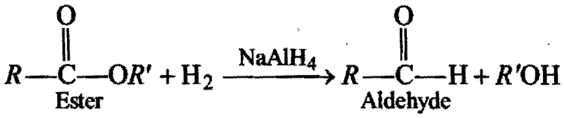
The catalyst is also poisoned to small extent by sulphur compounds to prevent further reduction of aldehydes to 1° alcohols. Generally, a small amount of quinoline and sulphur is also added.

Acid chlorides are readily reduced to aldehydes by weaker reducing agents like lithium tri-*t*-butoxyaluminium hydride, $[LiAlH(O\text{-}t\text{-}C_4H_9)_3]$ or tri *n*-butyl tin hydride, $Sn(C_4H_9)_3H$.



$$R-\overset{\overset{O}{\|}}{C}-Cl + LiAl[OC(CH_3)_3]_3H \longrightarrow \underset{\text{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} + Al[OC(CH_3)_3]_3 + LiCl$$

Sodium aluminium hydride, $NaAlH_4$ or di-isobutyl aluminium hydride **(DIBAL-H)** also reduces esters into aldehydes.



$$\underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'} + H_2 \xrightarrow{NaAlH_4} \underset{\text{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} + R'OH$$

(ii) Ketones can be prepared by the action of dialkylcadmium on acid chlorides.

$$\underset{\text{Acid chloride}}{2RCOCl} + R'_2Cd \longrightarrow 2RCOR' + CdCl_2$$

$$2CH_3COCl + (CH_3)_2Cd \longrightarrow 2CH_3COCH_3 + CdCl_2$$

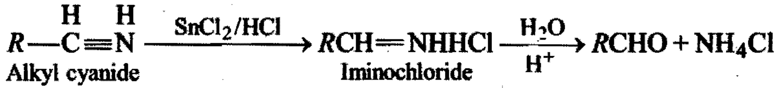
$$2CH_3COCl + (C_2H_5)_2Cd \longrightarrow \underset{\text{Butanone}}{2CH_3COC_2H_5} + CdCl_2$$

$$2C_6H_5COCl + (CH_3)_2Cd \longrightarrow \underset{\text{Acetophenone}}{2C_6H_5COCH_3} + CdCl_2$$

[Grignard reagents also react with acid chloride to form a ketone but the ketone formed reacts further to form tertiary alcohol.]

8. From nitriles (only for aldehydes)

An alkyl cyanide is dissolved in ether and reduced with stannous chloride and conc. hydrochloric acid. The iminochloride, thus, formed when hydrolysed with water yields aldehyde.



$$\underset{\text{Alkyl cyanide}}{R{-}\overset{H}{C}\equiv\overset{H}{N}} \xrightarrow{SnCl_2/HCl} \underset{\text{Iminochloride}}{RCH{=}NHHCl} \xrightarrow[H^+]{H_2O} RCHO + NH_4Cl$$

$$[SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2(H)]$$

$$\underset{\text{Acetonitrile}}{CH_3{-}C\equiv N} + 2[H] + HCl \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Acetaldimine}\\ \text{Hydrochloride}}}{CH_3CH{=}NH\cdot HCl} \xrightarrow[\text{Boiling}]{H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO} + NH_4Cl$$

Here, $H_2[SnCl_4]$ is formed, which is very strong reducing agent.

This reaction is known as **Stephen's reduction.**

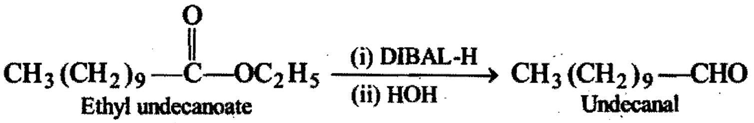
Alternatively, nitriles can be selectively reduced by di-isobutyl aluminium hydride, $[(CH_3)_2CH_2CH]_2AlH$, **[DIBAL-H]** to imines which upon hydrolysis gives aldehyde.

$$\underset{\text{Alkyl nitrile}}{R{-}C\equiv N} \xrightarrow[\text{Dry ether}]{AlH(i\text{-}Bu)_2} \underset{\text{Aldimine}}{R{-}CH{=}NH} \xrightarrow[\text{Hydrolysis}]{H_2O} \underset{\text{Aldehyde}}{R{-}CH{=}O} + NH_3$$

DIBAL-H does not reduced ethylenic double bonds and hence unsaturated nitriles can be reduced to corresponding unsaturated aldehydes by using this reagent.

$$\underset{\text{Hex-4-en-1-nitrile}}{CH_3CH{=}CHCH_2CH_2CN} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(i\text{-}Bu)_2} \underset{\text{Hex-4-en-1-al}}{CH_3CH{=}CHCH_2CH_2CHO}$$

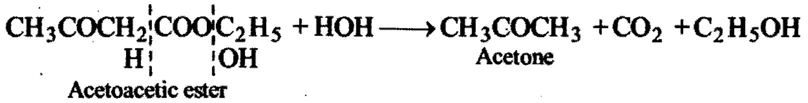
Similarly, esters are also reduced to aldehydes with **DIBAL-H.**



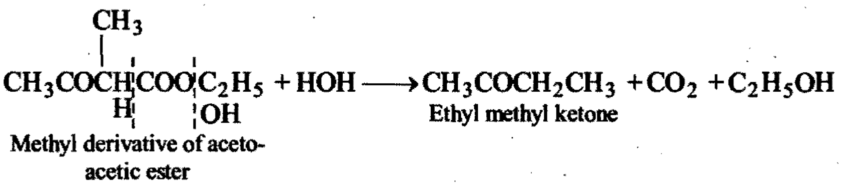
$$\underset{\text{Ethyl undecanoate}}{CH_3(CH_2)_9{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5} \xrightarrow[\text{(ii) HOH}]{\text{(i) DIBAL-H}} \underset{\text{Undecanal}}{CH_3(CH_2)_9{-}CHO}$$

9. From acetoacetic ester (only for ketones)

Ketones are prepared by the ketonic hydrolysis of acetoacetic ester or its alkyl derivatives by heating with dilute aqueous acid or dilute alcoholic solution of alkali, preferably acid solution.



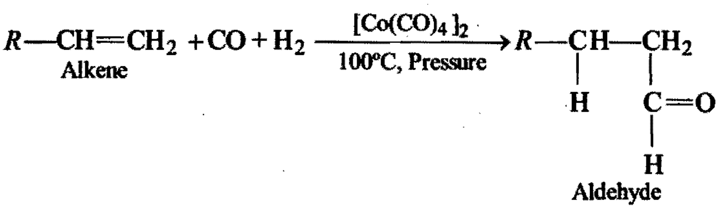
$$\underset{\text{Acetoacetic ester}}{CH_3CO\underset{H}{CH_2}\vdots CO\underset{OH}{O}\vdots C_2H_5} + HOH \longrightarrow \underset{\text{Acetone}}{CH_3COCH_3} + CO_2 + C_2H_5OH$$



$$\underset{\substack{\text{Methyl derivative of aceto-}\\ \text{acetic ester}}}{CH_3CO\underset{H}{\overset{\overset{\displaystyle CH_3}{|}}{CH}}\vdots CO\underset{OH}{O}\vdots C_2H_5} + HOH \longrightarrow \underset{\text{Ethyl methyl ketone}}{CH_3COCH_2CH_3} + CO_2 + C_2H_5OH$$

10. Oxo process (only for aldehydes)

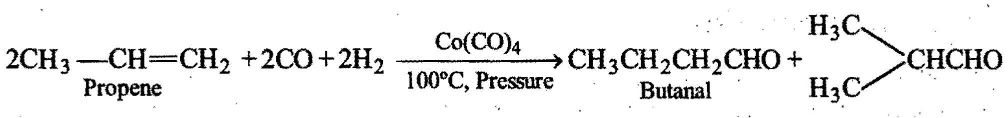
It is an industrially important method for forming aldehydes and also called **carbonylation** or **hydroformylation** reaction. Under the influence of high temperature and pressure, an alkene reacts with CO and H_2 (water gas) in presence of cobalt carbonyl which acts as a catalyst.



$$\underset{\text{Alkene}}{R{-}CH{=}CH_2} + CO + H_2 \xrightarrow[100^\circ C,\ \text{Pressure}]{[Co(CO)_4]_2} \underset{\text{Aldehyde}}{R{-}\underset{H}{\overset{}{CH}}{-}\underset{\underset{\displaystyle H}{|}}{\underset{C=O}{\underset{|}{CH_2}}}}$$

The net reaction appears to be an addition of formaldehyde through anti-Markownikoff's rule.

The reaction always gives isomeric straight chain and branched aldehyde, straight chain aldehyde is a dominant product.



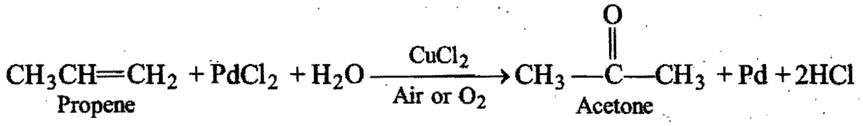
11. Wacker process

This is a recent method for the manufacturing of acetaldehyde from ethylene. Both aldehydes and ketones can be prepared by this method. Alkenes are directly oxidised to their corresponding aldehydes and ketones by treating with an acidified aqueous solution of palladium chloride and cupric chloride in presence of oxygen or air.

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + PdCl_2 + H_2O \xrightarrow[\text{Air or } O_2]{CuCl_2} \underset{\text{Acetaldehyde}}{CH_3CHO} + Pd + 2HCl$$

$$[Pd + 2HCl \longrightarrow PdCl_2 + H_2$$

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl\,]$$

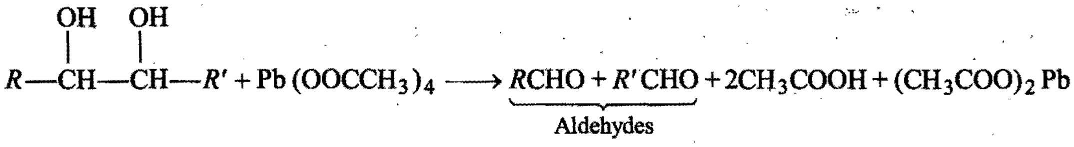


$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + PdCl_2 + H_2O \xrightarrow[\text{Air or } O_2]{CuCl_2} \underset{\text{Acetone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + Pd + 2HCl$$

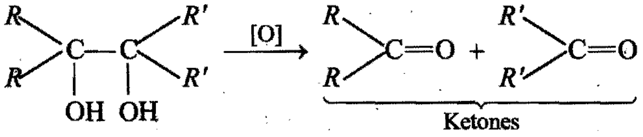
During the reaction, $PdCl_2$ is reduced to metallic Pd in presence of $CuCl_2$.

12. By oxidation of 1,2-glycols with lead tetra-acetate or periodic acid (HIO_4)

1,2-Glycols undergo cleavage to form carbonyl compounds. This reaction is not observed with non-vicinal glycols.



$$R-\overset{\overset{\displaystyle OH}{|}}{CH}-\overset{\overset{\displaystyle OH}{|}}{CH}-R' + Pb(OOCCH_3)_4 \longrightarrow \underbrace{RCHO + R'CHO}_{\text{Aldehydes}} + 2CH_3COOH + (CH_3COO)_2Pb$$



13. Aldehydes from alkyl halides

In this method **DMSO** (dimethyl sulphoxide) reagent is used. 1° alkyl halides give aldehyde, 2° alkyl halides give ketone, but 3° alkyl halides do not participate in this reaction.

$$\underset{1^\circ\text{ alkyl halide}}{R-CH_2X} + (CH_3)_2SO \longrightarrow RCHO + (CH_3)_2S + HX$$

$$\underset{2^\circ\text{alkyl halide}}{R_2-CHX} + (CH_3)_2SO \longrightarrow R_2CO + (CH_3)_2S + HX$$

$$\underset{3^\circ\text{alkyl halide}}{R_3-CX} + (CH_3)_2SO \longrightarrow \text{No product}$$

3° alkyl halides cannot undergo oxidation due to absence of reducing 'H' atom.

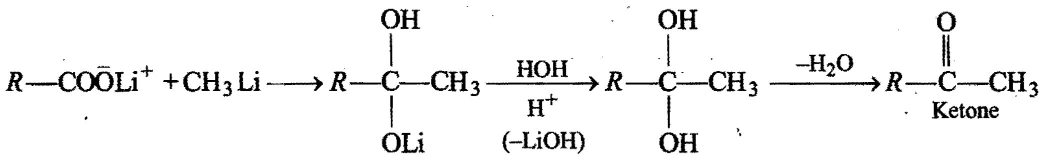
14. Aldehydes and ketones from cadmium and lithium salts

Dialkyl cadmium can be synthesized using Grignard reagents.

$$2RMgX + CdCl_2 \longrightarrow R_2Cd + MgCl_2 + MgX_2$$

$$R_2Cd + R'COCl \longrightarrow RCOR' + RCdCl$$

Similarly, aryl carbonyl compounds can also be synthesized. Lithium salt of carboxylic acid can be used to synthesize carbonyl compound.



$$R-CO\bar{O}Li^+ + CH_3Li \longrightarrow R-\underset{\underset{\displaystyle OLi}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 \xrightarrow[\substack{H^+ \\ (-LiOH)}]{HOH} R-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 \xrightarrow{-H_2O} \underset{\text{Ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

11.5 GENERAL CHARACTERISTICS

Physical : (i) The first member of the aldehyde series, formaldehyde, is a gas while next ten members of the aldehyde series are colourless volatile liquids at ordinary temperature. Ketones up to eleven carbon atoms are also colourless volatile liquids. The higher members of both the series are solids.

(ii) Lower aldehydes have unpleasant odour but the higher members have fruity odour. Ketones possess pleasant smell.

(iii) Lower members of aldehyde and ketone series are soluble in water, as they can form hydrogen bond with water. However, the solubility decreases as the molecular mass increases. The members having more than five carbon atoms are somewhat insoluble. These compounds are freely soluble in organic solvents such as alcohol, ether, etc.

(iv) The boiling points of aldehydes and ketones are comparatively higher than alkanes of similar molecular masses due to appreciable intermolecular attraction (dipole-dipole interaction) as the aldehydes and ketones are polar compounds. However, their boiling points are lower than corresponding alcohols due to absence of intermolecular hydrogen bonding. Boiling points increase with increase in molecular mass.

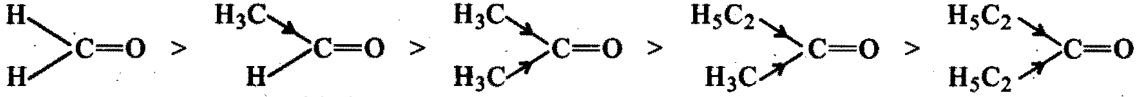
(v) Density of aldehydes and ketones is less than that of water.

Relative reactivity of aldehydes and ketones

Aldehydes are more reactive than ketones on account of the following facts:

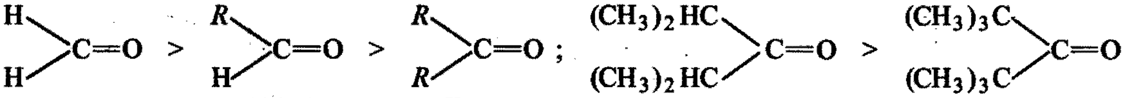
(a) Aliphatic aldehydes and ketones

(i) Inductive effect: The reactivity of the carbonyl group towards the addition reactions depends upon the magnitude of the positive charge on the carbonyl carbon atom. Hence, any substituent that increases the positive charge on the carbonyl carbon must increase its reactivity towards addition reactions. The introduction of negative group (–*I* effect) increases the reactivity while introduction of alkyl group (+*I* effect) decreases the reactivity, therefore, greater the number of alkyl groups attached to the carbonyl group and hence, lower is its reactivity towards nucleophilic addition reactions. Thus, the following decreasing order of reactivity is observed:



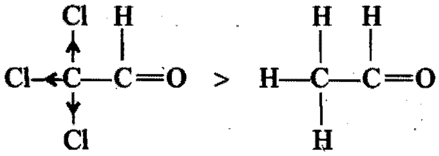
Formaldehyde Acetaldehyde Acetone Ethyl methyl ketone Diethyl ketone

(ii) Stearic effect: In formaldehyde, there is no alkyl group while in all other aldehydes there is one alkyl group so here the nucleophile attack is relatively more easy but in ketones there are two alkyl groups attached to carbonyl group and these cause hindrance, to the attacking group. This factor is also called stearic hindrance (crowding). In other words, as the hindrance increases, the reactivity decreases accordingly. Thus, the order of reactivity is:



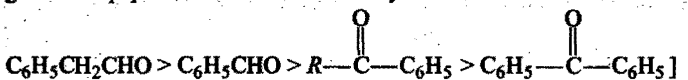
Formaldehyde Aldehyde Ketone Di-isopropyl ketone Di-*tert*-butyl ketone

The chloral is more reactive than acetaldehyde as chlorine atoms increase the positive charge on the carbonyl carbon (–*I* effect).



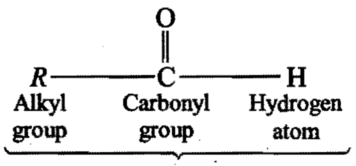
Chloral (High –*I* effect) Acetaldehyde

[Note : In aromatic carbonyl compounds, the —*R* group present in benzene ring at *o*- and *p*-position increases reactivity and + *R* group present in benzene ring at *o*- and *p*-position decreases reactivity.

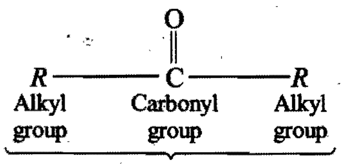


$$C_6H_5CH_2CHO > C_6H_5CHO > R-\overset{O}{\overset{\|}{C}}-C_6H_5 > C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5\,]$$

Chemical : Both aldehydes and ketones contain a carbonyl group in their structures and their chemical properties are mainly governed by this group.

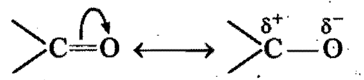


An aldehyde



A ketone

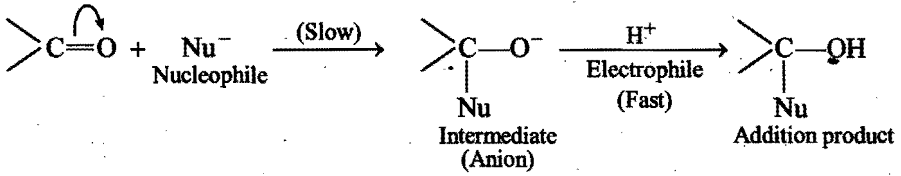
The carbonyl group is a highly reactive polar group due to resonance and permanent $-I$ effect of the negative oxygen atom, as the π-electrons of the double bond are shifted to the more electronegative oxygen atom.



The high dipole moments of methanal (2.27D) and acetone (2.85D) are in agreement with the polar nature of $>C=O$ group.

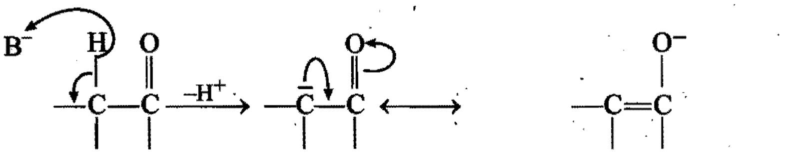
Mechanism of nucleophilic addition reactions

The carbonyl group has two active centres which can be easily attacked. The positively charged carbon is readily attacked by electron rich nucleophiles. The negatively charged oxygen is attacked by electron deficient electrophiles. **However, during addition reaction nucleophilic attack precedes the electrophilic attack because the anion produced is more stable than the cation.**



If however, the attacking nucleophiles are weak *e.g.*, ammonia and its derivatives, the reactions of aldehydes and ketones are usually carried out in weakly acidic medium. Such reactions are called **acid catalysed nucleophilic addition reactions.**

Another point of similarity between aldehydes and ketones is that hydrogen atoms attached to α-carbon are reactive (acidic in nature). The release of hydrogen from α-carbon results in the formation of carbanion which is resonance stabilised. This is called **enolate.** Its formation is facilitated by strong base.



Resonance stabilised enolate ion

The enolate ion can act as a nucleophile and can attack the carbonyl group of the other molecule, *i.e.*, giving condensation reactions. Thus, aldehydes and ketones show condensation reactions.

The common structural part of the aldehydes (except formaldehyde) and ketones is an alkyl group and the carbonyl group, hence, the reactions due to these groups are more or less similar. However, aldehydes differ from ketones in some respects due to the attachment of hydrogen to the carbonyl group.

Chemical reactions of aldehydes and ketones are, thus, studied under two broad headings:

(A) Reactions common to aldehydes and ketones, (B) Reactions in which aldehydes and ketones differ.

[A] Reactions Common to Aldehydes and Ketones

1. Substitution reactions of alkyl group (Halogenation).
2. Reactions of carbonyl group:
   (a) addition reactions, reduction reactions,
   (b) replacement of oxygen of carbonyl group.
3. Condensation reactions.

1. Substitution reactions of Alkyl Group

(i) Halogenation : The α-hydrogen atoms of the alkyl group of aldehydes and ketones can be replaced by halogen atoms when treated with halogens in presence of an acid. The moist chlorine or bromine reacts with acetaldehyde and acetone even at room temperature. For example,

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + Cl_2 \xrightarrow{CH_3COOH} \underset{\alpha\text{-Chloroacetaldehyde}}{ClCH_2CHO} + HCl$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3Cl_2 \xrightarrow{NaOH} \underset{\substack{\text{Trichloroacetaldehyde}\\ \text{(Chloral)}}}{CCl_3CHO} + 3HCl$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3COCH_3} + 3HCl$$

The excess of alkali decomposes the trihalogen compounds to give haloform.

$$CCl_3CHO + NaOH \longrightarrow CHCl_3 + HCOONa$$
$$CCl_3COCH_3 + NaOH \longrightarrow CHCl_3 + CH_3COONa$$

Similarly, when Cl_2 or Br_2 is bubbled through warm acetone, a mixture of α-halogeno derivatives is obtained.

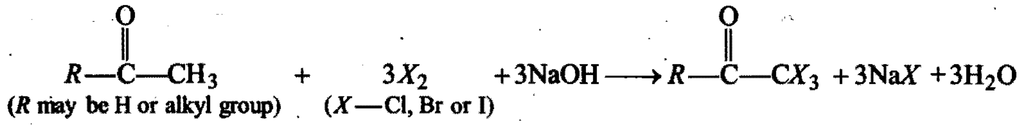
$$\underset{\text{Acetone}}{CH_3COCH_3} + Cl_2 \longrightarrow \underset{\alpha\text{-Chloroacetone}}{CH_3COCH_2Cl} + \underset{\alpha,\alpha\text{-Dichloroacetone}}{CH_3COCHCl_2}$$

$$CH_3COCH_3 + Br_2 \xrightarrow{\text{Acetic acid}} \underset{\alpha\text{-Bromoacetone}}{CH_3COCH_2Br} + HBr$$

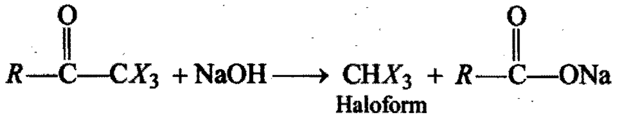
The halogenation is always facilitated by the presence of an alkali.

(ii) Haloform reaction : When an organic compound forms a haloform, CHX_3 (X is Cl, Br or I), by the action of halogen and an alkali ($NaOH + X_2$) or sodium hypohalite ($NaOX$) and the reaction is known as haloform reaction.

Acetaldehyde, acetone and methyl ketones having CH_3CO— group undergo haloform reaction. The hydrogen atoms of the methyl group are first replaced by halogen atoms. The trihalo derivative formed is then hydrolysed into haloform and an acid (containing one carbon atom less than the parent compound).



$$\underset{(R\text{ may be H or alkyl group})}{R—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3} + \underset{(X—\text{Cl, Br or I})}{3X_2} + 3NaOH \longrightarrow R—\overset{\overset{\displaystyle O}{\|}}{C}—CX_3 + 3NaX + 3H_2O$$



$$R—\overset{\overset{\displaystyle O}{\|}}{C}—CX_3 + NaOH \longrightarrow \underset{\text{Haloform}}{CHX_3} + R—\overset{\overset{\displaystyle O}{\|}}{C}—ONa$$

Note : The relative stability of carbanions is : $\bar{C}Cl_3 > \bar{C}F_3 > \bar{C}Br_3 > \bar{C}I_3$

or with sodium hypoiodite, the reaction may be written as:

$$2NaOH + I_2 \longrightarrow NaI + \underset{\text{Sod. hypoiodite}}{NaOI} + H_2O$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3NaOI \longrightarrow \underset{\text{Tri-iodoacetone}}{CH_3COCI_3} + 3NaOH$$

$$CH_3COCI_3 + NaOH \xrightarrow{\text{Hydrolysis}} \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3} + \underset{\text{Sod. acetate}}{CH_3COONa}$$

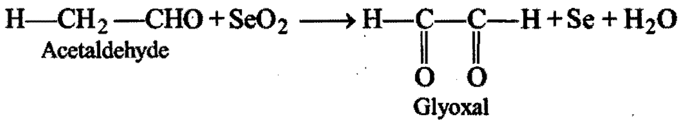
Haloform test is given by those alcohols also which on oxidation give either acetaldehyde or methyl ketones. This reaction is used as a test of CH_3CO— group. Generally, a mixture of iodine and sodium hydroxide (NaOI) is used.

$$CH_3CHO + 3I_2 \xrightarrow[\text{(Iodination)}]{NaOH} CI_3CHO + 3HI$$

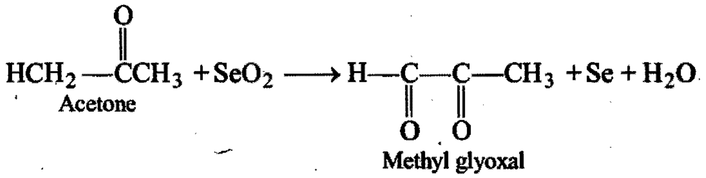
$$\underset{\text{Iodal}}{CI_3CHO} + NaOH \xrightarrow{\text{Hydrolysis}} \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3} + \underset{\text{Sod. formate}}{HCOONa}$$

The mixture is added to the compound, if yellow crystals of iodoform (CHI_3) are formed, it will confirm that $CH_3CO—$ group is present in the compound. This test is known as iodoform test. The test is given by **ethyl alcohol** and those **secondary alcohols** ($CH_3—CHOH—R$) which on oxidation give methyl ketones.

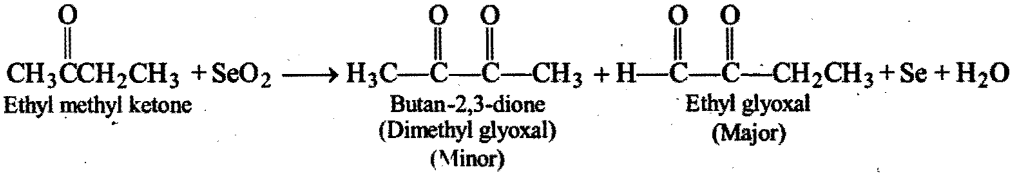
(iii) Oxidation by selenium dioxide (SeO_2) : Selenium dioxide oxidises the reactive methylene group adjacent to carbonyl group at the α-carbon to form dicarbonyl compounds. For example,



$$\underset{\text{Acetaldehyde}}{H—CH_2—CHO} + SeO_2 \longrightarrow \underset{\text{Glyoxal}}{H—\underset{\|}{\underset{O}{C}}—\underset{\|}{\underset{O}{C}}—H} + Se + H_2O$$

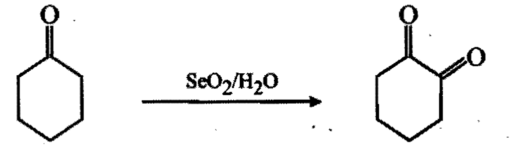


$$\underset{\text{Acetone}}{HCH_2—\overset{O}{\overset{\|}{C}}CH_3} + SeO_2 \longrightarrow \underset{\text{Methyl glyoxal}}{H—\underset{\|}{\underset{O}{C}}—\underset{\|}{\underset{O}{C}}—CH_3} + Se + H_2O$$



$$\underset{\text{Ethyl methyl ketone}}{CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3} + SeO_2 \longrightarrow \underset{\substack{\text{Butan-2,3-dione}\\\text{(Dimethyl glyoxal)}\\\text{(Minor)}}}{H_3C—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—CH_3} + \underset{\substack{\text{Ethyl glyoxal}\\\text{(Major)}}}{H—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—CH_2CH_3} + Se + H_2O$$

A reactive methylene group adjacent to $>C=O$ group at the α-carbon forming a part of the ring also oxidises to a ketonic group. For example,



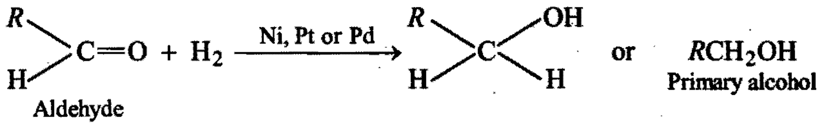
Cyclohexanone Cyclohexa-1,2-dione

2. Reactions of Carbonyl Group

(a) Addition reactions :

(i) Addition of hydrogen : Aldehydes and ketones react with hydrogen in a number of ways when different products are formed.

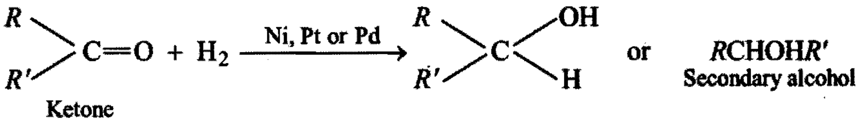
Molecular hydrogen in presence of a metallic catalyst such as Pt, Pd, or Ni reduces aldehydes and ketones into primary and secondary alcohols respectively.



Aldehyde

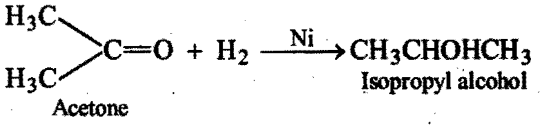
RCH_2OH
Primary alcohol

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + H_2 \xrightarrow{\text{Ni, Pt or Pd}} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$



Ketone

$RCHOHR'$
Secondary alcohol



Acetone

Isopropyl alcohol

$$>C=O \xrightarrow[\text{or LiAlH}_4 \text{ or NaBH}_4]{\text{H}_2\text{/Ni, Pt or Pd}} >CHOH$$

Reduction reactions

Reagents which produce nascent hydrogen such as Zn and CH_3COOH, sodium and water, sodium and alcohol, Zn and alcoholic NaOH, $LiAlH_4$, $NaBH_4$ or $LiBH_4$, etc., also reduce aldehydes and ketones to primary and secondary alcohols, respectively **(Reduction to alcohols).**

$$\underset{\text{Aldehyde}}{RCHO} + 2[H] \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Primary alcohol}}{RCH_2OH}$$

$$CH_3CHO + 2[H] \xrightarrow{LiAlH_4} CH_3CH_2OH$$

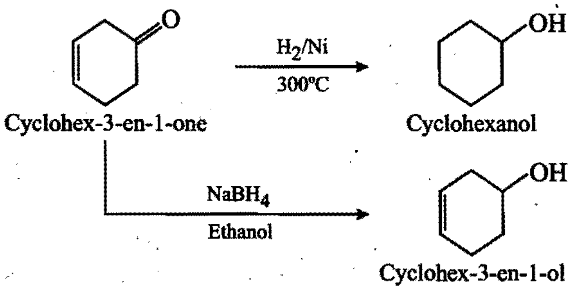
$$\underset{\text{Acrolein}}{H_2C{=}CHCHO} \xrightarrow[H^+]{LiAlH_4} \underset{\text{Allyl alcohol}}{H_2C{=}CHCH_2OH}$$

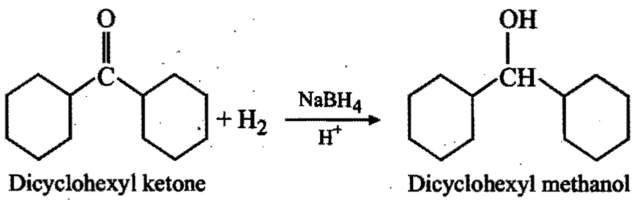
Unsaturated aldehydes can be reduced to unsaturated alcohols (1°) without affecting C=C in presence of reducing agents $LiAlH_4$ in dry ether or $NaBH_4$ in alcohol. Catalytic hydrogenation however, reduces both C=C and >C=O group simultaneously.

$$\underset{\substack{\text{But-2-en-1-al}\\\text{(Crotonaldehyde)}}}{CH_3CH{=}CHCHO} + H_2 \xrightarrow[\text{or } NaBH_4]{LiAlH_4} \underset{\substack{\text{But-2-en-1-ol}\\\text{(Crotyl alcohol)}}}{CH_3CH{=}CHCH_2OH}$$

$$CH_3CH{=}CHCHO + H_2 \xrightarrow{H_2/Ni} \underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH}$$

$$\underset{\substack{\text{Cinnamaldehyde}\\\text{(3-Phenylprop-2-en-1-al)}}}{C_6H_5CH{=}CHCHO} + H_2 \xrightarrow[\text{or } NaBH_4]{LiAlH_4} \underset{\substack{\text{Cinnamyl alcohol}\\\text{(3-Phenylprop-2-en-1-ol)}}}{C_6H_5CH{=}CHCH_2OH}$$

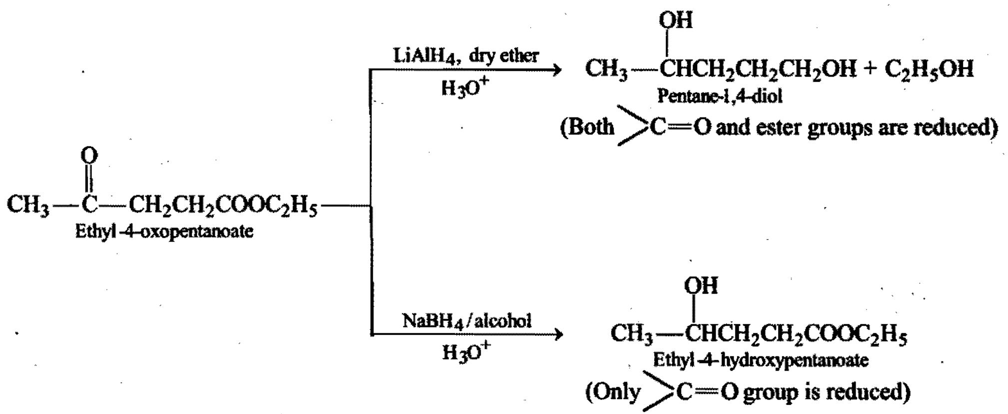




$NaBH_4$ has also the similar function.

$$\underset{\text{Ketone}}{RCOR'} + 2[H] \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Secondary alcohol}}{RCHOHR'}$$

Note: $LiAlH_4$ reduces acid chlorides and esters to alcohol but $NaBH_4$ does not reduce acid chlorides and esters to alcohol.



(Both $>C=O$ and ester groups are reduced)

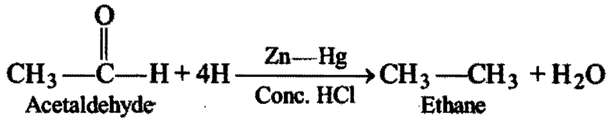
(Only $>C=O$ group is reduced)

Reduction to hydrocarbons : The carbonyl ($>C=O$) group of aldehydes and ketones can be reduced to methylene ($>CH_2$) group to form hydrocarbons by the following methods.

$$>C=O \xrightarrow{\text{Reduction}} >CH_2$$

Using reducing agents such as:
(i) Zn-Hg/Conc. HCl—**Clemmensen's reduction**
(ii) HI/Red phosphorus at 150°C
(iii) $H_2N\text{-}NH_2$/KOH at 180-200°C—**Wolff-Kishner reduction**

Clemmensen's reduction : Aldehydes and ketones are converted into alkanes when treated with amalgamated zinc and concentrated HCl. This reaction is known as **Clemmensen's reduction.**



$$\underset{\text{Acetaldehyde}}{CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—H} + 4H \xrightarrow[\text{Conc. HCl}]{\text{Zn—Hg}} \underset{\text{Ethane}}{CH_3—CH_3} + H_2O$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 4H \xrightarrow[\text{Conc. HCl}]{\text{Zn—Hg}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$

Clemmensen's reduction is not applicable to keto alcohols (containing acid sensitive —OH group), α-hydroxy ketones, unsaturated cyclic ketones and high molecular weight substrates in which activated Zn and gaseous HCl in organic solvents (ether or acetic anhydride) can be used.

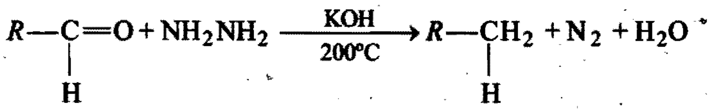
Clemmensen's reduction may also be carried out with Zn-Hg and DCl in D_2O in place of HCl in H_2O.

The same conversion ($>C=O \longrightarrow >CH_2$) can be made by heating aldehydes and ketones with red phosphorus and conc. hydroiodic acid or basic solution of hydrazine.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 4HI \xrightarrow[150^\circ C]{\text{Red P}} \underset{\text{Ethane}}{CH_3—CH_3} + H_2O + 2I_2$$

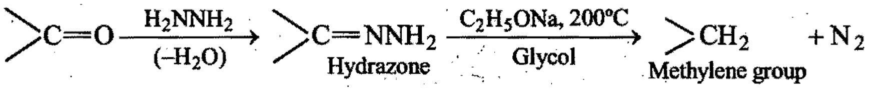
$$\underset{\text{Acetone}}{CH_3COCH_3} + 4HI \xrightarrow[150^\circ C]{\text{Red P}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + 2I_2$$

Wolff-Kishner reduction : Aldehydes and ketones are conveniently reduced to hydrocarbons in the presence of excess of hydrazine and strong base, KOH or potassium *tert.* butoxide on heating. The best solvent for the reaction is diethylene glycol ($HOCH_2CH_2OCH_2CH_2OH$). This reaction is also called **Hung-Milnon reaction.**

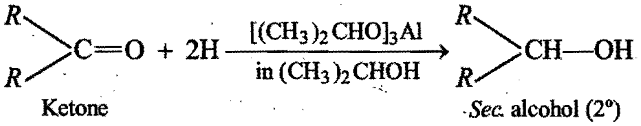


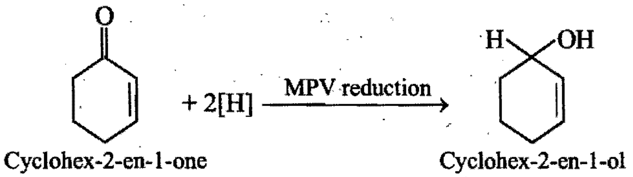
$$R—\underset{\underset{\displaystyle H}{|}}{C}=O + NH_2NH_2 \xrightarrow[200^\circ C]{\text{KOH}} R—\underset{\underset{\displaystyle H}{|}}{C}H_2 + N_2 + H_2O$$

This reaction can be carried with sodium ethoxide or NaOH at hight temperature. Besides hydrazones, phenylhydrazones and semicarbazones respond to this reaction.

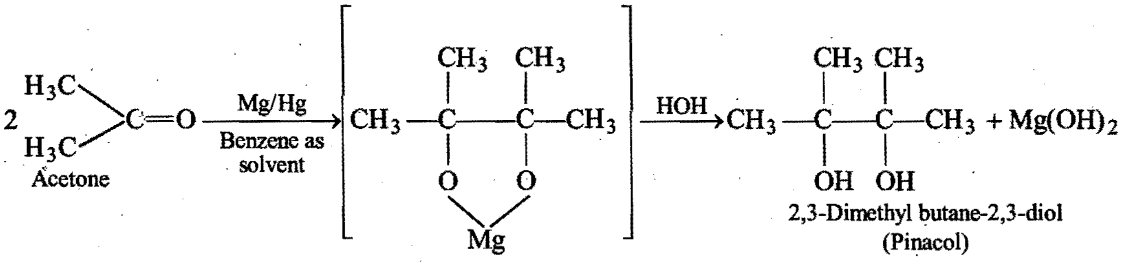


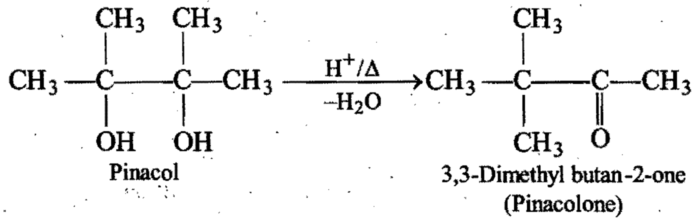
Ketones can also be reduced to secondary alcohols with aluminium isopropoxide in propan-2-ol solution and this is **Meerwein-Ponndorf-Verley (MPV) reduction.** The mechanism of this reaction is the reverse of oppenauer oxidation.



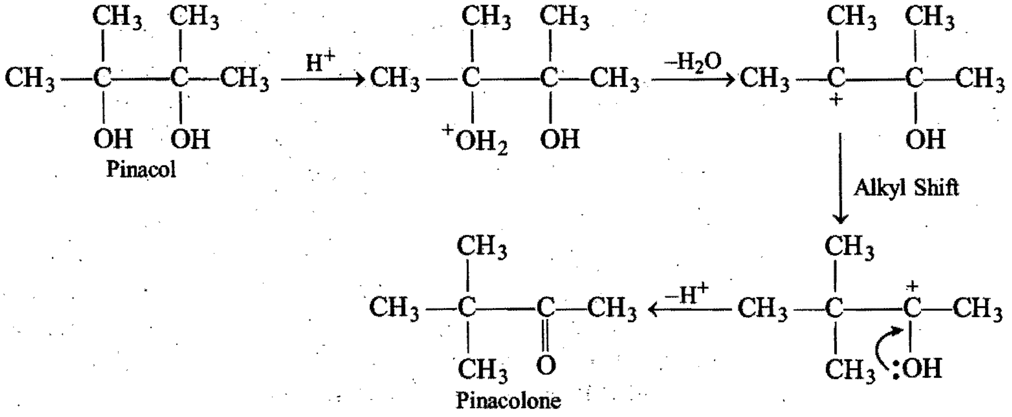


Bimolecular reduction or Pinacol formation : Two molecules of ketones undergo reduction in the presence of Mg/Hg to form pinacol. Upon treatment with mineral acids, pinacol is converted into pinacolone. This transformation involves dehydration and rearrangement called **pinacol-pinacolone rearrangement.**





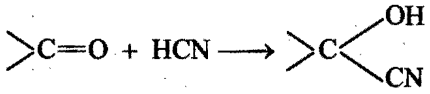
Mechanism : This reaction involves : 1-Protonation, 2-deprotonation, 3-alkyl shift and 4-dehydration.

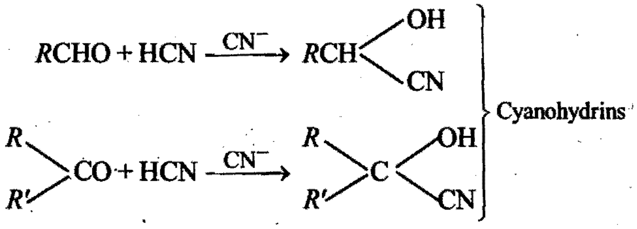


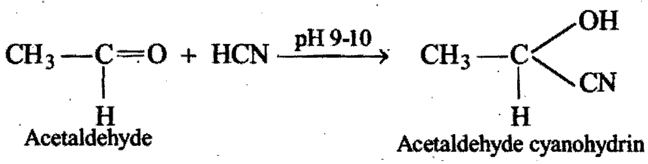
Migratory attitude of alkyl group lies in following sequence:

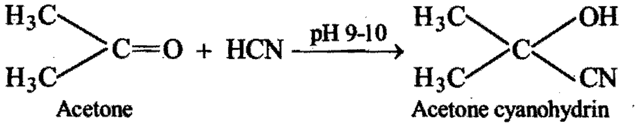
$$C_6H_5— > (CH_3)_3C— > (CH_3)_2CH— > —C_2H_5 > —CH_3$$

(ii) Addition of hydrogen cyanide : Aldehydes and ketones react with hydrogen cyanide (KCN or NaCN + dil. H_2SO_4) to form cyanohydrins. This reaction occurs very slowly with pure HCN. Therefore, it is catalysed at a pH 9-10 in presence of a base **(Nucleophilic addition reaction).**

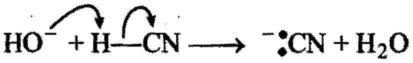






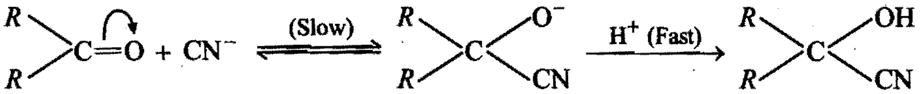


HCN is too weak an acid, to add directly to a $>C{=}O$ group. It requires slightly alkaline reaction conditions such as those found in NaCN-HCN buffer solution. In this way, the concentration of CN^- ion is increased and the CN^- ion thus generated being a stronger nucleophile readily adds to carbonyl carbon to yield corresponding cyanohydrin.



$$HO^- + H{-}CN \longrightarrow {}^-{:}CN + H_2O$$

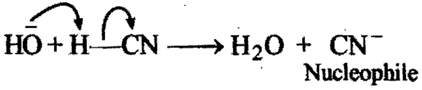
Addition of CN^- is in a slow step (rate determining step) and hence, nucleophilic addition.



Mechanism

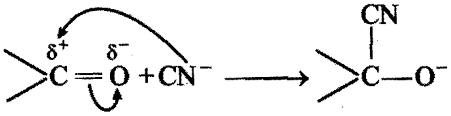
Addition of hydrogen cyanide to $>C{=}O$ group involves the following steps:

Step 1. The hydrogen cyanide interacts with the base to form nucleophile, *i.e.*, cyanide ion,

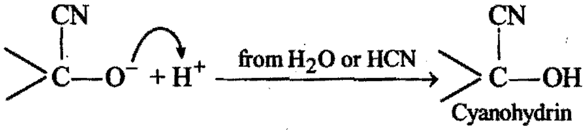


$$H\ddot{O} + H{-}CN \longrightarrow H_2O + \underset{\text{Nucleophile}}{CN^-}$$

Step 2. The nucleophile attacks the carbonyl carbon to form an anion,

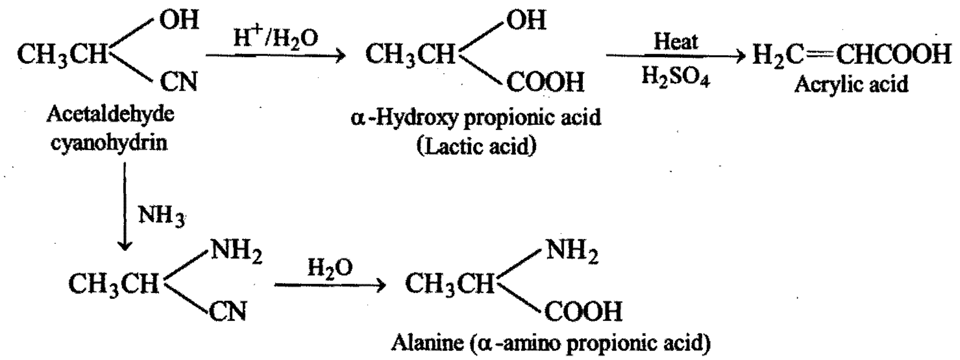


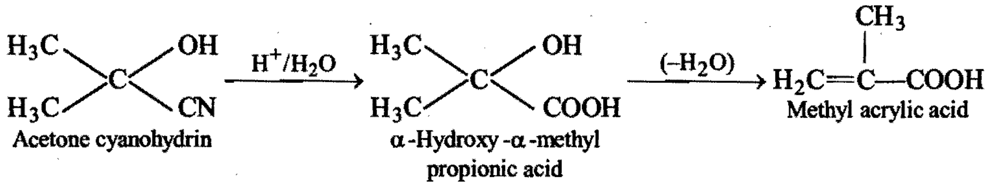
Step 3. The proton from the solvent (usually water) combines with the anion to form cyanohydrin (the addition product).



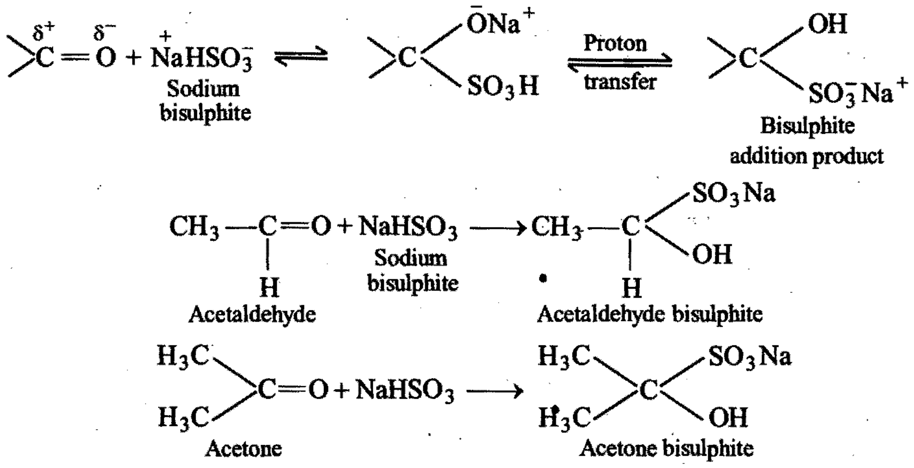
Note: All aldehydes form cyanohydrins but in ketones, only acetone, butanone, pentan-3-one and pinacolone form cyanohydrins.

The cyanohydrins are good synthetic reagents as they can be converted into α-hydroxy acids and α-amino acids (Strecker's synthesis).





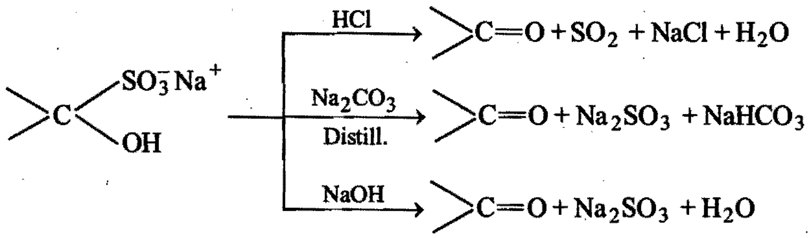
(iii) Addition of sodium bisulphite ($NaHSO_3$) : Crystalline solid derivatives are formed when aldehydes and aliphatic methyl ketones are shaken with saturated aqueous solution of sodium bisulphite.



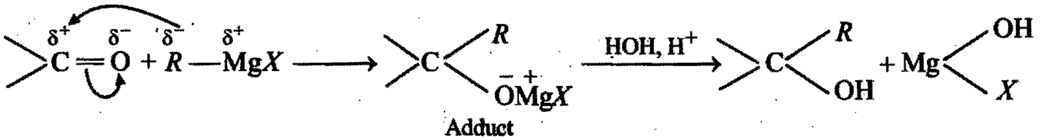
Note : All ketones do not undergo this reaction. Only methyl ketones form addition products with sodium bisulphite.

These bisulphite compounds on heating with NaCN yield cyanohydrins.

On reacting the bisulphite derivative with dilute HCl or alkali, the original aldehyde or ketone is regenerated. Hence, this property is used in the separation and purification of aldehydes and ketones.

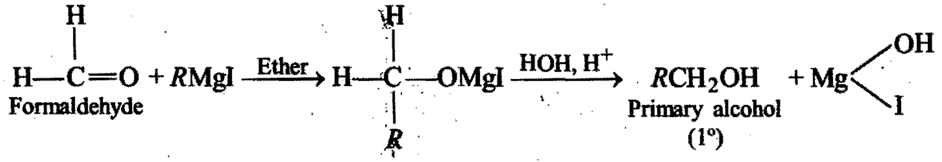


(iv) Addition of Grignard reagent : In these reactions, the alkyl (*R*—) group of Grignard reagent is transferred to the carbon atom of the carbonyl group and Mg*X* adds to oxygen to form an addition product (Adduct) which on hydrolysis decomposes to yield alcohol (1°, 2° or 3° depending upon the nature of carbonyl compound).



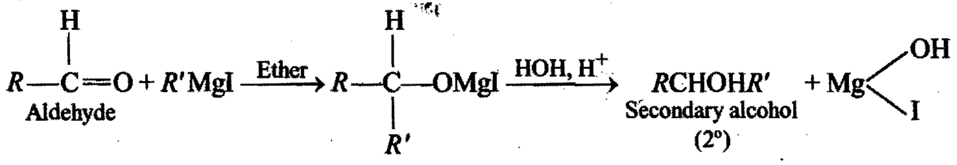
$$\overset{\delta^+}{>C}=\overset{\delta^-}{O}+\overset{\delta^-}{R}-\overset{\delta^+}{MgX}\longrightarrow \underset{\text{Adduct}}{>C\begin{smallmatrix}R\\ \overset{-}{O}\overset{+}{Mg}X\end{smallmatrix}}\xrightarrow{HOH,\,H^+}>C\begin{smallmatrix}R\\ OH\end{smallmatrix}+Mg\begin{smallmatrix}OH\\ X\end{smallmatrix}$$

For example, formaldehyde forms a primary alcohol.



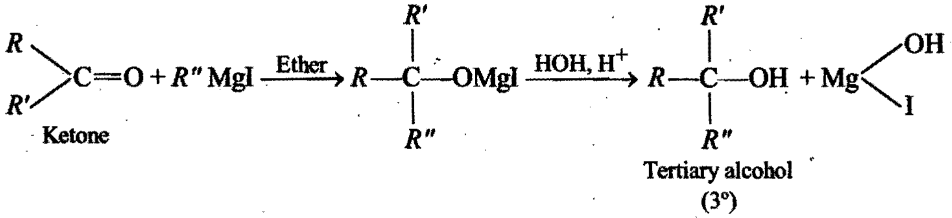
$$\underset{\text{Formaldehyde}}{H-\overset{\overset{H}{|}}{C}=O}+RMgI\xrightarrow{\text{Ether}}H-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-OMgI\xrightarrow{HOH,\,H^+}\underset{\substack{\text{Primary alcohol}\\ (1^\circ)}}{RCH_2OH}+Mg\begin{smallmatrix}OH\\ I\end{smallmatrix}$$

Higher aldehydes give secondary alcohols.



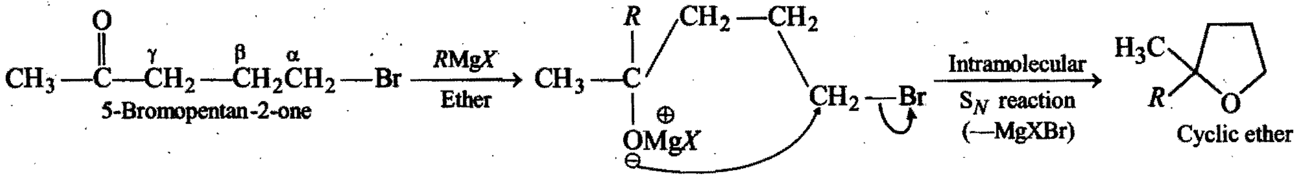
$$\underset{\text{Aldehyde}}{R-\overset{\overset{H}{|}}{C}=O}+R'MgI\xrightarrow{\text{Ether}}R-\overset{\overset{H}{|}}{\underset{\underset{R'}{|}}{C}}-OMgI\xrightarrow{HOH,\,H^+}\underset{\substack{\text{Secondary alcohol}\\ (2^\circ)}}{RCHOHR'}+Mg\begin{smallmatrix}OH\\ I\end{smallmatrix}$$

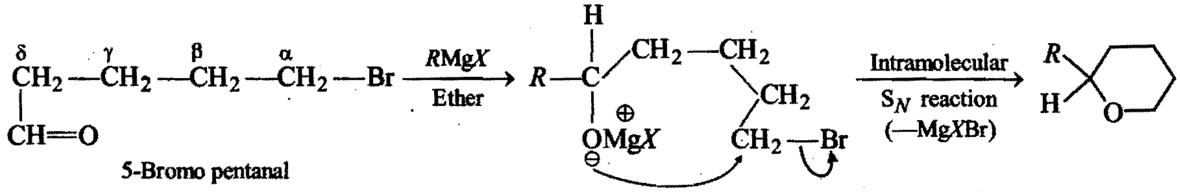
Ketones give tertiary alcohols.



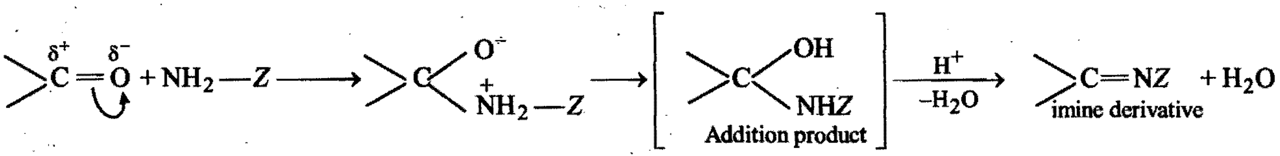
$$\underset{\text{Ketone}}{\begin{smallmatrix}R\\ R'\end{smallmatrix}>C=O}+R''MgI\xrightarrow{\text{Ether}}R-\overset{\overset{R'}{|}}{\underset{\underset{R''}{|}}{C}}-OMgI\xrightarrow{HOH,\,H^+}\underset{\substack{\text{Tertiary alcohol}\\ (3^\circ)}}{R-\overset{\overset{R'}{|}}{\underset{\underset{R''}{|}}{C}}-OH}+Mg\begin{smallmatrix}OH\\ I\end{smallmatrix}$$

γ or δ-Halogenated carbonyl compounds on treatment with Grignard reagent form a five or six-membered cyclic ether. For example,





(b) Replacement of carbonyl oxygen : Some ammonia derivatives (NH_2—***Z***), *i.e.*, hydroxylamine (NH_2—**OH**), hydrazine (H_2N—$\mathbf{NH_2}$), phenylhydrazine (H_2N—$\mathbf{NHC_6H_5}$) and semicarbazide (H_2N—$\mathbf{NHCONH_2}$), etc., react with aldehydes and ketones in weak acidic medium (pH = 3-4) to form compounds containing carbon nitrogen double bond (C=N) with elimination of water molecule.



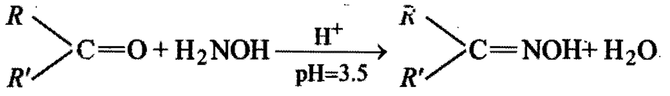
$$\overset{\delta^+}{>C}=\overset{\delta^-}{O}+NH_2-Z\longrightarrow>C\begin{smallmatrix}O^-\\ \overset{+}{N}H_2-Z\end{smallmatrix}\longrightarrow\underset{\text{Addition product}}{\left[>C\begin{smallmatrix}OH\\ NHZ\end{smallmatrix}\right]}\xrightarrow[-H_2O]{H^+}\underset{\text{imine derivative}}{>C=NZ}+H_2O$$

(where Z = OH, NH_2, NHC_6H_5, $NHCONH_2$, etc.). These derivatives are crystalline solids and used for the identification of carbonyl compounds.

(i) Reaction with hydroxylamine ($\mathbf{NH_2OH}$) : Aldehydes and ketones react with hydroxylamine (at pH = 3.5) to form **oximes** with the evolution of water.

$$RCH{=}O + H_2\ddot{N}OH \xrightarrow{H^+} RCH{=}NOH + H_2O$$

Aldehyde Aldoxime

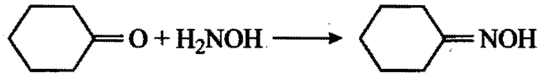

Ketone Ketoxime

$$CH_3CHO + H_2NOH \xrightarrow[pH=3.5]{H^+} CH_3CH{=}NOH + H_2O$$

Acetaldehyde Acetaldoxime

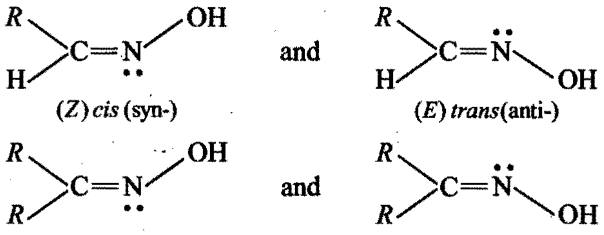
$$(CH_3)_2C{=}O + H_2NOH \xrightarrow[pH=3.5]{H^+} (CH_3)_2C{=}NOH + H_2O$$

Acetone Acetone oxime


Cyclohexanone Cyclohexanoneoxime

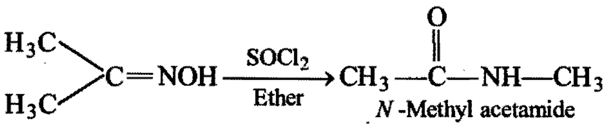
These oximes can be hydrolysed back to aldehydes and ketones by reaction with acids.

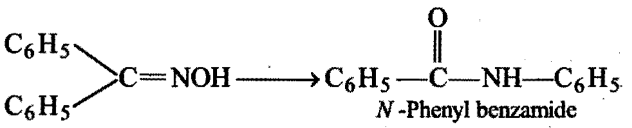
The reaction of H_2NOH with a symmetrical ketone, $R_2C{=}O$ gives one oxime, but the two isomeric oximes may form from the reaction of an aldehyde or non-symmetrical ketone because the rotation about the pi-bond in $>C{=}N$ is not free and therefore, geometrical isomerism is possible when the two groups on the carbonyl carbon are different. For example,



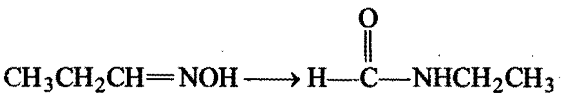
Oximes are solids having specific melting points, so these are used for the separation and identification of aldehydes and ketones.

Beckmann rearrangement : Ketoximes on treatment with acid catalyst such as conc. H_2SO_4, PCl_5, H_3PO_4, $SOCl_2$ or $C_6H_5SO_2Cl$, etc., undergo Beckmann rearrangement to form a **substituted amide.** For example,

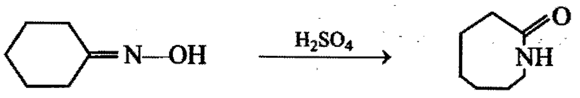

Acetoxime N-Methyl acetamide


Benzophenone oxime N-Phenyl benzamide

This rearrangement is intramolecular and involves 1,2-shift. It has been demonstrated that it is always the anti —R group that migrates in the Beckmann rearrangement.


$$CH_3CH_2CH{=}NOH \longrightarrow H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NHCH_2CH_3$$

Propionaldoxime N-Ethyl formamide


Cyclohexanoneoxime Caprolactum

(ii) Reaction with hydrazine (NH_2NH_2) : Aldehydes and ketones form **hydrazones** with hydrazine (at pH = 3.5). A water molecule is eliminated.

$$\underset{\text{Acetaldehyde}}{CH_3CH{=}O} + H_2NNH_2 \xrightarrow{H^+} \underset{\text{Acetaldehyde hydrazone}}{CH_3CH{=}NNH_2} + H_2O$$

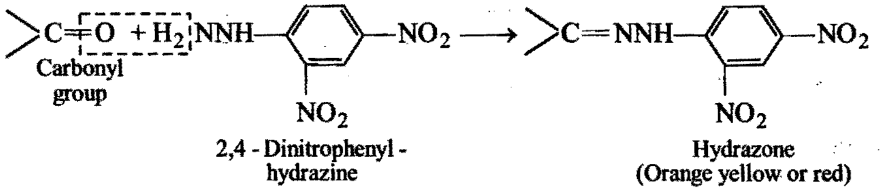
$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + H_2NNH_2 \xrightarrow{H^+} \underset{\text{Acetone hydrazone}}{(CH_3)_2C{=}NNH_2} + H_2O$$

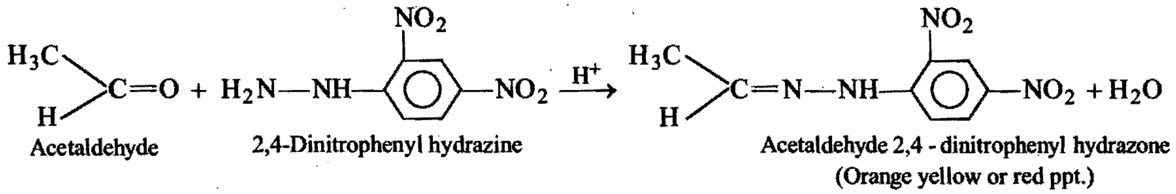
(iii) Reaction with phenylhydrazine ($H_2NNHC_6H_5$) : Aldehydes and ketones react with phenylhydrazine (at pH = 3.5) and form corresponding **phenylhydrazones.**

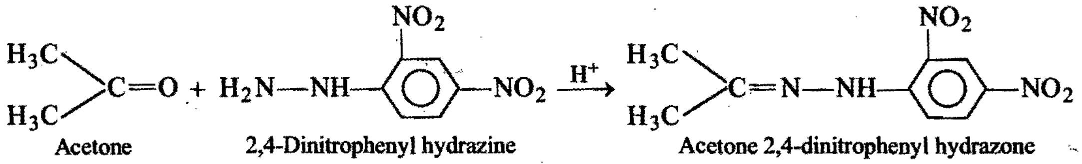
$$\underset{\text{Acetaldehyde}}{CH_3CH{=}O} + \underset{\text{Phenylhydrazine}}{H_2N{-}NHC_6H_5} \xrightarrow{H^+} \underset{\text{Acetaldehyde phenylhydrazone}}{CH_3CH{=}NNHC_6H_5} + H_2O$$

$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + H_2N{-}NHC_6H_5 \xrightarrow{H^+} \underset{\text{Acetone phenylhydrazone}}{(CH_3)_2C{=}NNHC_6H_5} + H_2O$$

Substituted phenylhydrazines like **2,4-dinitrophenylhydrazine (DNP, Brady's reagent)** react similarly with carbonyl compounds to form the corresponding hydrazones. These hydrazones have specific melting points and hence used for the identification of aldehydes and ketones.







(iv) Reaction with semicarbazide ($H_2NNHCONH_2$) : Aldehydes and ketones combine with semicarbazide to form crystalline compounds called semicarbazones.

$$\underset{\text{Acetaldehyde}}{CH_3CH{=}O} + \underset{\text{Semicarbazide}}{H_2NNHCONH_2} \xrightarrow{H^+} \underset{\text{Acetaldehyde semicarbazone}}{CH_3CH{=}NNHCONH_2} + H_2O$$

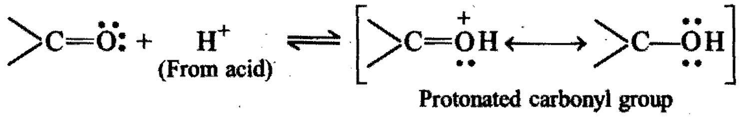
$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + H_2NNHCONH_2 \xrightarrow{H^+} \underset{\text{Acetone semicarbazone}}{(CH_3)_2C{=}NNHCONH_2} + H_2O$$

Control of pH during addition of ammonia derivatives to aldehydes and ketones.

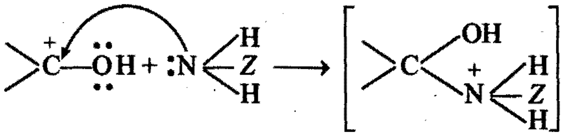
The reaction of ammonia derivatives to aldehydes and ketones is catalysed by acids. In acidic medium, the carbonyl oxygen gets protonated. Due to the presence of positive charge on the carbonyl carbon, the weak nucleophiles like ammonia derivatives attack the carbonyl group very easily.

Mechanism : The addition-elimination reactions with ammonia derivatives (NH_2—Z) are carried out in **weakly acidic medium (pH = 3-4).**

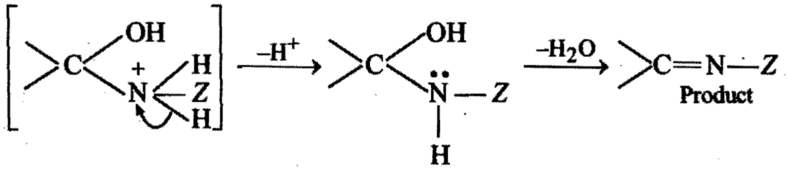
Step 1. In acidic medium, the carbonyl oxygen gets protonated.



Step 2. In ammonia derivative, the nitrogen atom has a lone pair of electrons (Nucleophile) attack the positively charged carbonyl carbon and results the positive charge on nitrogen atom.

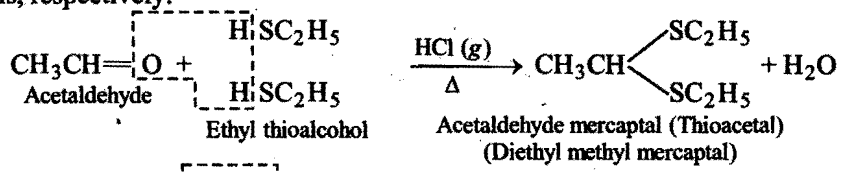


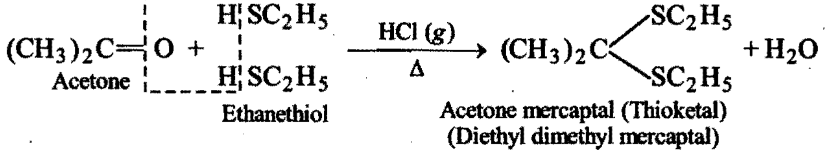
Step 3. The unstable intermediate loses a proton, H^+ and water molecule to form a stable product (imines).

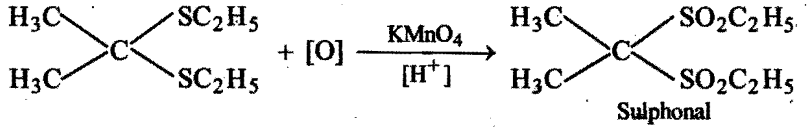


Now, if the medium is **highly acidic** then the ammonia derivatives being basic in nature, may form their respective salts ($\overset{+}{N}H_3ZX^-$) which cannot act as nucleophiles and consequently, the reaction does not occur. However, if the medium is basic, the protonation of carbonyl group will not occur and hence, the reaction is not favoured. Thus, to carry out such reactions we have to properly control the pH of the medium. The optimum pH of the medium is around 3.5.

(v) Reaction with thioalcohols : Aldehydes and ketones combine with thioalcohols more rapidly than alcohols and form thioacetals and thioketals, respectively.

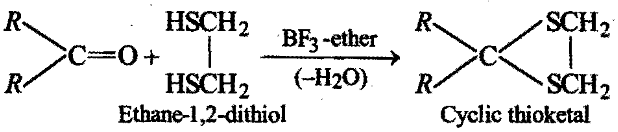




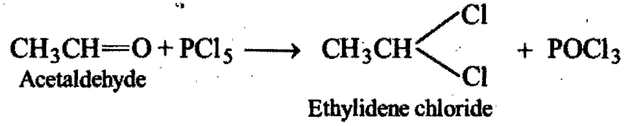


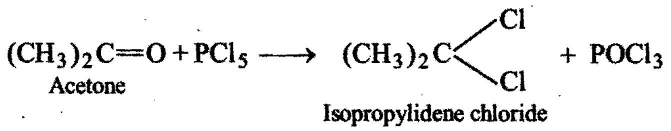
These sulphur derivatives of carbonyl compounds are used as sedative sulpha drug.

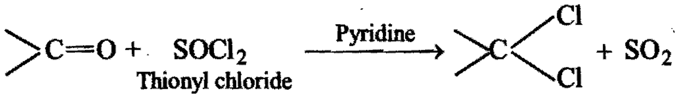
Alkane dithiol reacts with both aldehydes and ketones in presence of BF_3-ether to give corresponding cyclic thioacetals **(dithianes)** and cyclic thioketals.



(vi) Reaction with phosphorus pentachloride (PCl_5) or thionyl chloride ($SOCl_2$) : Oxygen atom of the carbonyl group is replaced by two chlorine atoms to form gem-dihalides. For example,

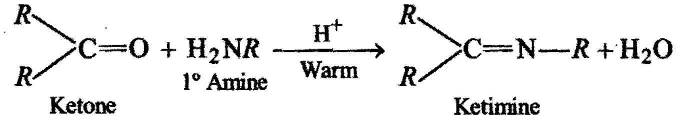






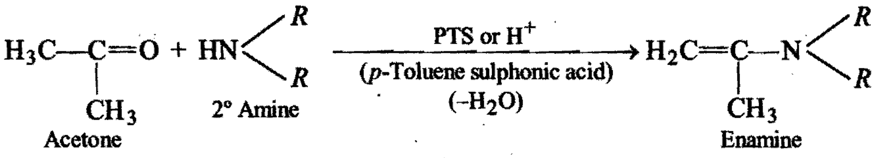
(vii) Reaction with primary amines (R—NH_2) : Aldehydes and ketones react with primary (1°) amines to form azomethines (imines) known as **Schiff's base.**

$$\underset{\text{Aldehyde}}{R{-}CH{=}O} + \underset{\text{Alkylamine (1°)}}{H_2NR} \xrightarrow[\Delta]{H^+} \underset{\substack{\text{Aldimine}\\\text{(A Schiff's base)}}}{RCH{=}N{-}R} + H_2O$$



Schiff's base is pink in colour and it can be decolourised by passing SO_2 gas. The colourless solution obtained is known as **Schiff's reagent.**

(viii) Reaction with secondary amines (R_2NH) : Aldehydes and ketones that have at least one α-hydrogen reacts with secondary amines to form **enamines** (α, β-unsaturated tertiary amine).



In enamines, the double bond is present between carbonyl carbon and α-carbon of carbonyl compound part.

3. Condensation Reactions

Aldol condensation (Reactions involving α-hydrogen) : It is a chemical reaction in which two or more molecules of same or different carbonyl compounds containing α-hydrogen atom unite together in the presence of dilute bases such as NaOH, $Ba(OH)_2$ or K_2CO_3, etc., to form compounds called aldols. The term aldol is derived from the combination of words aldehyde and alcohol, the two functional groups present in the product. In such condensation, the hydrogen of one molecule in α-position with respect to the carbonyl group enters into combination with the oxygen of the carbonyl group of the other molecule forming a hydroxy group. So, aldol condensation is an important reaction based on the acidity of α-hydrogens of aldehydes and ketones.

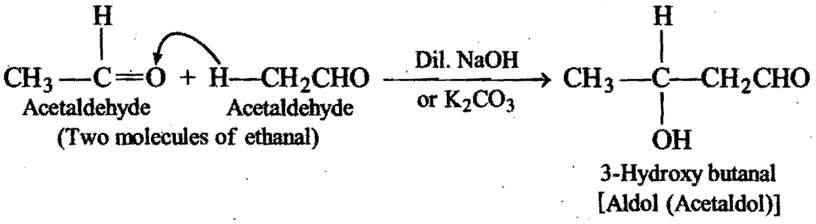
Characteristics of Aldol Condensation

(i) This reaction may take place between (a) same or different aldehydes, (b) an aldehyde and a ketone, and (c) same or different ketones. The carbonyl compound must contain an α-hydrogen atom which is involved in aldol condensation in presence of dilute alkali (dil. NaOH, Na_2CO_3 or $Ba(OH)_2$, etc.). However, formaldehyde though contains no α-hydrogen atom yet undergoes abnormal aldol condensation in presence of lime water.

(ii) New carbon to carbon linkage is formed (an irreversible process).

(iii) The condensation product, *i.e.*, aldol, loses a molecule of water to form unsaturated aldehyde or ketone.

Examples : (i) Acetaldehyde undergoes aldol condensation in presence of dilute caustic alkali or potassium carbonate to form β-hydroxy butyraldehyde or aldol.

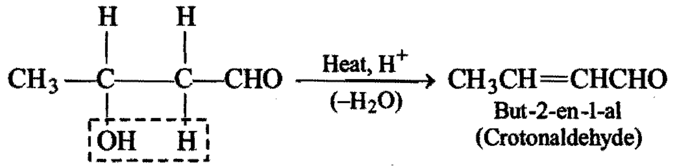


$$\underset{\text{Acetaldehyde}}{CH_3{-}\overset{\overset{\displaystyle H}{|}}{C}{=}O} + \underset{\text{Acetaldehyde}}{H{-}CH_2CHO} \xrightarrow[\text{or } K_2CO_3]{\text{Dil. NaOH}} CH_3{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}{-}CH_2CHO$$

(Two molecules of ethanal)

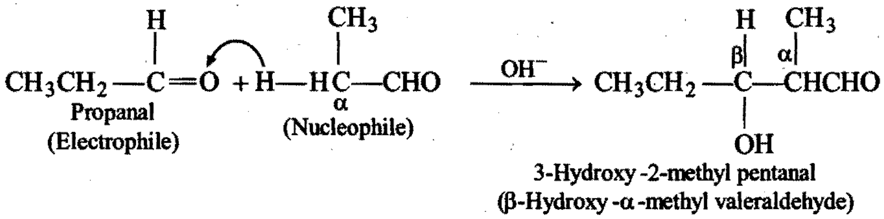
3-Hydroxy butanal
[Aldol (Acetaldol)]

On heating with dilute acids, aldol loses a molecule of water to give α,β-unsaturated aldehyde (Crotonaldehyde).



$$CH_3-CH(OH)-CH_2-CHO \xrightarrow[(-H_2O)]{\text{Heat, } H^+} CH_3CH=CHCHO$$

But-2-en-1-al
(Crotonaldehyde)

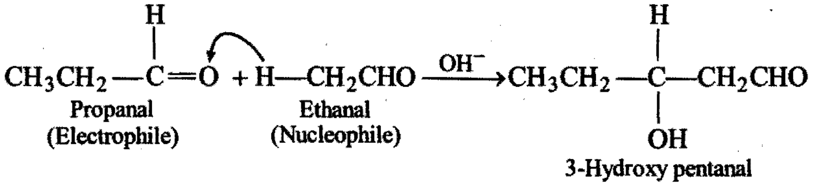


$$CH_3CH_2-CH=O + H-CH(CH_3)-CHO \xrightarrow{OH^-} CH_3CH_2-CH(OH)-CH(CH_3)CHO$$

Propanal (Electrophile) + Propanal (Nucleophile)

3-Hydroxy-2-methyl pentanal
(β-Hydroxy-α-methyl valeraldehyde)

The aldol condensation of two molecules of same aldehydes or ketones is called **self condensation.** It can also takes place between two different aldehydes or ketones or between one aldehyde and one ketone is called **crossed (mixed) aldol condensation.**

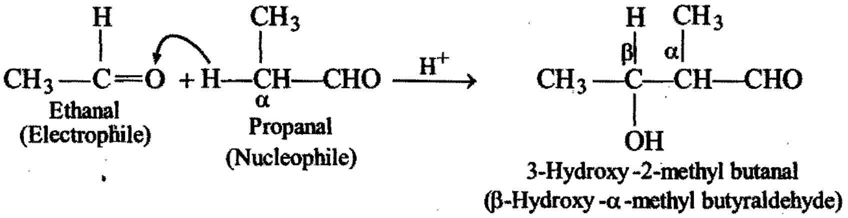


$$CH_3CH_2-CH=O + H-CH_2CHO \xrightarrow{OH^-} CH_3CH_2-CH(OH)-CH_2CHO$$

Propanal (Electrophile) + Ethanal (Nucleophile)

3-Hydroxy pentanal

In presence of base, the α-hydrogen atom in lower aldehyde is more acidic and so migrates, while in presence of an acid, the α-hydrogen atom in higher aldehyde is more basic.



$$CH_3-CH=O + H-CH(CH_3)-CHO \xrightarrow{H^+} CH_3-CH(OH)-CH(CH_3)-CHO$$

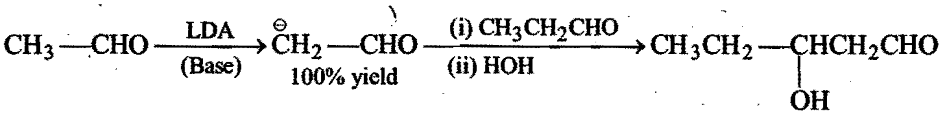
Ethanal (Electrophile) + Propanal (Nucleophile)

3-Hydroxy-2-methyl butanal
(β-Hydroxy-α-methyl butyraldehyde)

These β-hydroxy aldehydes or ketones are collectively called **aldols** and the reaction is known as **aldol condensation.**

Generally with two different aldehydes, all possible condensation products are obtained; but by using different catalysts, one product may be made to predominate in the mixture.

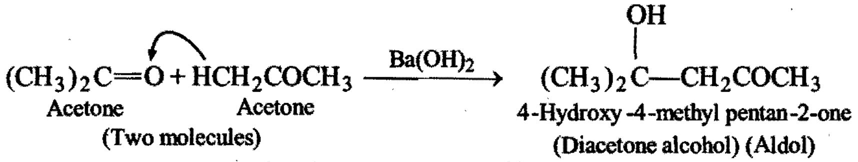
A common method used to obtained a single aldol product is to use LDA to remove the α-hydrogen when creating the enolate. Because LDA is a strong base, all the carbonyl compounds will be converted into an enolate, so there will be no carbonyl compound left with which to react. Addition will occur when the second carbonyl compound is added slowly to the reaction mixture. This aldol reaction is known as **directed aldol addition.**



$$CH_3-CHO \xrightarrow[\text{(Base)}]{LDA} \overset{\ominus}{C}H_2-CHO \xrightarrow[\text{(ii) HOH}]{\text{(i) } CH_3CH_2CHO} CH_3CH_2-CH(OH)CH_2CHO$$

100% yield

(ii) Acetone undergoes aldol condensation in the presence of $Ba(OH)_2$ to form diacetone alcohol.

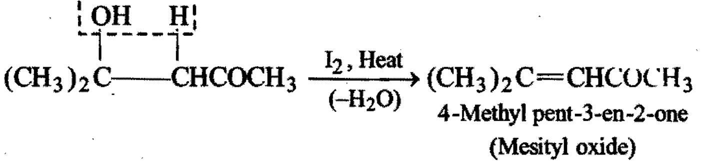


$$(CH_3)_2C=O + HCH_2COCH_3 \xrightarrow{Ba(OH)_2} (CH_3)_2C(OH)-CH_2COCH_3$$

Acetone + Acetone
(Two molecules)

4-Hydroxy-4-methyl pentan-2-one
(Diacetone alcohol) (Aldol)

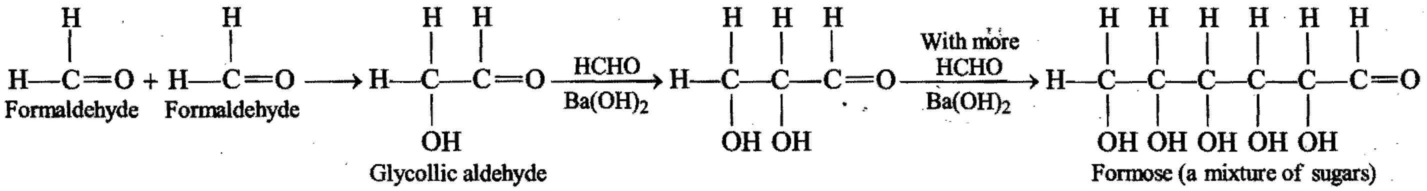
Diacetone alcohol loses a water molecule on heating in presence of little iodine and forms mesityl oxide.



$$(CH_3)_2C(OH)-CH_2COCH_3 \xrightarrow[(-H_2O)]{I_2,\text{ Heat}} (CH_3)_2C=CHCOCH_3$$

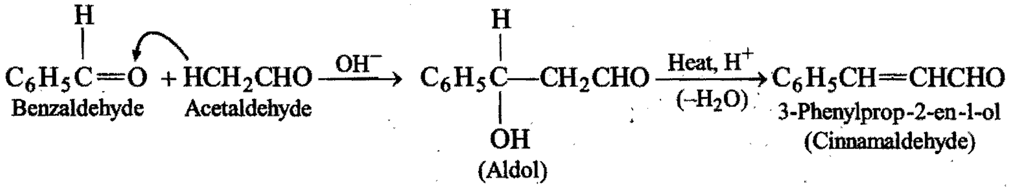
4-Methyl pent-3-en-2-one
(Mesityl oxide)

(iii) Formaldehyde undergoes abnormal repeated aldol type condensation in presence of $Ba(OH)_2$ or $Ca(OH)_2$ to form formose sugar.



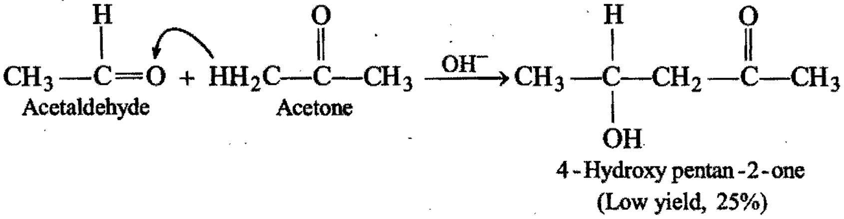
$$\underset{\text{Formaldehyde}}{H{-}\overset{H}{C}{=}O} + \underset{\text{Formaldehyde}}{H{-}\overset{H}{C}{=}O} \longrightarrow \underset{\text{Glycollic aldehyde}}{H{-}\underset{OH}{\overset{H}{C}}{-}\overset{H}{C}{=}O} \xrightarrow[Ba(OH)_2]{HCHO} H{-}\underset{OH}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\overset{H}{C}{=}O \xrightarrow[Ba(OH)_2]{\text{With more HCHO}} \underset{\text{Formose (a mixture of sugars)}}{H{-}\underset{OH}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\overset{H}{C}{=}O}$$

(iv) Acetaldehyde reacts with benzaldehyde (which has no α-hydrogen) in the presence of a base to form an aldol which on heating yields cinnamaldehyde.



$$\underset{\text{Benzaldehyde}}{C_6H_5\overset{H}{C}{=}O} + \underset{\text{Acetaldehyde}}{HCH_2CHO} \xrightarrow{OH^-} \underset{\text{(Aldol)}}{C_6H_5\underset{OH}{\overset{H}{C}}{-}CH_2CHO} \xrightarrow[(-H_2O)]{\text{Heat, }H^+} \underset{\substack{\text{3-Phenylprop-2-en-1-ol}\\ \text{(Cinnamaldehyde)}}}{C_6H_5CH{=}CHCHO}$$

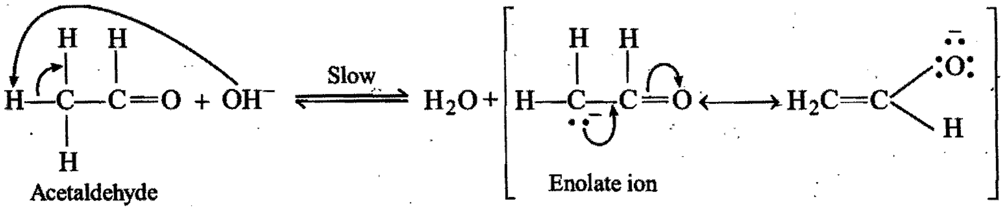
(v) When aldehyde condensed with ketone, it is the α-hydrogen atom of the ketone which is involved in the condensation (crossed aldol condensation), *e.g.*,



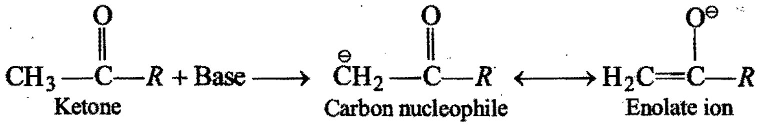
$$\underset{\text{Acetaldehyde}}{CH_3{-}\overset{H}{C}{=}O} + \underset{\text{Acetone}}{HH_2C{-}\overset{O}{\overset{\|}{C}}{-}CH_3} \xrightarrow{OH^-} \underset{\substack{\text{4-Hydroxy pentan-2-one}\\ \text{(Low yield, 25\%)}}}{CH_3{-}\underset{OH}{\overset{H}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$$

Mechanism of aldol condensation (Acidity of α-hydrogen) : Aldol condensation involves the following steps through the formation of carbanion or the enolate ion which is stabilized by resonance in Step 1:

Step 1. The base (OH^-) ion removes one of the α-hydrogen atom (which is somewhat acidic) from aldehydes and ketones to form a carbanion or the enolate ion.



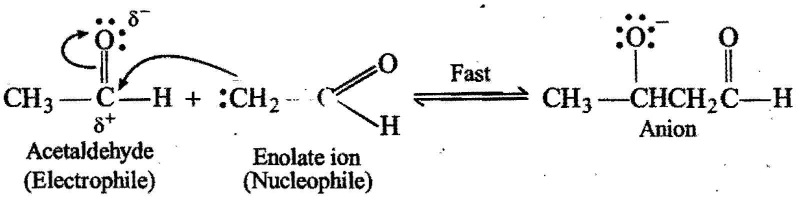
$$\underset{\text{Acetaldehyde}}{H{-}\underset{H}{\overset{H}{C}}{-}\overset{H}{C}{=}O} + OH^- \overset{\text{Slow}}{\rightleftharpoons} H_2O + \underset{\text{Enolate ion}}{\left[H{-}\overset{H}{\underset{\bullet\bullet}{C}}{-}\overset{H}{C}{=}O \longleftrightarrow H_2C{=}C\begin{smallmatrix}\ddot{O}:^-\\ H\end{smallmatrix}\right]}$$



$$\underset{\text{Ketone}}{CH_3{-}\overset{O}{\overset{\|}{C}}{-}R} + \text{Base} \longrightarrow \underset{\text{Carbon nucleophile}}{\overset{\ominus}{C}H_2{-}\overset{O}{\overset{\|}{C}}{-}R} \longleftrightarrow \underset{\text{Enolate ion}}{H_2C{=}\overset{O^{\ominus}}{\overset{|}{C}}{-}R}$$

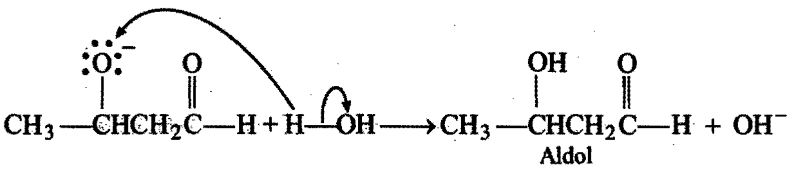
The acidity of α-hydrogen is due to resonance stabilization of enolate anion.

Step 2. The enolate ion (nucleophile) attacks the carbonyl carbon of another aldehyde molecule to form the anion.



$$\underset{\substack{\text{Acetaldehyde}\\ \text{(Electrophile)}}}{CH_3{-}\overset{\ddot{O}:^{\delta-}}{\overset{\|}{\underset{\delta^+}{C}}}{-}H} + \underset{\substack{\text{Enolate ion}\\ \text{(Nucleophile)}}}{:CH_2{-}C\begin{smallmatrix}O\\ H\end{smallmatrix}} \overset{\text{Fast}}{\rightleftharpoons} \underset{\text{Anion}}{CH_3{-}\overset{:\ddot{O}:^-}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}{-}H}$$

Step 3. A proton from water is accepted by anion to form aldol and the OH^- ion is regenerated.



$$CH_3-\overset{:\ddot{O}:^-}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}-H+H-OH\longrightarrow \underset{\text{Aldol}}{CH_3-\overset{OH}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}-H}+OH^-$$

(B) Reactions in which Aldehydes and Ketones Differ

(i) Oxidation of aldehydes : Aldehydes are easily oxidised and thus act as strong **reducing agents.** Aldehydes on oxidation form corresponding carboxylic acids containing the same number of carbon atoms.

$$\underset{\text{Aldehyde}}{RCHO}\xrightarrow[\text{[O]}]{\text{Oxidant}}\underset{\text{Acid}}{RCOOH}$$

Oxidising agents may be strong (such as acidified $K_2Cr_2O_7$ or acidified $Na_2Cr_2O_7$ or acidified $KMnO_4$) or mild (such as Tollens' reagent or Fehling's solution or Benedict's solution).

Reduction of Tollens' reagent : It is an ammoniacal solution of silver nitrate. It is prepared by adding NH_4OH to silver nitrate solution till the precipitates of Ag_2O first formed just redissolves. When aldehyde is added to Tollens' reagent, silver oxide is reduced to metallic silver which deposits as a mirror **(Reducing character of aldehydes).**

$$\begin{bmatrix} 2AgNO_3+2NH_4OH\longrightarrow Ag_2O+2NH_4NO_3+H_2O \\ Ag_2O+4NH_4OH\longrightarrow \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]OH}+3H_2O \end{bmatrix}$$

$$\underset{\text{Aldehyde}}{RCHO}+Ag_2O\longrightarrow \underset{\text{Acid}}{RCOOH}+\underset{\text{Silver mirror}}{2Ag}$$

$$[RCHO+\underset{\text{Amm. silver nitrate soln.}}{2Ag(NH_3)_2^+}+3OH^-\longrightarrow RCOO^-+\underset{\text{Silver mirror}}{2Ag}+4NH_3+2H_2O]$$

This reaction is known as **silver mirror test** for aldehydes. Both aliphatic and aromatic aldehydes reduce Tollens' reagent. Unsaturated aldehydes can also be oxidised to unsaturated acids (C=C is not affected).

$$CH_3CH{=}CHCHO\xrightarrow{\text{Tollens' reagent}}CH_3CH{=}CHCOOH$$

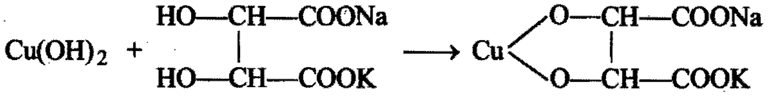
Reduction of Fehling's solution : It is an alkaline solution of cupric ion complexed with sodium potassium tartrate. Aldehydes reduce the cupric ion (deep blue) to cuprous oxide (red). Two solutions are kept in laboratory in the name of Fehling solution I and Fehling solution II. Fehling solution I contains dilute solution of copper sulphate and solution II contains sodium potassium tartrate and sodium hydroxide. Equal volumes of both the solutions are taken and heated with organic compound. If a red brown precipitate of cuprous oxide appears, it confirms that the organic compound is an aldehyde.

Fehling solution I ⟶ $CuSO_4$ solution.

Fehling solution II ⟶ Alkaline solution of sodium potassium tartrate also called **Rochelle salt.**

When both these solutions are mixed, we get deep blue coloured solution.

$$CuSO_4+2NaOH\longrightarrow Cu(OH)_2+Na_2SO_4$$



$$Cu(OH)_2+\begin{matrix}HO-CH-COONa\\ |\\ HO-CH-COOK\end{matrix}\longrightarrow Cu\begin{matrix}O-CH-COONa\\ |\\ O-CH-COOK\end{matrix}$$

Rochelle salt (Deep blue coloured solution)

$$\underset{\text{Aldehyde}}{RCHO}+\underset{\text{Blue}}{2CuO}\xrightarrow{\Delta}RCOOH+\underset{\text{Cuprous oxide (Red ppt.)}}{Cu_2O}$$

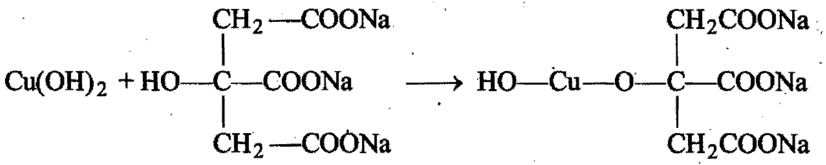
$$[RCHO+2Cu^{2+}+3OH^-\longrightarrow RCOO^-+\underset{\text{Red ppt.}}{2Cu^+}+2H_2O]$$

Reduction of Benedict's solution : It is solution of copper sulphate, sodium citrate and sodium carbonate. When heated with an aldehyde, a reddish brown precipitate appears. So, all the organic compounds which give positive test with Fehling's solution, also give same test with Benedict's solution [CuO or $Cu(OH)_2$].

Solution I ⟶ Alkaline solution of potassium or sodium citrate.

Solution II ⟶ $CuSO_4$

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$



$$Cu(OH)_2 + HO-\overset{\substack{CH_2-COONa\\|}}{\underset{\substack{|\\CH_2-COONa}}{C}}-COONa \longrightarrow HO-Cu-O-\overset{\substack{CH_2COONa\\|}}{\underset{\substack{|\\CH_2COONa}}{C}}-COONa$$

Blue coloured complex

Note: Benzaldehyde does not respond to Fehling's or Benedict tests due to alkaline nature of these reagents. Ketones also do not reduce Tollens' reagent, Fehling's solution and Benedict's solution. Hence, these reagents can be used to distinguish between aldehydes and ketones.

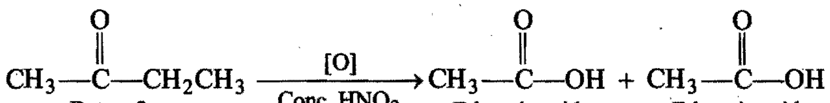
Oxidation of ketones : Unlike aldehydes, ketones do not have any hydrogen atom attached to $>C=O$ group and hence, they cannot be oxidised by weak oxidising agents such as Tollens' reagent or Fehling's solution.

Ketones are, however, oxidised by strong oxidising agents like acidified dichromate, acidified or alkaline $KMnO_4$, hot concentrated HNO_3, etc., to a mixture of carboxylic acids with lesser number of carbon atoms.

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow[+4[O]]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2 + H_2O$$

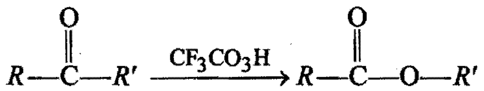
$$\underset{\substack{\text{Pentan-2-one}\\\text{(Methyl propyl ketone)}}}{CH_3CH_2CH_2COCH_3} \xrightarrow[[O]]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Propionic acid}}{CH_3CH_2COOH} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Oxidation of mixed ketones is governed by **Popoff's rule** according to which carbonyl group of the unsymmetrical ketone remains with the smaller alkyl group preferentially.



$$\underset{\text{Butan-2-one}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3} \xrightarrow[\text{Conc. }HNO_3]{[O]} \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH}$$

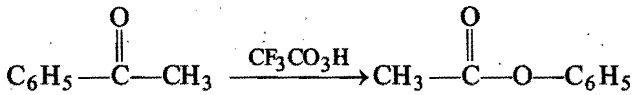
Baeyer-Villiger oxidation : Aliphatic ketones undergo oxidation with Caro's acid (per monosulphuric acid, H_2SO_5) or per benzoic acid ($C_6H_5CO_3H$) or *m*-chloro perbenzoic acid or per acetic acid (CH_3CO_3H) or CF_3CO_3H, etc., to form esters or their hydrolysed products.



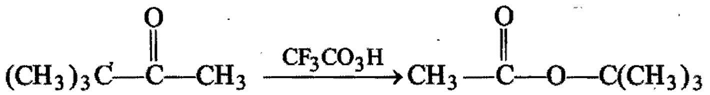
$$\underset{\text{Ketone}}{R-\overset{\overset{O}{\|}}{C}-R'} \xrightarrow{CF_3CO_3H} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-O-R'}$$

This oxidation of ketones into ester is known as Baeyer-Villiger Oxidation. In case of unsymmetrical ketones, the preference of insertion of oxygen atom between carbonyl carbon and alkyl group in decreasing order is as follows:

$$H > 3° \text{ alkyl} > 2° \text{ alkyl} > C_6H_5 > CH_3$$



$$\underset{\text{Methyl phenyl ketone}}{C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow{CF_3CO_3H} \underset{\text{Phenyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-O-C_6H_5}$$



$$(CH_3)_3C-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{CF_3CO_3H} CH_3-\overset{\overset{O}{\|}}{C}-O-C(CH_3)_3$$

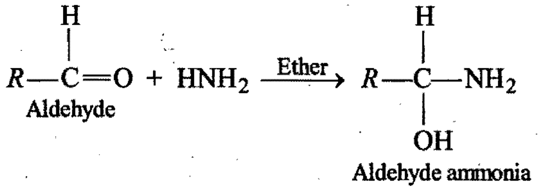
$$[RCOOR' \xrightarrow{H^+} RCOOH + R'OH]$$

$$\underset{\text{Ketone}}{R_2CO} + \underset{\text{Per acid}}{R'COOOH} \longrightarrow \underset{\text{Ester}}{RCOOR'} + \underset{\text{Acid}}{RCOOH}$$

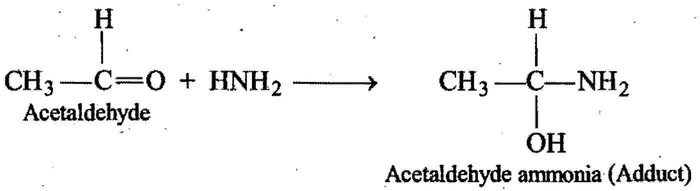
(ii) Schiff's test of aldehydes : Schiff's reagent is a dilute solution of *para*-rosaniline hydrochloride whose red colour has been discharged by passing sulphur dioxide gas. Aldehydes when treated with Schiff's reagent (magenta solution in sulphurous acid, H_2SO_3) restore its pink colour.

Ketones do not give this test.

(iii) Reaction with ammonia : Except formaldehyde, other aldehydes form addition products with an etheral solution of ammonia. These addition compounds on heating with dilute acids regenerate the aldehyde.

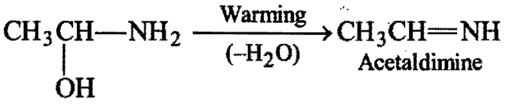


$$\underset{\text{Aldehyde}}{R-\overset{\overset{\large H}{|}}{C}=O} + HNH_2 \xrightarrow{\text{Ether}} \underset{\text{Aldehyde ammonia}}{R-\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}-NH_2}$$



$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\large H}{|}}{C}=O} + HNH_2 \longrightarrow \underset{\text{Acetaldehyde ammonia (Adduct)}}{CH_3-\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}-NH_2}$$

This addition product on warming with water, decomposes to give **imines.**

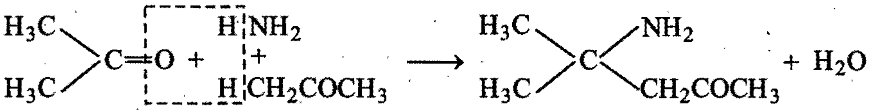


$$CH_3\underset{\underset{\large OH}{|}}{CH}-NH_2 \xrightarrow[(-H_2O)]{\text{Warming}} \underset{\text{Acetaldimine}}{CH_3CH=NH}$$

However, formaldehyde forms a complex product with ammonia. The product is called hexamethylene tetramine or **urotropine,** used as an urinary antiseptic.

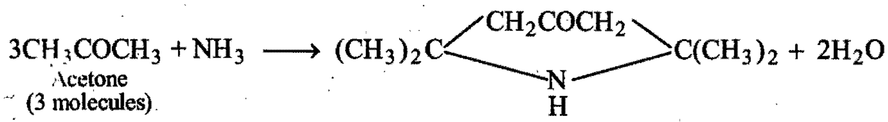
$$\underset{\text{Formaldehyde}}{6HCHO} + 4NH_3 \longrightarrow \underset{\text{Hexamethylene tetramine}}{(CH_2)_6N_4} + 6H_2O$$

Ketones form complex ketonic amines.



Two molecules of acetone

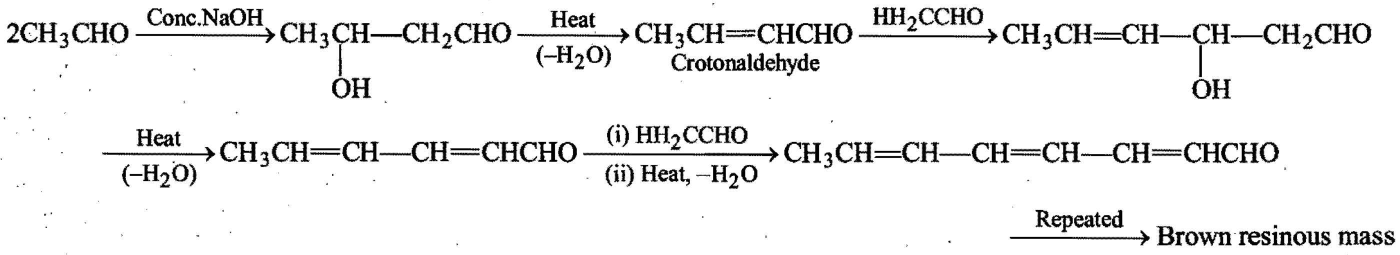
4-Amino-4-methyl pentan-2-one (Diacetone amine)



Acetone (3 molecules)

Triacetone amine

(iv) Reaction with alkali : Aldehydes having α-hydrogen atom on heating with concentrated alkali (except formaldehyde) give a brown resinous mass of characteristic odour. The **aldehyde-resin** is formed (resinification) probably through a series of condensation reactions.



$$2CH_3CHO \xrightarrow{\text{Conc.NaOH}} CH_3\underset{\underset{\large OH}{|}}{CH}-CH_2CHO \xrightarrow[(-H_2O)]{\text{Heat}} \underset{\text{Crotonaldehyde}}{CH_3CH=CHCHO} \xrightarrow{HH_2CCHO} CH_3CH=CH-\underset{\underset{\large OH}{|}}{CH}-CH_2CHO$$

$$\xrightarrow[(-H_2O)]{\text{Heat}} CH_3CH=CH-CH=CHCHO \xrightarrow[\text{(ii) Heat, }-H_2O]{\text{(i) }HH_2CCHO} CH_3CH=CH-CH=CH-CH=CHCHO$$

$$\xrightarrow{\text{Repeated}} \text{Brown resinous mass}$$

Ketones do not give this reaction.

Formaldehyde, benzaldehyde and other aldehydes containing **no α-hydrogen atoms** on heating **with concentrated alkali solution** (50%) undergo **Cannizzaro's reaction.** In this reaction, one molecule is oxidised to carboxylic acid at the expense of other which is reduced to 1° alcohol, *e.g.*, formaldehyde undergoes disproportionation (oxidation-reduction), *i.e.*,

$$\underset{\text{Formaldehyde}}{2HCHO} + \underset{(50\%)}{NaOH} \longrightarrow \underset{\text{Sodium formate}}{HCOONa} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

Some other examples of Cannizzaro's reactions are:

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + \underset{(50\%)}{NaOH} \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodium benzoate}}{C_6H_5COO^-Na^+}$$

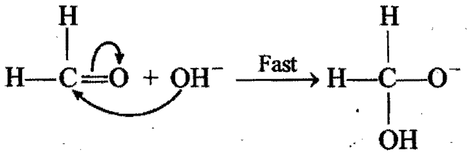
$$\underset{\text{Chloral}}{2CCl_3CHO} + KOH \longrightarrow \underset{\text{Trichloroethanol}}{CCl_3CH_2OH} + \underset{\text{Trichloropotassium acetate}}{CCl_3COOK}$$

$$\underset{\text{2,2-Dimethyl propanal}}{2(CH_3)_3CCHO} + \underset{(50\%)}{NaOH} \longrightarrow \underset{\text{2,2-Dimethyl propan-1-ol}}{(CH_3)_3CCH_2OH} + (CH_3)_3CCOONa$$

The usual reagent for bringing about the Cannizzaro's reaction is 50 per cent aqueous or ethanolic alkali.

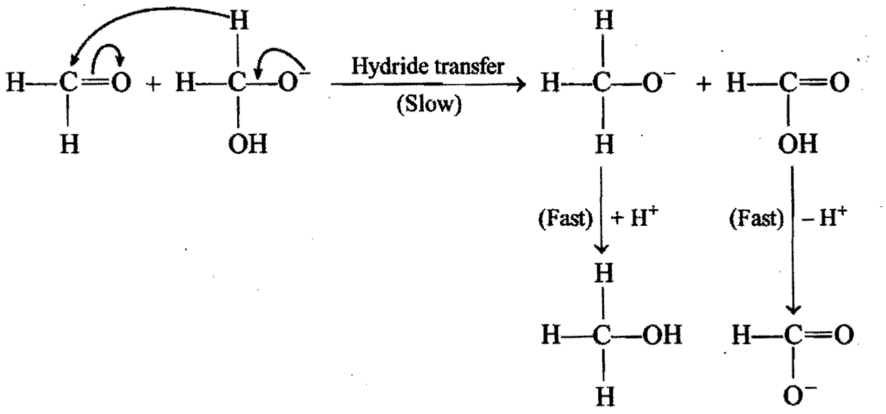
Mechanism : The mechanism involves hydride ion transfer and one possibility being as follows:

Step 1. The OH^- ion attacks the carbonyl carbon to form hydroxy alkoxide (Nucleophilic attack), an anion (I).



Anion (I)

Step 2. The anion (I) acts as hydride ion donor to the second molecule of aldehyde. In the final step of the reaction the acid and the alkoxide ion transfer H^+ to acquire stability.



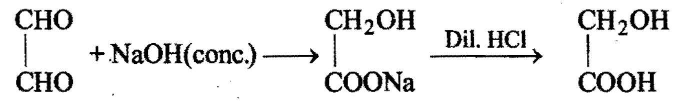
(Alcohol) (Salt of an acid)

Cannizzaro's reaction involves same or different aldehydes having no α-hydrogen atoms and is **proton (H^+)-hydride (H^-) transfer** reaction.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + NaOH + \underset{\text{Formaldehyde}}{HCHO} \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodium formate}}{HCOONa}$$

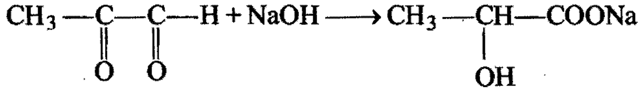
This reaction is called **crossed Cannizzaro's reaction.**

In compounds containing two carbonyl groups, the **intramolecular** or **internal Cannizzaro's reaction** takes place, where one-half part of the molecule is reduced and the other half part (of the same molecule) is oxidised.



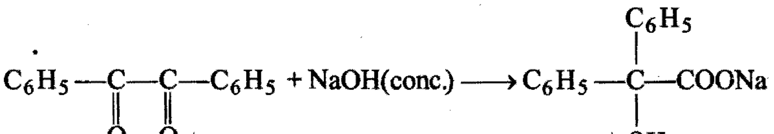
$$\begin{matrix} CHO \\ | \\ CHO \end{matrix} + NaOH(conc.) \longrightarrow \begin{matrix} CH_2OH \\ | \\ COONa \end{matrix} \xrightarrow{\text{Dil. HCl}} \begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}$$

Glyoxal Glycollic acid



$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H + NaOH \longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-COONa$$

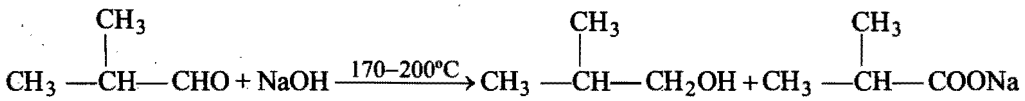
Methyl glyoxal Sodium lactate



$$C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-C_6H_5 + NaOH(conc.) \longrightarrow C_6H_5-\overset{\overset{C_6H_5}{|}}{\underset{\underset{OH}{|}}{C}}-COONa$$

Diphenyl glyoxal Sodium benzillate

Exception : Certain aliphatic monoalkylated aldehydes (having α-hydrogen atoms) may undergo Cannizzaro's reaction (quantitative disproportionation) when heated with aqueous NaOH. For example,



$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-CHO + NaOH \xrightarrow{170\text{–}200°C} CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2OH + CH_3-\overset{CH_3}{\overset{|}{C}}H-COONa$$

2-Methyl propanal 2-Methyl propan-1-ol Sod. 2-methyl propanoate

This exceptional behaviour is probably due to $+I$ effect of the two alkyl groups.

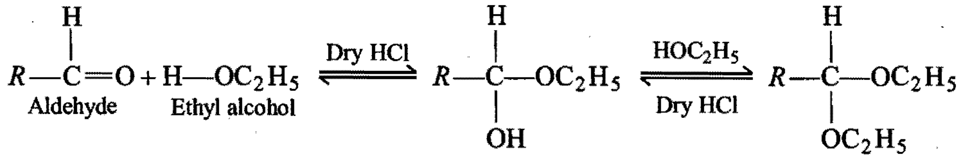
(v) Tischenko's reaction : This is a modified form of Cannizzaro's reaction. All aldehydes with or without α-hydrogen atoms undergo Cannizzaro's reaction in presence of aluminium ethoxide. The acid (by oxidation) and the alcohol (by reduction) formed react together to give the ester.

$$\underset{\text{Acetaldehyde}}{2CH_3CHO} \xrightarrow{(C_2H_5O)_3Al} [CH_3COOH + C_2H_5OH] \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

$$\underset{\text{Propionaldehyde}}{2CH_3CH_2CHO} \xrightarrow{(C_2H_5O)_3Al} [CH_3CH_2COOH + C_3H_7OH] \longrightarrow \underset{\text{Propyl propionate}}{C_2H_5COOC_3H_7}$$

$$\underset{\text{Acrolein}}{H_2C{=}CHCHO} \xrightarrow{(C_2H_5O)_3Al} \underset{\text{Allyl acrylate}}{H_2C{=}CHCOOCH_2CH{=}CH_2}$$

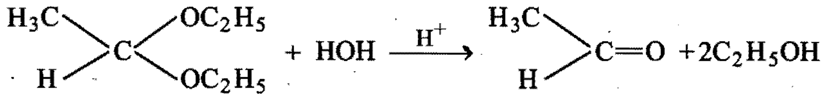
(vi) Reaction with alcohols : Aldehydes combine with alcohols in presence of dry hydrogen chloride gas forming first hemi-acetals (unstable) and then the acetals (dialkoxy alkanes). The acid catalyst in most of the cases is p-toluene sulphonic acid (Ts—OH).



$$\underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} + \underset{\text{Ethyl alcohol}}{H-OC_2H_5} \underset{}{\overset{\text{Dry HCl}}{\rightleftharpoons}} R-\overset{H}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-OC_2H_5 \underset{\text{Dry HCl}}{\overset{HOC_2H_5}{\rightleftharpoons}} R-\overset{H}{\overset{|}{\underset{OC_2H_5}{\underset{|}{C}}}}-OC_2H_5$$

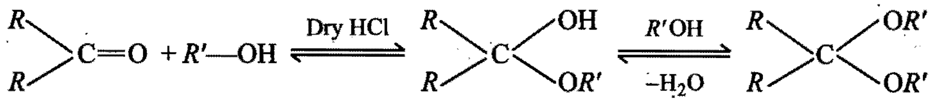
(Hemi-acetal) Acetal

The reaction is reversible and therefore, the acetal formed can be decomposed by dilute mineral acids to give back to original aldehyde.



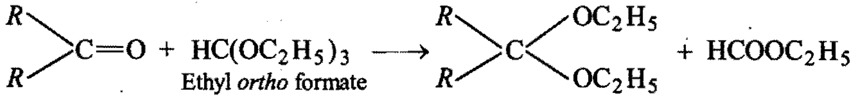
Acetal Acetaldehyde

A large excess of alcohol is used to shift the equilibrium in favour of acetal formation. Ketones do not readily react with monohydric alcohols.

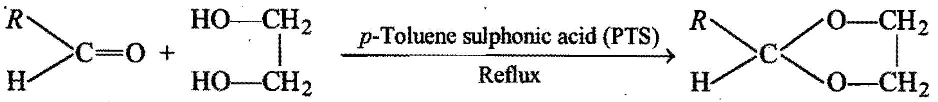


(Hemi-ketal) Ketal

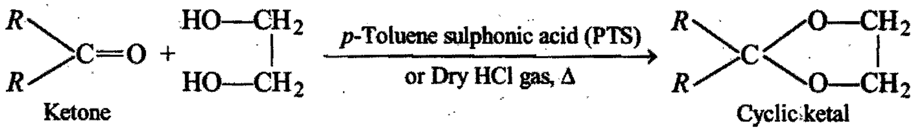
Ketals may however, be prepared by treating the ketone with ethyl *ortho* formate.



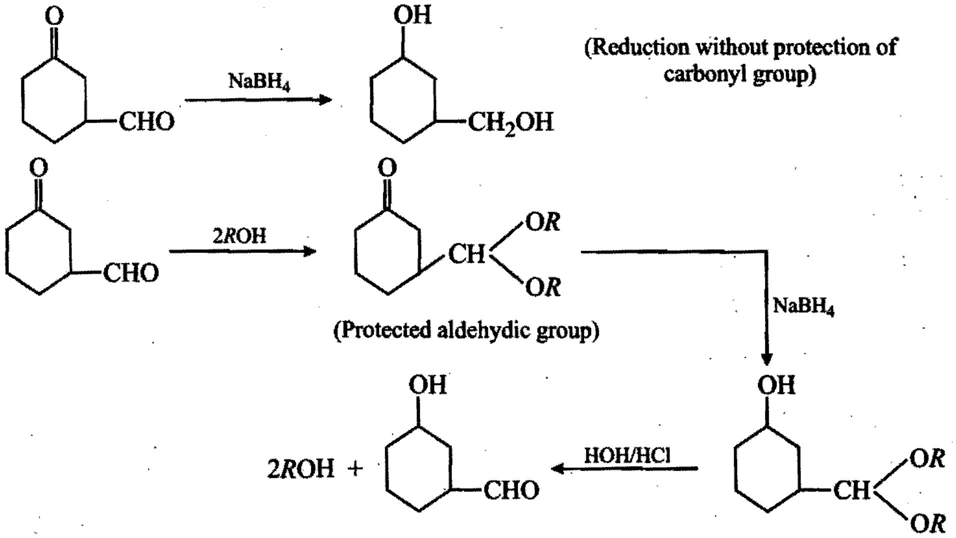
However, On treatment with ethylene glycol, cyclic acetal and cyclic ketal (1,3-dioxolans) are formed.



Aldehyde Ethylene glycol Cyclic acetal



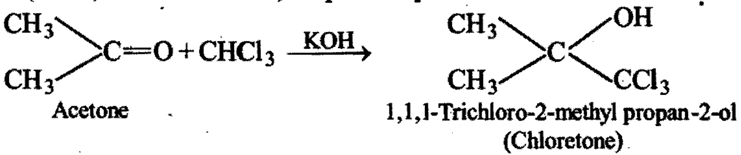
Acetal and ketal formation is used for protection of carbonyl group. Aldehydic group is found more reactive than ketonic group. Let us illustrate application of protection of carbonyl groups.



(Thus, this method can be used for preferential reduction of ketonic group.)

(vii) Polymerisation : The lower aldehydes show a marked tendency to polymerise forming compounds in which several molecules are linked together through oxygen. [For details see formaldehyde and acetaldehyde]. Ketones do not form polymers.

(viii) Condensation with chloroform : Ketones condense with chloroform/bromoform in presence of caustic potash to form chlorohydroxy compounds (chloretone/brometone) respectively.



Aldehydes do not respond to this reaction.

(ix) Formation of sodio-derivatives : Ketones yield sodio-derivatives when treated with sodium or sodamide in ether solution.

$$\underset{\text{Acetone}}{CH_3COCH_3} + \underset{\text{Sodamide}}{NaNH_2} \xrightarrow{\text{Ether}} \underset{\text{Sodio-derivative}}{CH_3COCH_2Na} + NH_3$$

These sodio-derivatives can be treated with alkyl halides to produce higher methyl alkyl ketones.

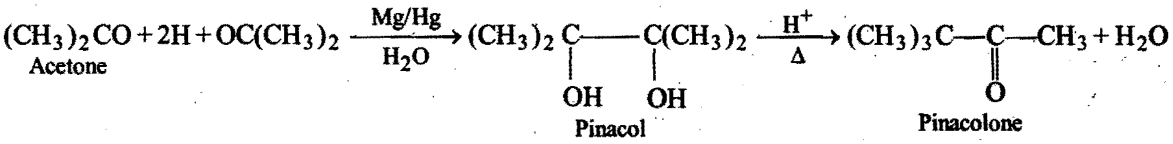
Aldehydes do not respond to this reaction.

(x) Reaction with nitrous acid : Ketones when treated with nitrous acid form isonitroso derivatives.

$$\underset{\text{Acetone}}{CH_3COCHH_2} + O{=}N{-}OH \longrightarrow \underset{\text{Isonitrosoacetone (Oximino acetone)}}{CH_3COCH{=}NOH} + H_2O$$

This reaction is used for detecting the presence of —$COCH_2$— group and not observed in aldehydes.

(xi) Reduction in neutral or alkaline medium : When ketones are reduced with Mg-Hg and water, pinacols are the main product which on heating with dil. H_2SO_4 give pinacolone. This reaction is called as **Pinacol-Pinacolone rearrangement.**

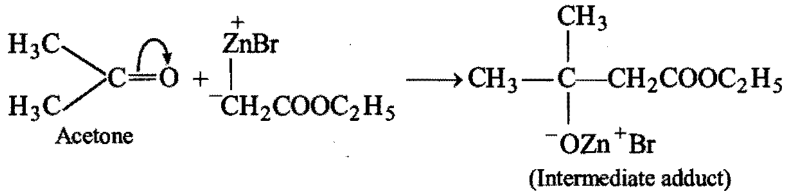


$$\underset{\text{Acetone}}{(CH_3)_2CO} + 2H + OC(CH_3)_2 \xrightarrow[H_2O]{Mg/Hg} \underset{\text{Pinacol}}{(CH_3)_2\underset{OH}{\underset{|}{C}}{-}\underset{OH}{\underset{|}{C}}(CH_3)_2} \xrightarrow[\Delta]{H^+} \underset{\text{Pinacolone}}{(CH_3)_3C{-}\underset{O}{\underset{\|}{C}}{-}CH_3} + H_2O$$

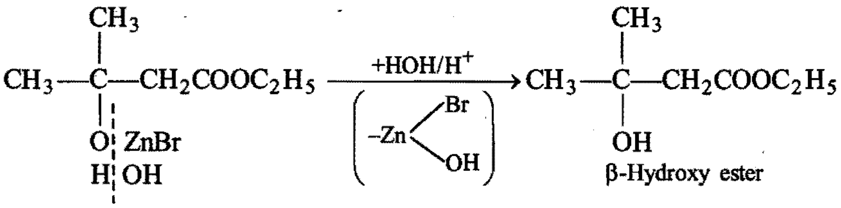
(xii) Reformatsky reaction : This reaction involves the treatment of aldehydes or ketones with α-bromo acid ester in presence of metallic zinc to form β-hydroxy ester, which can be easily dehydrated into α, β-unsaturated ester.

(a) $$\underset{\alpha\text{-Bromoethyl acetate}}{BrCH_2COOC_2H_5} + Zn \xrightarrow{\text{(Benzene)}} \underset{\text{Organo zinc compound}}{Br{-}\overset{+}{Zn}{-}\overset{-}{C}H_2COOC_2H_5}$$

(b) Addition to carbonyl group,



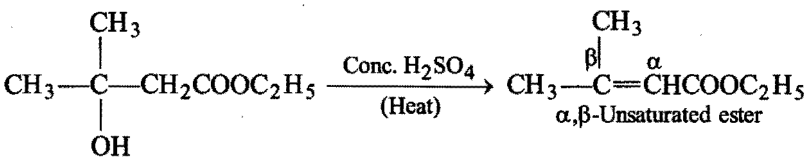
(c) Acid hydrolysis of the adduct,



$$CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{O\,ZnBr}{|}}{C}}{-}CH_2COOC_2H_5 \xrightarrow[-Zn(Br)(OH)]{+HOH/H^+} CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}{-}CH_2COOC_2H_5$$

β-Hydroxy ester

(d) Dehydration to form α,β-unsaturated ester,



$$CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}{-}CH_2COOC_2H_5 \xrightarrow[\text{(Heat)}]{\text{Conc. }H_2SO_4} CH_3{-}\overset{\overset{CH_3}{|\beta}}{C}{=}\overset{\alpha}{C}HCOOC_2H_5$$

α,β-Unsaturated ester

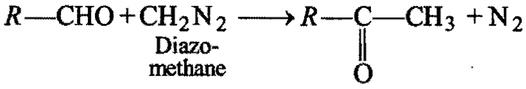
(xiii) Claisen-Schmidt reaction : This condensation reaction (also known as **Claisen reaction**) is between an aliphatic aldehyde or ketone containing α-hydrogen with benzaldehyde in the presence of dilute alkali to form an α,β-unsaturated compound.

$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + \underset{\text{Acetaldehyde}}{H_2HCCHO} \xrightarrow{NaOH} \underset{\text{Cinnamaldehyde}}{C_6H_5CH{=}CHCHO}$$

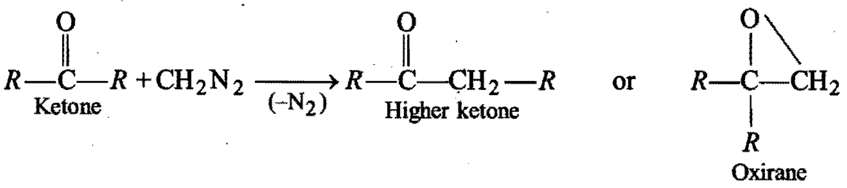
$$C_6H_5CH{=}O + \underset{\text{Acetone}}{H_2HCCOCH_3} \longrightarrow \underset{\substack{\text{Benzylidene acetone}\\ \text{(used in perfumery)}}}{C_6H_5CH{=}CHCOCH_3}$$

This reaction is similar to aldol condensation.

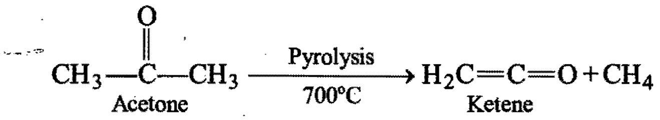
(xiv) Reaction with diazomethane : In this reaction, aldehydes can be converted to ketone and lower ketones can be converted to higher ketones or oxiranes.



$$R{-}CHO + \underset{\substack{\text{Diazo-}\\ \text{methane}}}{CH_2N_2} \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + N_2$$

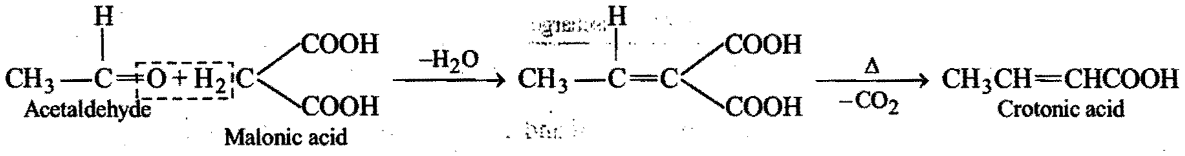


(xv) Pyrolysis of ketones : Pyrolysis of ketones give ketene.



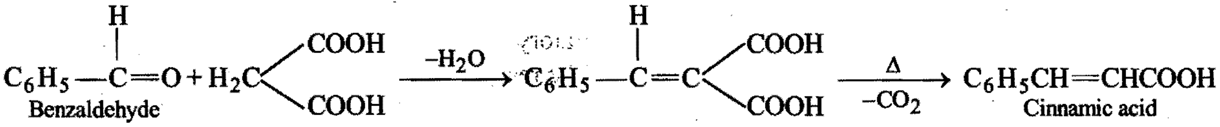
$$\underset{\text{Acetone}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3} \xrightarrow[700°C]{\text{Pyrolysis}} \underset{\text{Ketene}}{H_2C{=}C{=}O} + CH_4$$

(xvi) Knoevenagel's reaction : This reaction involves condensation between active methylene group and carbonyl group in presence of base (pyridine).



$$CH_3-\overset{H}{C}=O+H_2C(COOH)_2 \xrightarrow{-H_2O} CH_3-\overset{H}{C}=C(COOH)_2 \xrightarrow[-CO_2]{\Delta} CH_3CH=CHCOOH$$

Acetaldehyde, Malonic acid, Crotonic acid

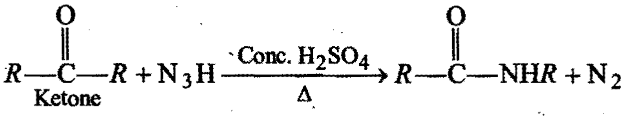


$$C_6H_5-\overset{H}{C}=O+H_2C(COOH)_2 \xrightarrow{-H_2O} C_6H_5-\overset{H}{C}=C(COOH)_2 \xrightarrow[-CO_2]{\Delta} C_6H_5CH=CHCOOH$$

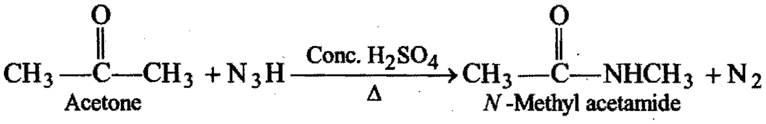
Benzaldehyde, Cinnamic acid

(xvii) Schmidt reaction : This is a reaction between a carbonyl compound and hydrazoic acid in presence of conc. H_2SO_4.

$$\underset{}{R\text{—}CHO} + \underset{\text{Hydrazoic acid}}{N_3H} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{\text{Alkyl cyanide}}{R\text{—}CN} + \underset{N\text{-Alkyl formamide}}{HCONHR} + N_2$$



$$\underset{\text{Ketone}}{R-\overset{O}{\overset{\|}{C}}-R} + N_3H \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} R-\overset{O}{\overset{\|}{C}}-NHR + N_2$$



$$\underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + N_3H \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{N\text{-Methyl acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NHCH_3} + N_2$$

11.6 TESTS OF ALDEHYDES AND KETONES (Distinction)

Tests	Aldehydes	Ketones
1. With Schiff's reagent	Give pink colour.	No colour.
2. With Fehling's solution	Give red precipitate.	No precipitate is formed.
3. With Tollen's reagent	Black precipitate of silver or silver mirror is formed.	No black precipitate or silver mirror is formed.
4. With saturated sodium bisulphite solution in water	Crystalline compound (colourless) is formed.	Crystalline compound (colourless) is formed.
5. With 2,4-dinitrophenylhydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.
6. With sodium hydroxide	Give brown resinous mass (Formaldehyde does not give this test).	No reaction.
7. With sodium nitroprusside and few drops of sodium hydroxide	A deep red colour (Formaldehyde does not respond to this test).	Red colour which changes to orange.

11.7 SOME COMMERCIALLY IMPORTANT CARBONYL COMPOUNDS

1. Formaldehyde or Methanal (HCHO)

Formaldehyde is the first member of the aldehyde series. It is present in green leaves of plants where its presence is supposed to be due to the reaction of CO_2 with water in presence of sunlight and chlorophyll.

$$CO_2 + H_2O \longrightarrow HCHO + O_2$$

Traces of formaldehyde are formed when incomplete combustion of wood, sugar, coal, etc., occurs.

Manufacture : Formaldehyde is manufactured by controlled oxidation of methane by air in presence of various metallic oxides as catalyst.

$$\underset{\text{Methane}}{CH_4} + O_2 \xrightarrow[\text{Catalyst}]{\text{Mo-oxide}} \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

It is also prepared by passing water gas at low pressure through an electric discharge of low intensity.

$$\underbrace{CO + H_2}_{\text{Water gas}} \xrightarrow{\text{Elec. discharge}} \underset{\text{Formaldehyde}}{HCHO}$$

Formaldehyde is manufactured by oxidation of methyl alcohol and also by dehydrogenation of methyl alcohol in presence of copper or silver catalyst at 300-400°C.

Laboratory preparation : Formaldehyde is prepared in laboratory by catalytic oxidation of methyl alcohol.

Excess of methyl alcohol is removed by fractional distillation. The resulting mixture is called **formalin** which contains 40% formaldehyde, 8% methyl alcohol and 52% water.

Physical properties : (i) It is a colourless, pungent smelling gas and is extremely soluble in water. Its solubility in water may be due to hydrogen bonding between water molecules and its hydrate.

(ii) It can easily be condensed into liquid. The liquid formaldehyde boils at −21°C.

(iii) It causes irritation to skin, eyes, nose and throat.

(iv) Its solution acts as antiseptic and disinfectant.

Chemical properties : Formaldehyde is structurally different from other aldehydes as it contains no alkyl group in the molecule. Though, it shows general properties of aldehydes, it differs in certain respects. The abnormal properties of formaldehyde are given below:

(i) Reaction with ammonia : Like other aldehydes, formaldehyde does not form addition product with ammonia but a crystalline compound, hexamethylene tetramine (Urotropine).

$$\underset{\text{Formaldehyde}}{6HCHO} + 4NH_3 \longrightarrow \underset{\substack{\text{Hexamethylene tetramine}\\ \text{(Urotropine)}}}{(CH_2)_6N_4} + 6H_2O$$

The reaction may be given as,

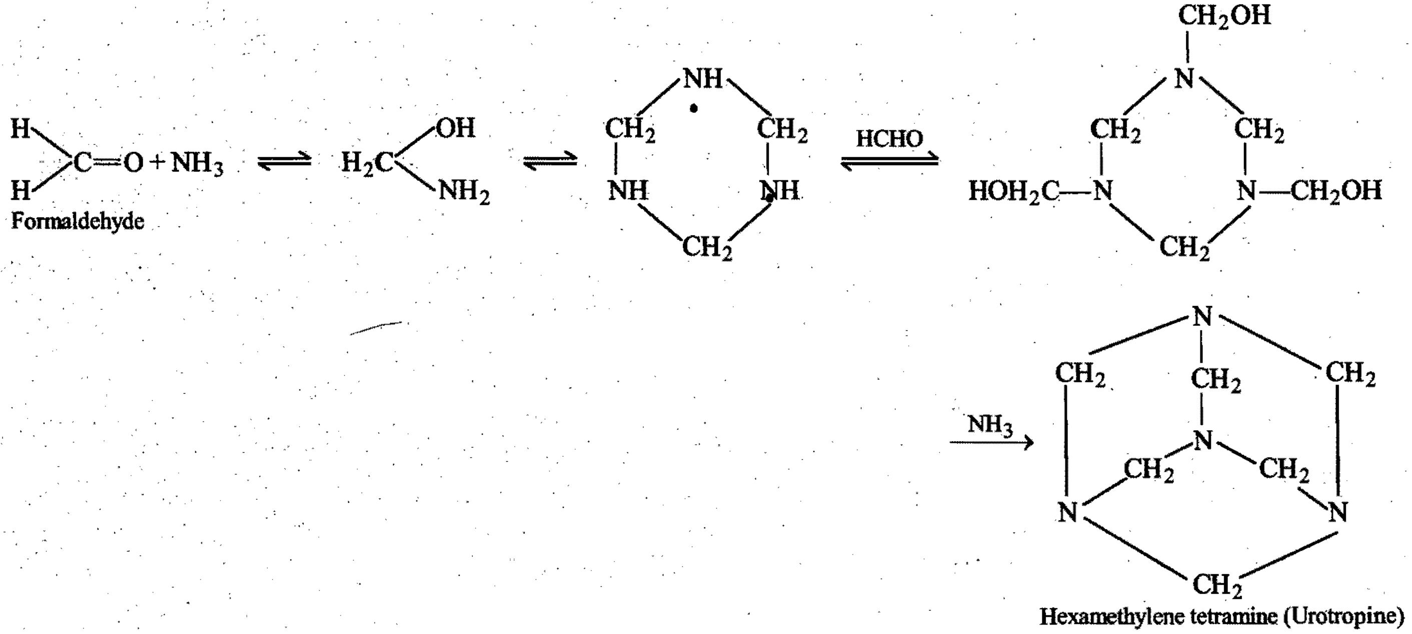


Fig. 11.1 . Urotropine

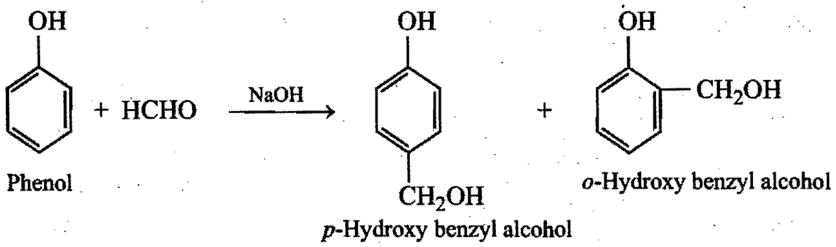
Hexamethylene tetramine has a cyclic structure. It is used as medicine in case of urinary troubles under the name of **Urotropine** or hexamine. Nitration of urotropine under controlled conditions gives an explosive **RDX (Research and Development Explosive).**

(ii) Reaction with sodium hydroxide (Cannizzaro's reaction).

(iii) Aldol condensation : Formation of **formose (hexose).**

(iv) Condensation with phenol : Formaldehyde condenses with phenol to give a synthetic plastic, bakelite. The condensation occurs in presence of dilute sodium hydroxide or ammonia at 80–90°C. Bakelite is used for preparing electrical insulators, electric switches and toys, etc.

When phenol is treated with 40% formaldehyde in presence of dilute acid or alkali, a mixture of *ortho* and *para*-hydroxy benzyl alcohol is formed. This reaction is called **Lederer Manase's reaction.**



Cross linking of these compounds result into **Bakelite.** Overall equation can be represented as:

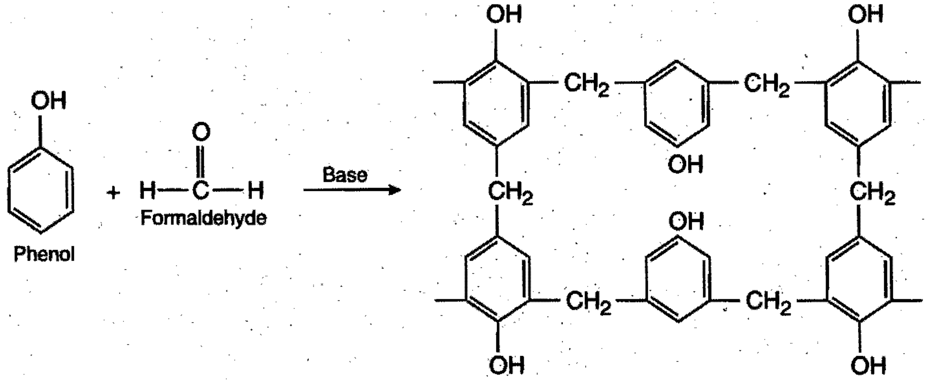
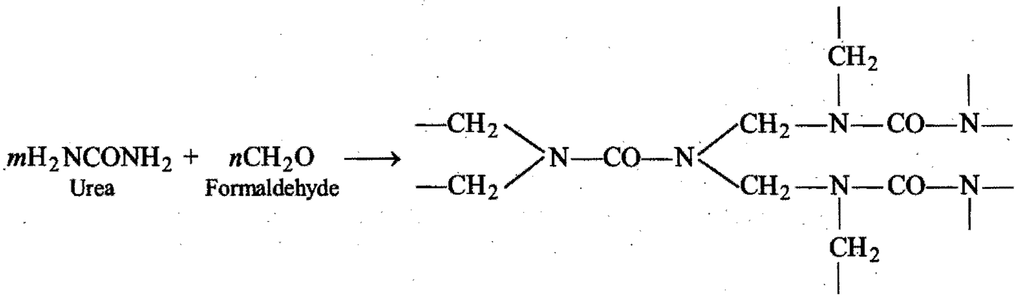


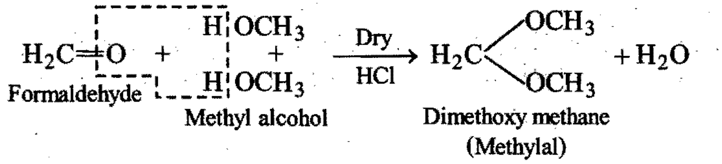
Fig. 11.2 Bakelite (Three dimensional product)

(v) Condensation with urea : Formaldehyde also condenses with urea in acidic solution to form a plastic like product.



Formaldehyde-Urea plastic

(vi) Reaction with alcohol : Formaldehyde reacts with methyl alcohol in presence of dry hydrogen chloride or fused calcium chloride forming methylal which is used as soporific.



(vii) Polymerisation : Formaldehyde readily undergoes polymerisation.

(a) *Para*-formaldehyde : When an aqueous solution of formaldehyde (formalin) is evaporated to dryness, a white crystalline solid with fishy odour is obtained. It is a long chain polymer.

$$\underset{\text{(Aq. solution)}}{n\text{HCHO}} \rightleftharpoons \underset{\textit{Para}\text{-formaldehyde}}{(\text{CH}_2\text{O})_n} \quad \text{or} \quad -\!\!(\text{CH}_2\text{O—CH}_2\text{O—CH}_2\text{O})\!\!-_n \qquad (n = 6 \text{ to } 50)$$

On rapid heating, it gives back gaseous formaldehyde.

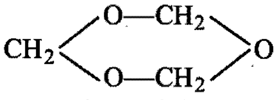
When a formaldehyde solution is treated with conc. H_2SO_4, a white solid, polyoxy methylene $(CH_2O)_n \cdot H_2O$ is formed.

$$n\text{HCHO} \xrightleftharpoons[\text{Heat}]{\text{Conc. H}_2\text{SO}_4} \underset{\text{Polyoxy methylene}}{(\text{CH}_2\text{O})_n\cdot\text{H}_2\text{O}} \qquad n > 100$$

This on heating gives back formaldehyde.

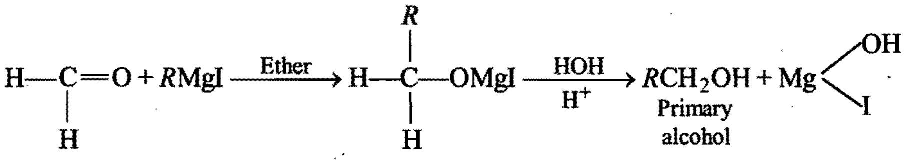
(b) *Meta*-formaldehyde : On allowing formaldehyde gas to stand at room temperature, it slowly polymerises to *meta*-formaldehyde, $(HCHO)_3$. It is a white solid (m.pt. 61–62°C). It does not show reducing character and on heating gives back gaseous formaldehyde.

$$\underset{\text{Formaldehyde}}{3HCHO} \rightleftharpoons \underset{\substack{\textit{Meta}\text{-formaldehyde}\\ \text{or Trioxane}}}{(HCHO)_3} \quad \text{or}$$



Trioxymethylene

(viii) Reaction with Grignard reagent : Formaldehyde forms primary alcohol with Grignard reagent.



$$H-\underset{\underset{H}{|}}{C}=O + RMgI \xrightarrow{\text{Ether}} H-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-OMgI \xrightarrow[H^+]{HOH} \underset{\substack{\text{Primary}\\ \text{alcohol}}}{RCH_2OH} + Mg\begin{matrix}OH\\ I\end{matrix}$$

Formaldehyde does not react with chlorine and phosphorus pentachloride. It does not give iodoform test.

Uses : (i) The 40% solution of formaldehyde in water (formalin) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens.

(ii) It is used in the preparation of hexamethylene tetramine (urotropine) which is used as an antiseptic and germicide.

(iii) It is used in silvering of mirror and decolouring vat dyes.

(iv) It is employed in the manufacture of synthetic dyes such as *para*-rosaniline, indigo, etc.

(v) It is used in the manufacture of **formamint** (by mixing formaldehyde with lactose)—a throat lozenge.

(vi) It is used for making synthetic plastics like bakelite, urea-formaldehyde resin, etc.

(vii) Rongalite—a product obtained by reducing formaldehyde sodium bisulphite derivative with zinc dust and ammonia and is used as a reducing agent in vat dyeing.

(viii) As a methylating agent for primary and secondary amines, *e.g.*,

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + 2HCHO \longrightarrow \underset{\text{Ethyl methylamine}}{C_2H_5NH-CH_3} + HCOOH$$

2. Acetaldehyde or Ethanal (CH_3CHO)

Acetaldehyde occurs in certain fruits and was first prepared by Scheele in 1774 by oxidation of ethyl alcohol.

It may be prepared by any of the general methods already dealt in section 11.4.

Laboratory preparation : Acetaldehyde is prepared in the laboratory by oxidation of ethyl alcohol with acidified potassium dichromate or acidified sodium dichromate.

Manufacture : Acetaldehyde can be manufactured by one of the following methods:

(i) By air oxidation of ethyl alcohol.
(ii) By dehydrogenation of alcohol.
(iii) By hydration of acetylene.
(iv) From ethylene (Wacker process).

Physical properties : (i) Acetaldehyde is a colourless volatile liquid, b.pt is 21°C and has a characteristic pungent smell.

(ii) It is soluble in water, chloroform, ethyl alcohol and ether. Its aqueous solution has a pleasant odour. In water, it is hydrated to a considerable extent to form ethylidene glycol.

$$CH_3CHO + H_2O \longrightarrow CH_3CH(OH)_2$$

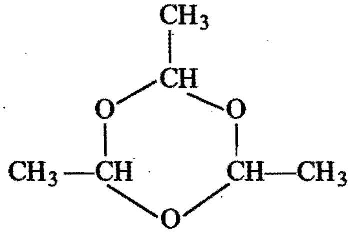
Chemical properties : It gives all characteristic reactions of aldehydes (already discussed in section 11.5). Besides general reactions, acetaldehyde shows the following reactions also:

(i) Haloform reaction : It responds to iodoform reaction due to the presence of CH_3CO group.

(ii) Polymerisation : Acetaldehyde undergoes polymerisation forming different products under different conditions.

(a) Paraldehyde : It is formed, when anhydrous acetaldehyde is treated with a few drops of conc. sulphuric acid.

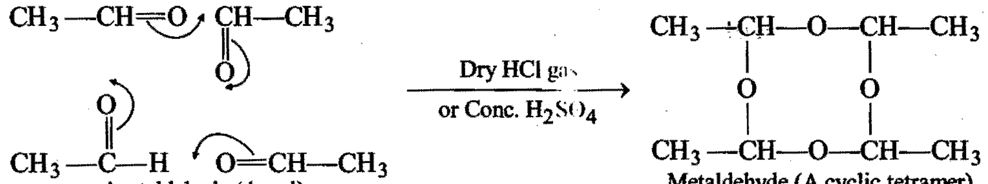
$3CH_3CHO \rightleftharpoons (CH_3CHO)_3$;
Acetaldehyde Paraldehyde, (trimer)



Paraldehyde
(A cyclic trimer)

It is a pleasant smelling liquid (b.pt. 124°C). It has cyclic structure and when heated with dilute sulphuric acid, it changes again into acetaldehyde. It is used in the medicine as a **hypnotic** and **soporific** (sleep producing).

(b) Metaldehyde : Acetaldehyde on treatment with dry hydrogen chloride gas or a few drops of conc. H_2SO_4 is converted into metaldehyde $(CH_3CHO)_4$. It is a white solid (m.pt. 246°C). On heating it sublimes but changes again into acetaldehyde when distilled with dilute sulphuric acid. It is used as a solid fuel.



Acetaldehyde (4 mol)

Metaldehyde (A cyclic tetramer)

It is used for killing slugs and snails.

Uses : Acetaldehyde is used:

(i) in the preparation of acetic acid, acetic anhydride, ethyl acetate, chloral, buta-1,3-diene (used in rubbers), dyes and drugs.

(ii) as an antiseptic inhalant in nose troubles.

(iii) in the preparation of paraldehyde (hypnotic) and metaldehyde (solid fuel).

(iv) in the preparation of acetaldehyde ammonia (a rubber accelerator).

(v) as a reducing agent in silvering of mirrors.

Analytical Tests of Formaldehyde and Acetaldehyde

(A) Common to both:

(i) Both restore the pink colour of Schiff's reagent.

(ii) Both reduce Tollen's reagent to silver mirror.

(iii) Both give red precipitate with Fehling's solution.

(B) Special tests of formaldehyde:

(i) Pyrogallol test : When formalin is added to freshly prepared solution of pyrogallol containing excess of hydrochloric acid, a white precipitate is formed which soon acquires pink colour.

(ii) Schryver's test : 1 mL of 1% phenylhydrazine hydrochloride and 1 mL of 5% potassium ferricyanide solution is added to formalin. It is acidified by adding 5 mL of concentrated hydrochloric acid. Appearance of rosy red colour confirms formaldehyde.

(iii) Remini's test : 1 mL of 1% phenylhydrazine solution is mixed with 1 mL of freshly prepared solution of sodium nitroprusside. It is now added to 5 mL of formalin. The solution is made alkaline by adding excess of sodium hydroxide solution. A deep blue colour develops which changes via green brown to red with time.

(iv) Formaldehyde renders protein hard and insoluble. This property can also be used as a special test of formaldehyde as other aldehydes do not have this property.

(C) Special tests of acetaldehyde:

(i) It gives iodoform test.

(ii) With sodium nitroprusside and piperidine, acetaldehyde gives blue colour.

(iii) Acetaldehyde produces a deep red colour with freshly prepared sodium nitroprusside solution and excess of dilute sodium hydroxide.

Conversion of HCHO into CH_3CHO and *vice-versa*

Ascent of Series : Conversion of formaldehyde into acetaldehyde

(i) $$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{H_2/Ni} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{PCl_5} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow[\text{(Alc.)}]{KCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{\text{Na/Alcohol}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[HCl]{NaNO_2}$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7]{H_2SO_4\text{(dil.)}} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(ii) $$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow[\text{Ether}]{CH_3MgI} CH_3CH_2OMgI \xrightarrow{H_3^+O} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[300°C]{Cu} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(iii) $$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Formic acid}}{HCOOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium formate}}{(HCOO)_2Ca} \xrightarrow[\text{Heat}]{(CH_3COO)_2Ca} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

Descent of Series : Conversion of acetaldehyde into formaldehyde

(i) $$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow[HCl]{NaNO_2}$$

$$CH_3OH \xrightarrow[300°C]{Cu} \underset{\text{Formaldehyde}}{HCHO}$$

(ii) $$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} \underset{\text{Sod. acetate}}{CH_3COONa} \xrightarrow[\text{Heat}]{\text{Sodalime}} \underset{\text{Methane}}{CH_4} \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow{AgOH}$$

$$CH_3OH \xrightarrow[300°C]{Cu} \underset{\text{Formaldehyde}}{HCHO}$$

3. Acetone or Propanone, CH_3COCH_3 or Dimethyl Ketone

It is a symmetrical (simple) ketone and is the first member of the homologous series of ketones. In traces, it is present in blood and urine. It may be prepared by any of the general methods already dealt in section 11.4.

Laboratory preparation : Acetone is prepared in laboratory by heating anhydrous calcium acetate.

Manufacture : Acetone is manufactured by following methods:

(i) By air-oxidation of isopropyl alcohol.

(ii) By dehydrogenation of isopropyl alcohol.

(iii) From propene : (a) Wacker's process.

(b) Propene is absorbed in concentrated sulphuric acid and the resulting product is boiled with water when isopropyl alcohol is formed. Isopropyl alcohol on dehydrogenation yields acetone.

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + H_2SO_4 \longrightarrow CH_3CH(HSO_4)CH_3 \xrightarrow[\text{Boil}]{H_2O} \underset{\text{Isopropyl alcohol}}{CH_3CH(OH)CH_3} \xrightarrow[300°C]{Cu} \underset{\text{Acetone}}{CH_3COCH_3}$$

(iv) From ethyl alcohol : By passing a mixture of ethyl alcohol vapour and steam over a catalyst, zinc chromite at 500°C, acetone is obtained. The yield is about 80%.

$$2C_2H_5OH + H_2O \xrightarrow{Zn(CrO_2)_2} CH_3COCH_3 + CO_2 + 4H_2$$

(v) From acetylene : By passing a mixture of acetylene and steam over a catalyst, magnesium or zinc vanadate at 420°C, acetone is obtained.

$$2HC{\equiv}CH + 3H_2O \longrightarrow CH_3COCH_3 + CO_2 + 2H_2$$

(vi) From pyroligneous acid : Pyroligneous acid containing acetic acid, acetone and methyl alcohol is distilled in copper vessel and the vapours are passed through hot milk of lime. Acetic acid combines to form non-volatile calcium acetate. The unabsorbed vapours of methanol and acetone are condensed and fractionally distilled. Acetone distills at 56°C.

The acetone thus obtained is purified with the help of sodium bisulphite as described in laboratory preparation.

Physical properties : (i) It is a colourless liquid with characteristic pleasant odour.

(ii) It is inflammable liquid and boils at 56°C.

(iii) It is highly miscible with water, alcohol and ether.

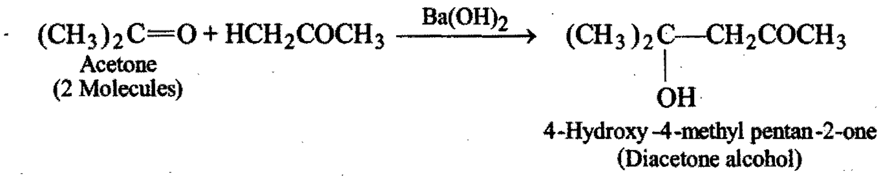
Chemical properties : It shows general properties of ketones. Some special properties of acetone are described below:

(i) Haloform reaction : When heated with iodine and sodium hydroxide, it forms yellow crystals of iodoform.

(ii) Acetone forms chloroform when heated with bleaching powder.

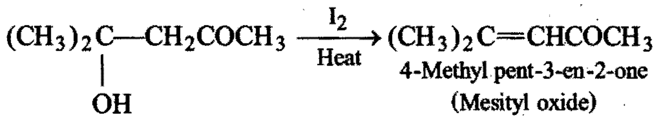
(iii) Condensation reactions : Acetone forms a number of condensation products under different conditions.

(a) Two molecules of acetone condense together in presence of barium hydroxide to form diacetone alcohol.



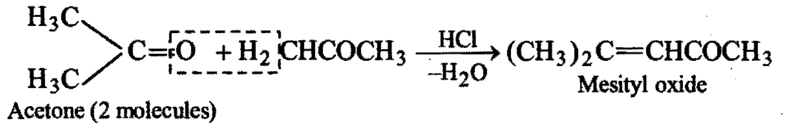
$$\underset{\substack{\text{Acetone}\\\text{(2 Molecules)}}}{(CH_3)_2C{=}O + HCH_2COCH_3} \xrightarrow{Ba(OH)_2} \underset{\substack{\text{4-Hydroxy-4-methyl pentan-2-one}\\\text{(Diacetone alcohol)}}}{(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}CH_2COCH_3}$$

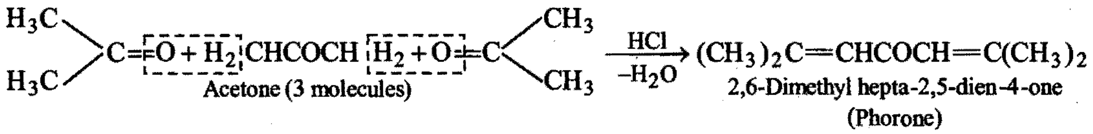
When diacetone alcohol is heated in presence of a little iodine, mesityl oxide is formed.



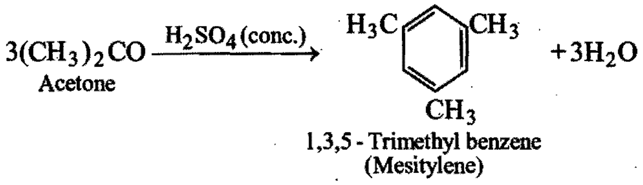
$$(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}CH_2COCH_3 \xrightarrow[\text{Heat}]{I_2} \underset{\substack{\text{4-Methyl pent-3-en-2-one}\\\text{(Mesityl oxide)}}}{(CH_3)_2C{=}CHCOCH_3}$$

(b) When acetone saturated with HCl gas is kept at low temperature for few days, it forms mesityl oxide and phorone which can be separated by distillation.





(c) When acetone is distilled with concentrated sulphuric acid it forms mesitylene.



Uses : (i) As a solvent for cellulose acetate, cellulose nitrate, celluloid, lacquers, resins, etc.

(ii) For storing acetylene.

(iii) In the manufacture of cordite—a smokeless powder explosive.

(iv) In the preparation of chloroform, iodoform, sulphonal and chloretone.

(v) As a nail polish remover.

(vi) In the preparation of an artificial scent (ionone), plexiglas (a tough transparent plastic) and synthetic rubber.

Tests : (i) Legal's test : When a few drops of freshly prepared sodium nitroprusside and sodium hydroxide solution are added to an aqueous solution of acetone, a wine colour is obtained which changes to yellow on standing.

(ii) Indigo test : A small amount of *ortho*-nitrobenzaldehyde is added to about 2 mL of acetone and it is diluted with KOH solution and stirred. A blue colour of indigotin is produced.

(iii) Iodoform test : Acetone gives iodoform test with iodine and sodium hydroxide or iodine and ammonium hydroxide.

11.8 POLYMERISATION AND CONDENSATION

Polymerisation : The process which involves union of two or more molecules of the same compound, without the elimination of a small molecule such as H_2O, NH_3 or alcohol, etc., resulting in the formation of a new compound whose molecular mass is simple multiple of the original compound is called **polymerisation.** The new compound formed is termed polymer (Greek: *poly* + *meros* = many parts). The original simple compounds from which polymers are made are called monomers.

Characteristics of Polymerisation

(i) It is generally a reversible reaction, *i.e.*, the polymer can be converted easily into original compound.

(ii) No portion of reacting molecules is eliminated in any form.

(iii) No new C—C and C—N linkages are formed.

(iv) Polymer and the monomer both have the same empirical mass and formula but the molecular mass of the polymer is simple multiple of the molecular mass of the monomer.

(v) The monomer usually consists of a multiple bond (double or triple) in its molecule.

Alkenes, acetylenes and aldehydes undergo polymerisation reactions. The polymer may be straight chain or cyclic.

Examples : (i) On evaporation of formaldehyde solution, a solid *para*-formaldehyde is formed. On rapid heating, it is again converted into gaseous formaldehyde.

(ii) On allowing formaldehyde gas to stand at room temperature, it slowly polymerises to *meta*-formaldehyde $(HCHO)_3$, a white solid. This on heating is again converted into gaseous formaldehyde.

(iii) When acetaldehyde is treated with few drops of conc. H_2SO_4, a vigorous reaction takes place with the formation of paraldehyde, $(CH_3CHO)_3$. Acetaldehyde is regenerated when paraldehyde is distilled with dil. H_2SO_4.

(iv) Acetaldehyde on treatment with SO_2 or dry HCl gas at low temperature is converted into metaldehyde $(CH_3CHO)_4$. On distillation with dil. H_2SO_4, it yields back acetaldehyde.

Condensation : It is a process which involves union of two or more molecules of the same or different substances to form a more complex compound with or without the elimination of H_2O, HCl, NH_3 or alcohol, etc., with a new carbon-carbon or carbon-nitrogen linkages through functional groups.

Characteristics of Condensation

(i) Condensation is irreversible reaction.

(ii) Union occurs with or without elimination of H_2O, HCl, NH_3 or alcohol, etc.

(iii) New C—C or C—N linkages are formed.

(iv) Molecular mass of the final product may or may not be exact multiple of the molecular mass of the original substance.

Examples : (i) Condensation of aldehydes and ketones with H_2NOH, $H_2N—NH_2$, $H_2N—NHC_6H_5$, $H_2NNHCONH_2$, etc.

(ii) Acetone undergoes condensation under different conditions. [See page 607]

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Propene reacts with carbon monoxide and hydrogen in presence of cobalt carbonyl catalyst at high temperature and pressure, to form :
(a) propanal (b) butanal
(c) butanone (d) butanoic acid
[Ans. (b)]

2. If hexan-3-one is treated with $NaBH_4$ followed by hydrolysis with D_2O, the product will be:
(a) $CH_3CH_2CH(OD)CH_2CH_2CH_3$
(b) $CH_3CH_2CD(OH)CH_2CH_2CH_3$
(c) $CH_3CH_2CH(OH)CH_2CH_2CH_3$
(d) $CH_3CH_2CD(OD)CH_2CH_2CH_3$
[Ans. (a)]

3. The reaction,

$$R_2CO + 4[H] \xrightarrow[\text{Conc. HCl}]{\text{Zn-Hg}} R_2CH_2 + H_2O$$

is well known as:
(a) Wurtz reaction (b) Rosenmund reduction
(c) Kolbe reaction (d) Clemmensen reduction
[Ans. (d)]

4. Propyne on hydroboration-oxidation gives mainly:
(a) propanone (b) propanoic acid
(c) propanal (d) propane
[Ans. (c)]

5. Which of the following does not react with $NaHSO_3$?
(a) CH_3COCH_3 (b) CH_3CHO
(c) HCHO (d) None of these
[Ans. (d)]

6. $CH_3CHO \xrightarrow{HCN} (A) \xrightarrow{HOH} (B)$
The product (B) is:
(a) malonic acid (b) lactic acid
(c) glycolic acid (d) malic acid
[Ans. (b)]

7. Wolff-Kishner reduction, reduces:
   (a) —COOH group (b) —C≡C group
   (c) —CHO group (d) —O— group
   [Ans. (c)]
8. Aldol condensation will not occur in:
   (a) HCHO (b) CH_3CH_2CHO
   (c) CH_3COCH_3 (d) CH_3CHO
   [Ans. (a)]
9. Acetone reacts with butan-2-ol in presence of aluminium tertiary butoxide to form:
   (a) butanone + propan-1-ol (b) butanone + propan-2-ol
   (c) butanal + propan-1-ol (d) butanal + propan-2-ol
   [Ans. (b)]
10. Acetoxime on heating in presence of conc. H_2SO_4 undergo rearrangement and yields:
   (a) acetone hydrazone (b) acetone
   (c) acetone semicarbazone (d) *N*-methyl acetamide
   [Ans. (d)]

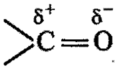
SOME SOLVED PROBLEMS

Problem 3. *Both* $>C=O$ *and* $>C=C<$ *bonds undergo addition reactions, give the basic difference in their nature.*

Solution : The $>C=O$ grouping undergoes nucleophilic addition while $>C=C<$ undergoes electrophilic addition reactions. The difference is due to the fact that C of $>C=O$ grouping is more electrophilic than C of $>C=C<$ grouping since oxygen is more electronegative than carbon. Thus, carbon of $>C=O$ reacts with nucleophiles. The $>C=C<$ grouping is nucleophile and hence reacts with electrophiles.

Problem 4. *Explain why aldehydes are more reactive than ketones.*

Solution : The carbonyl group is polar in nature.



$$>\overset{\delta^+}{C}=\overset{\delta^-}{O}$$

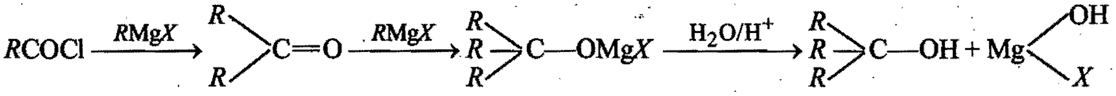
Lower positive charge on the carbon of carbonyl group makes the aldehyde or ketone less reactive towards nucleophiles. In ketones, the positive charge on the carbonyl carbon is lowered by high +*I* effect of two alkyl groups in comparison to aldehydes in which one alkyl group is present. Further increase in the number of alkyl groups also increases the steric hindrance making it less reactive. Thus, in general, aldehydes are more reactive than ketones.

Problem 5. *Under what circumstances may an aldehyde be prepared by oxidation of primary alcohol,* ROH, *with acid dichromate?*

Solution : If the aldehyde product is more volatile than the reactant alcohol and H_2O, it may be removed from the reaction mixture by distillation as it is formed. For example, acetaldehyde (b.pt. 21°C) can be prepared from ethyl alcohol (b.pt. 78°C) by this method.

Problem 6. RCOCl *fails to give ketone when treated with R*—Mg—*X but with* R_2Cd, *a ketone is obtained easily. Explain.*

Solution : No doubt, Grignard reagent reacts with acid halide to form a ketone but Grignard reagent further reacts with ketone readily and ultimately forms a tertiary alcohol.



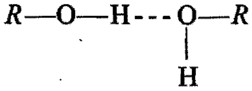
$$RCOCl \xrightarrow{RMgX} R_2C=O \xrightarrow{RMgX} R_3C—OMgX \xrightarrow{H_2O/H^+} R_3C—OH + Mg\begin{smallmatrix}OH\\X\end{smallmatrix}$$

R_2Cd reacts with *R*COCl and forms ketone easily as Cd of R_2Cd is sufficiently electrophilic to initiate the reaction.

$$RCOCl + R_2Cd \longrightarrow [R_2Cd\overset{-}{Cl} + R\overset{+}{C}=O] \longrightarrow RCOR + RCdCl$$

Problem 7. *Account for the boiling points of 2-propanol, propanone and 2-methyl propene (the molecular masses are approximately the same) are 82°C, 57°C and –7°C respectively.*

Solution : The high boiling point of alcohol is due to hydrogen bonding.



$$R—O—H\cdots\underset{\underset{H}{|}}{O}—R$$

The dipole-dipole attractive forces of carbonyl compounds cause them to have higher boiling points than alkenes.

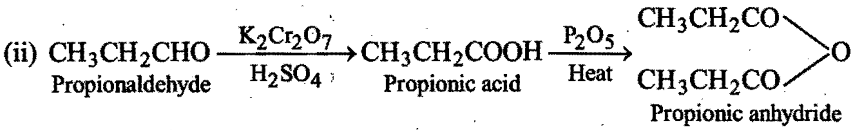
Problem 8. *How will you prepare the following?*

(i) Acetoxime from acetaldehyde, *(ii) Propionic anhydride from propionaldehyde,*

(iii) Acetone from acetylene, *(iv) α-Hydroxy propionic acid from acetaldehyde.*

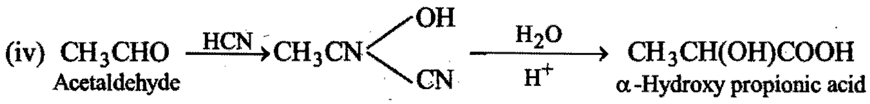
Solution :

$$\text{(i)}\ \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4\,(\text{dil.})]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow[\text{Distillation}]{\text{Dry}} \underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{NH_2OH} \underset{\text{Acetoxime}}{(CH_3)_2C{=}NOH}$$



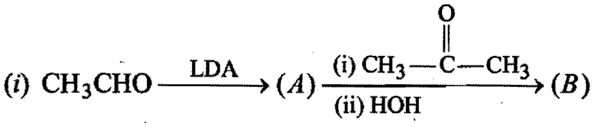
$$\text{(ii)}\ \underset{\text{Propionaldehyde}}{CH_3CH_2CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Propionic anhydride}}{(CH_3CH_2CO)_2O}$$

$$\text{(iii)}\ \underset{\text{Acetylene}}{HC{\equiv}CH} \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow[\text{Distillation}]{\text{Dry}} \underset{\text{Acetone}}{CH_3COCH_3}$$

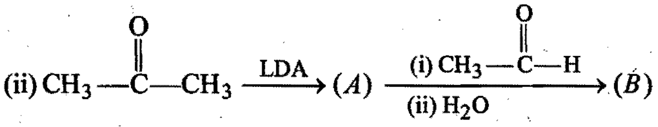


$$\text{(iv)}\ \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{HCN} CH_3CH(OH)CN \xrightarrow[H^+]{H_2O} \underset{\alpha\text{-Hydroxy propionic acid}}{CH_3CH(OH)COOH}$$

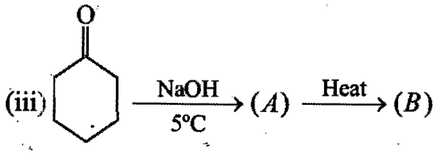
Problem 9. Complete the following reactions :



$$(i)\ CH_3CHO \xrightarrow{LDA} (A) \xrightarrow[\text{(ii) HOH}]{\text{(i) } CH_3COCH_3} (B)$$

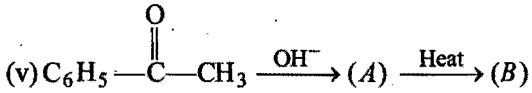


$$\text{(ii)}\ CH_3COCH_3 \xrightarrow{LDA} (A) \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3CHO} (B)$$



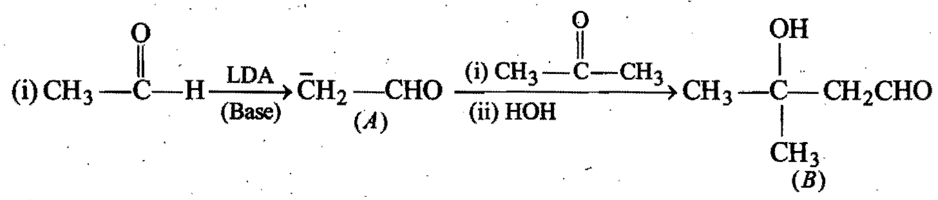
$$\text{(iii)}\ \text{Cyclohexanone} \xrightarrow[5°C]{NaOH} (A) \xrightarrow{\text{Heat}} (B)$$

$$\text{(iv)}\ C_6H_5CH_2CHO \xrightarrow[10°C]{KOH} (A) \xrightarrow{\text{Heat}} (B)$$

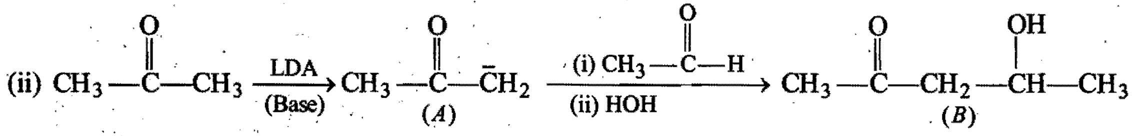


$$\text{(v)}\ C_6H_5COCH_3 \xrightarrow{OH^-} (A) \xrightarrow{\text{Heat}} (B)$$

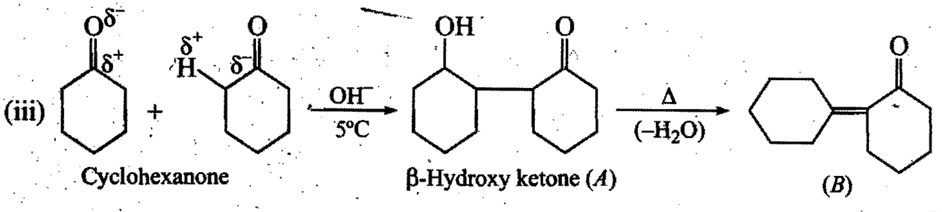
Solution :



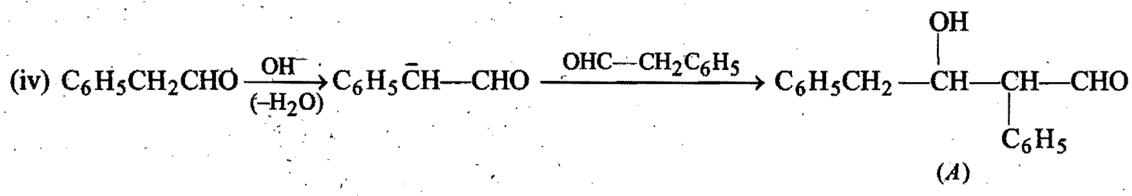
$$(i)\ CH_3CHO \xrightarrow[\text{(Base)}]{LDA} \underset{(A)}{\bar{C}H_2{-}CHO} \xrightarrow[\text{(ii) HOH}]{\text{(i) } CH_3COCH_3} \underset{(B)}{CH_3C(OH)(CH_3)CH_2CHO}$$



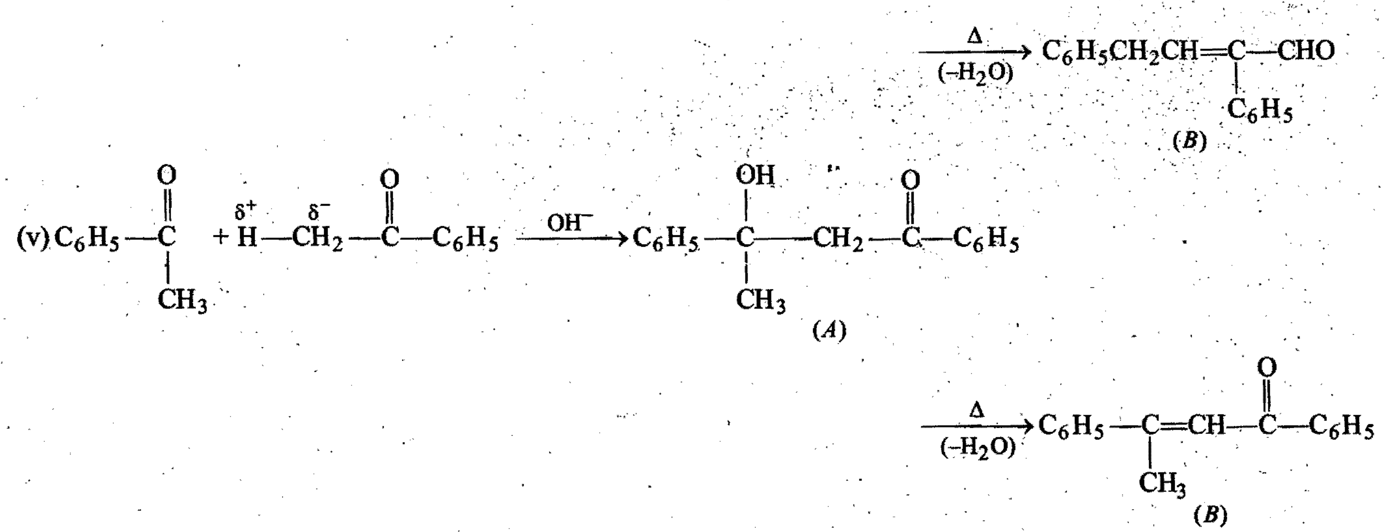
$$\text{(ii)}\ CH_3COCH_3 \xrightarrow[\text{(Base)}]{LDA} \underset{(A)}{CH_3CO\bar{C}H_2} \xrightarrow[\text{(ii) HOH}]{\text{(i) } CH_3CHO} \underset{(B)}{CH_3COCH_2CH(OH)CH_3}$$



Cyclohexanone β-Hydroxy ketone (*A*) (*B*)



$$\text{(iv)}\ C_6H_5CH_2CHO \xrightarrow[(-H_2O)]{OH^-} C_6H_5\bar{C}H{-}CHO \xrightarrow{OHC{-}CH_2C_6H_5} \underset{(A)}{C_6H_5CH_2CH(OH)CH(C_6H_5)CHO}$$



$$\xrightarrow[(-H_2O)]{\Delta} C_6H_5CH_2CH{=}\underset{\underset{(B)}{C_6H_5}}{C}{-}CHO$$

$$(v)\ C_6H_5{-}\underset{CH_3}{\overset{O}{\overset{\|}{C}}} + \overset{\delta^+}{H}{-}\overset{\delta^-}{CH_2}{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \xrightarrow{OH^-} C_6H_5{-}\underset{CH_3}{\overset{OH}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \quad (A)$$

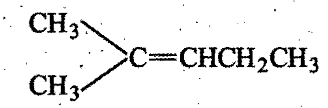
$$\xrightarrow[(-H_2O)]{\Delta} C_6H_5{-}\underset{CH_3}{C}{=}CH{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \quad (B)$$

Problem 10. *An alkene, C_6H_{12}, after ozonolysis yielded two products. One of these gave a positive iodoform reaction but a negative Tollens' test. The other product gave a positive Tollens' test but a negative iodoform reaction. What is the structure and name of the alkene?*

Solution : One product is methyl ketone as it gives positive iodoform test while other product is an aldehyde. The aldehyde does not have methyl group as it does not respond to iodoform test. Hence, the products of ozonolysis are,

$$CH_3COCH_3 \quad \text{and} \quad CH_3CH_2CHO$$

Therefore, the alkene is,

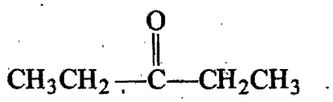


$$(CH_3)_2C{=}CHCH_2CH_3$$

2-Methyl pent-2-ene

Problem 11. *Compound (A), $C_5H_{10}O$, forms a phenylhydrazone, gives negative Tollens' and iodoform tests and is reduced to pentane. What is the compound?*

Solution : (*A*) forms a hydrazone, it is a carbonyl compound. It is a ketone as it does not reduce Tollens' reagent. The ketone does not have methyl group as it does not respond to iodoform test. Thus, the compound is:

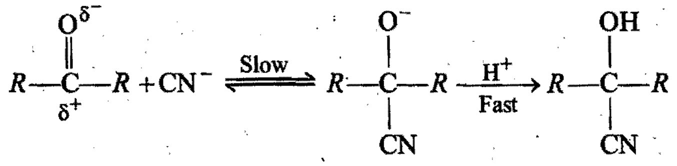


$$CH_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_3$$

Pentan-3-one

Problem 12. *Explain why the addition of hydrogen cyanide to carbonyl compounds is accelerated by bases and retarded by acids.* **[IIT 2003]**

Solution : The addition of HCN to $>C{=}O$ compounds proceeds as follows:



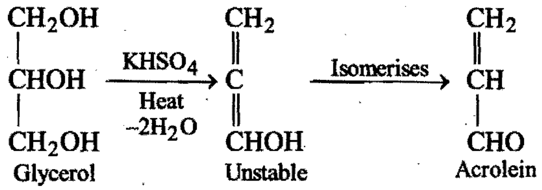
$$R{-}\underset{\delta^+}{\overset{O^{\delta^-}}{\overset{\|}{C}}}{-}R + CN^- \overset{\text{Slow}}{\rightleftharpoons} R{-}\underset{CN}{\overset{O^-}{C}}{-}R \xrightarrow[\text{Fast}]{H^+} R{-}\underset{CN}{\overset{OH}{C}}{-}R$$

In bases, CN^- is formed from HCN while in acidic medium, the ionization of HCN to give CN^- is suppressed.

SUPPLEMENTARY READING

11.9 ACROLEIN, ACRALDEHYDE OR PROP-2-EN-1-AL ($H_2C{=}CHCHO$)

It is obtained by dehydration of glycerol. Dehydration is done with the help of $KHSO_4$ or P_2O_5 or conc. H_2SO_4.



Commercially, it is prepared by passing a mixture of ethanal and methanal vapours over sodium silicate (catalyst).

$$HCH\boxed{O+H_2}CHCHO \xrightarrow{\text{Sodium silicate}} H_2C{=}CHCHO + H_2O$$

It is also obtained by direct oxidation of propylene over copper oxide.

$$H_2C{=}CHCH_3 + O_2 \longrightarrow H_2C{=}CHCHO + H_2O$$

Acrolein is a colourless pungent liquid. It has very irritating smell. It causes watering of eyes and nose.

It is the simplest unsaturated aldehyde. It shows properties of a double bond and aldehydic group. It gives addition reactions with halogens and halogen acids but contrary to Markownikoff's rule.

$$H_2C{=}CHCHO + Br_2 \longrightarrow CH_2Br{-}CHBrCHO$$

$$H_2C{=}CHCHO + HCl \longrightarrow ClCH_2{-}CH_2CHO$$

[This is due to resonance. $H_2C{=}CH{-}CH{=}O \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{O}$]

Acrolein undergoes oxidation with ammoniacal silver nitrate to give acrylic acid without affecting the double bond.

$$\underset{\text{Acrolein}}{H_2C{=}CH{-}CHO} + [O] \xrightarrow[NH_4OH]{AgNO_3} \underset{\text{Acrylic acid}}{H_2C{=}CHCOOH}$$

It undergoes reduction with $LiAlH_4$ to give allyl alcohol, without affecting the double bond.

$$H_2C{=}CH{-}CHO \xrightarrow[2H]{LiAlH_4} \underset{\text{Allyl alcohol}}{H_2C{=}CH{-}CH_2OH}$$

It undergoes Tischenko's reaction to form allyl acrylate.

$$2H_2C{=}CHCHO \xrightarrow{(C_2H_5O)_3Al} H_2C{=}CHCOOCH_2CH{=}CH_2$$

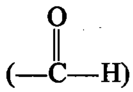
It does not show normal aldol condensation with alkalies. The chain breaks at double bond. This type of reaction is characteristic of α, β-unsaturated aldehydes.

$$H_2C{=}CHCHO \xrightarrow{NaOH} HCHO + CH_3CHO$$

It finds use as tear gas, in the manufacture of insecticides and in the manufacture of resins.

IMPORTANT POINTS TO REMEMBER (SUMMARY)

☐ Both aldehydes and ketones possess the same general formula $C_nH_{2n}O$ and contain a common **carbonyl** **($>C=O$) group.** In aldehydes, the carbonyl group is linked to an alkyl group and a hydrogen atom (except formaldehyde, having no alkyl group), while in ketones it is attached with two alkyl (aryl) groups (same or different).



☐ Aldehydes ($—\overset{\overset{O}{\|}}{C}—H$) may be regarded as the first oxidation product of primary (1°) alcohols and ketones are the first oxidation product of secondary (2°) alcohols.

☐ The carbon atom of $>C=O$ group is sp^2-hybridised and lie in the same plane **(planar).** The bond angles are approximately of 120° and $>C=O$ bond distance is 1.24 Å.

☐ The position of substituents on the parent chain is indicated by Greek letters α, β and γ etc. The α-carbon is one which is directly attached to the —CHO group. $\overset{\delta}{C}—\overset{\gamma}{C}—\overset{\beta}{C}—\overset{\alpha}{C}—CHO$

☐ The —CHO group is always present at the end of the carbon chain (C_1) and in IUPAC system it is named as **alkanal.** When —CHO group is present as side-chain (with some other main functional group like —COOH, —COO*R*, —CO*X*, —CN etc.), it is called **formyl** group.

☐ Aldehydes show chain isomerism amongst themselves and functional isomerism with ketones, cyclic ethers and unsaturated alcohols. Tautomerism with unsaturated alcohols is also observed. Ketones show chain isomerism, functional isomerism, metamerism (position isomerism) and tautomerism.

Methods of preparations for aldehydes and ketones (Carbonyl compounds)

☐ **From alcohols :** By **controlled oxidation** of 1° and 2° alcohols with acidified $K_2Cr_2O_7$ or $KMnO_4$ or MnO_2 or CrO_3 in CH_3COOH or chromic acid, H_2CrO_4, in aqueous acetone or pyridinium chlorochromate (PCC) etc.

☐ By **catalytic dehydrogenation** of 1° and 2° alcohols over reduced copper heated to 300°C.

☐ Ketones can be obtained from 2° alcohols by **Oppenauer oxidation** with aluminium *tert.*-butoxide $[(CH_3)_3CO]_3Al$. Unsaturated 2° alcohols can also be oxidised to unsaturated ketones (without affecting the $>C=C<$) by this reagent.

☐ **From carboxylic acids :** By **dry distillation of calcium salts** of fatty acids, *e.g.*, calcium formate gives formaldehyde and calcium acetate gives acetone. A equimolar mixture of calcium acetate and calcium formate gives acetaldehyde.

☐ Cyclic ketones are formed when calcium salts of dibasic acids are heated.

☐ By passing the vapours of fatty acids over heated MnO at 300°C or thoria (ThO_2) at 350°C or Al_2O_3 at 400°C, aldehydes and ketones are formed.

☐ **From gem-dihalides :** By **alkaline hydrolysis** of terminal gem-dihalides, the aldehydes are formed, while non-terminal one give ketones.

☐ **From alkenes :** By **reductive ozonolysis** with O_3 to give ozonide followed by decomposition with Zn/H_2O or reduction by H_2/Pd gives aldehydes and ketones. For example, but-2-ene (symmetrical alkene) gives only acetaldehyde and 2,3-dimethyl but-2-ene yields acetone only.

☐ **Oxoprocess (only for aldehydes) :** By reacting an alkene with CO and H_2 (water gas) in presence of cobalt carbonyl as catalyst at 100°C under pressure **(Hydroformylation).**

☐ **Wacker process :** Alkenes are directly oxidised to their corresponding aldehydes and ketones by treating with acidified aqueous solution of $PdCl_2$ and Cu_2Cl_2 in presence of oxygen or air.

☐ Alkenes can be oxidised to aldehyde by an oxidising agent $NaIO_4$ **(Lemieux reagent).**

☐ Alkenes can also be oxidised to aldehydes and ketones by an oxidising agent CrO_2Cl_2 in CH_2Cl_2.

☐ **From alkynes :** By hydration with dil (aq.) H_2SO_4 and $HgSO_4$ at about 60°C. Ethyne gives ethanal, propyne gives propanone and but-2-yne yields butan-2-one.

☐ **Hydroboration-oxidation :** Hydroboration (BH_3/THF) of terminal alkynes followed by oxidation with alk. H_2O_2 gives aldehyde, but non-terminal alkynes under similar conditions yield ketone.

☐ **From Grignard reagents :** On **reaction with nitriles,** *i.e.*, Grignard reagents give aldehydes with HCN and ketones with *R*CN.

☐ On **reaction with esters** *i.e.*, formic ester (HCOO*R*) is used to prepare aldehyde and all other esters (*R*COO*R*) give ketone on treatment with Grignard reagent.

☐ On **reaction with acid halide and acid anhydride,** *i.e.*, formyl chloride (HCOCl) gives an aldehyde and all other halides (*R*COCl) gives ketone. But acid anhydride $(RCO)_2O$ gives ketone only with Grignard reagent.

☐ On **reaction with *ortho* esters,** *i.e.*, *ortho*-formic ester or ethyl *ortho*-formate, $HC(OC_2H_5)_3$, gives an aldehyde with Grignard reagent while all other *ortho* esters $RC(OC_2H_5)_3$ give ketones.

☐ **Rosenmund's reduction :** Acid chlorides can be reduced into aldehydes with hydrogen in boiling xylene using Pd or Pt catalyst supported on $BaSO_4$. Ketones cannot be prepared by this method. The function of $BaSO_4$ is to poison the catalyst to prevent further reduction of aldehydes to 1° alcohol.

☐ Lithium *tri-t*-butoxy aluminium hydride $[LiAlH(O\text{-}t\text{-}Bu)_3]$ or *tri-n*-butyl tin $(C_4H_9)_3SnH$ also reduces *R*COCl into *R*CHO.

☐ Sodium aluminium hydride, $NaAlH_4$ also reduces esters into aldehyde.

☐ Ketones can be prepared by the action of dialkyl cadmium on acid chlorides.

☐ **Stephen's reduction :** The reduction of alkyl cyanide by $SnCl_2$ and conc. HCl followed by acid hydrolysis to give aldehyde is known as Stephen's reaction.

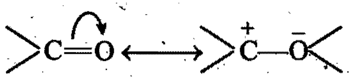
☐ **From acetoacetic ester :** Ketones are prepared by the hydrolysis of acetoacetic ester or its alkyl derivative with dilute aqueous acid or dilute alcoholic solution of alkali.

☐ **From 1,2-glycols :** By oxidation with lead *tetra*-acetate, $(CH_3COO)_4Pb$ or periodic acid, HIO_4.

☐ **From alkyl halides :** On treatment with dimethyl sulphoxide (DMSO), the 1° alkyl halides give aldehyde and 2° alkyl halides give ketone.

☐ **Physical properties :** Except HCHO (it is a gas), all other aldehydes and ketones are volatile liquids at ordinary temperature. Lower aldehydes have unpleasant odour while ketones possess pleasant smell. The carbonyl compounds are strongly polar in nature which results in appreciable intermolecular attraction. Therefore, their boiling points are higher than those of non-polar substances of comparable molecular weights. However, their boiling points are lower than corresponding alcohols due to the absence of intermolecular hydrogen bonding.

☐ **Chemical properties :** Both aldehydes and ketones contain a $>C=O$ group which is highly polar due to resonance and permanent $-I$ effect of the negative oxygen atom.



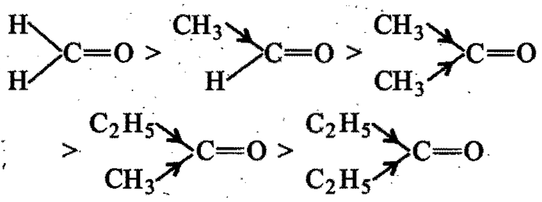
The positively charged carbon is readily attacked by the electron rich nucleophiles, while the negatively charged oxygen is attacked by electron deficient electrophiles.

☐ **Relative reactivity of aldehydes and ketones**

The reactivity of $>C=O$ group for nucleophilic addition depends mainly on:

(i) ability of carbonyl oxygen to carry a negative charge,
(ii) inductive effect of the groups attached to the carbonyl carbon atom and
(iii) size of substituent group (steric factor).

The decreasing order of reactivity of $>C=O$ group is as follows:



Thus, $+I$ effect of alkyl group decreases the reactivity whereas the introduction of negative group ($-I$ effect) increases the reactivity, *e.g.*, chloral (trichloroacetaldehyde) is more reactive than acetaldehyde as the chlorine atoms increase the positive charge on the carbonyl carbon.

The α-H atoms of aldehydes and ketones are reactive (acidic in nature). This is due to the fact that the anion resulting from removal of α-H atom by base gets stabilized by resonance.

Reactions common to aldehydes and ketones

☐ **Substitution reactions :** The α-H atom of alkyl group of $>C=O$ compounds can be replaced by halogen atoms (Cl_2 or Br_2) even at room temperature. Acetaldehyde on **halogenation** (chlorination) gives trichloroacetaldehyde (chloral) and acetone yields trichloroacetone. The excess of alkali decomposes the trihalogen compounds to give **haloform** (CHX_3).

☐ Acetaldehyde, acetone and methyl ketones $(—COCH_3)$ undergo haloform **(Iodoform)** reaction with X_2 (I_2) and NaOH.

☐ **Oxidation by SeO_2 :** Selenium dioxide oxidises the reactive methylene group adjacent to carbonyl group at the α-carbon to form dicarbonyl compounds. For example, acetaldehyde gives glyoxal and acetone yields methyl glyoxal.

Reactions of carbonyl group (Addition reactions)

☐ **Addition of hydrogen :** Different products are obtained depending on the nature of reducing agents.

☐ Molecular hydrogen in presence of metallic catalyst (such as Ni, Pt and Pd) reduces aldehydes and ketones into 1° and 2° alcohols respectively.

☐ With nascent hydrogen produced (such as $Zn + CH_3COOH$, $Na + C_2H_5OH$, $Na + H_2O$, Zn + alc. NaOH, etc.) gives 1° and 2° alcohols **(reduction to alcohols).**

☐ With $LiAlH_4$, $NaBH_4$ or $LiBH_4$ (complex metallic hydrides), aldehydes give 1° alcohol while ketones give 2° alcohol.

☐ Unsaturated aldehydes can be reduced to unsaturated alcohols (1°) without affecting C=C in presence of reducing agents $LiAlH_4$ in dry ether or $NaBH_4$ in alcohol.

☐ **Clemmensen's reduction :** Aldehydes and ketones are converted into alkanes, (*i.e.*, $>C=O$ group is reduced to $>CH_2$ group) when treated with Zn-Hg and conc. HCl. This reaction is known as Clemmensen's reduction.

- The same conversion ($>C{=}O$ into $>CH_2$) can be made by heating aldehydes and ketones with red P and conc. HI.
- **Wolff-Kishner reduction :** Aldehydes and ketones are conveniently reduced to hydrocarbons in presence of excess of hydrazine ($H_2N{-}NH_2$) and strong base (NaOH or C_2H_5ONa) on heating.

$$>C{=}O + H_2NNH_2 \xrightarrow{-H_2O} \underset{\text{(Hydrazone)}}{>C{=}NNH_2} \xrightarrow[\Delta,\ 200^\circ C]{C_2H_5ONa} >CH_2 + N_2$$

- **Meerwein-Ponndorf Verley (MPV) reduction :** Ketones can be reduced to sec. (2°) alcohols with aluminium isopropoxide $[(CH_3)_2CHO]_3Al$ in propan-2-ol.
- **Bimolecular reduction (Pinacol formation) :** Two moles of ketone undergo reduction in presence of Mg-Hg/HOH to pinacol which on heating with mineral acids, converted into pinacolone (Pinacol-pinacolone rearrangement).
- **Addition of HCN :** Both aldehydes and ketones add HCN (KCN + dil. H_2SO_4) in presence of basic catalyst to form cyanohydrins.
- Cyanohydrins are good synthetic reagents and can be converted into α-hydroxy acids, esters and amino acids.
- **Addition of $NaHSO_3$:** Aldehydes and ketones on shaking with a saturated solution of $NaHSO_3$ gives a solid derivative of sodium bisulphite compound.
- These bisulphite compounds on heating with NaCN yield cyanohydrins.
- **Addition of Grignard reagents :** The $>C{=}O$ group adds onto Grignard reagent and the addition product on hydrolysis decomposes to yield 1°, 2° or 3° alcohol depending on the nature of carbonyl compound. For example, HCHO forms 1° alcohol, higher aldehydes (*R*CHO) give 2° alcohols and ketones give 3° alcohol.
- **Reaction with alcohols :** Aldehydes and ketones combine with alcohols and form acetals and ketals respectively and can be easily hydrolysed by acids.
- **Reaction with thioalcohols :** Thioalcohols react more rapidly than alcohols and form thioacetals and thioketals.

Replacement of carbonyl oxygen (Condensation reactions)

- **Reaction with NH_2OH :** Aldehydes and ketones react with hydroxylamine (NH_2OH) to form **oximes** ($>C{=}NOH$).
- **Beckmann rearrangement :** Ketoximes on treatment with acid catalyst (conc. H_2SO_4, H_3PO_4, $SOCl_2$ or PCl_5 etc.) undergo Beckmann rearrangement to form a substituted amide (*R*CONH—*R*).
- **Reaction with NH_2NH_2 :** Aldehydes and ketones form **hydrazones** ($>C{=}NNH_2$) with hydrazine.
- **Reaction with $H_2NNHC_6H_5$:** Aldehydes and ketones react with phenylhydrazine ($H_2NNHC_6H_5$) to form **phenylhydrazones** ($>C{=}NNHC_6H_5$).
- **Reaction with 2,4-dinitrophenylhydrazine (DNP, Brady's reagent) :** DNP reacts similarly with carbonyl compounds to form corresponding **2,4-dinitrophenylhydrazone.**
- **Reaction with $H_2NNHCONH_2$:** Aldehydes and ketones combine with semicarbazide ($H_2NNHCONH_2$) to form **semicarbazone** ($>C{=}NNHCONH_2$).
- **Reaction with H_2S :** Carbonyl compounds react with H_2S to form **thioaldehydes** and **thioketones** respectively ($>C{=}S$).

Condensation reactions

- **Aldol condensation (Reactions involving α-hydrogen) :** It is a chemical reaction in which two or more molecules of same or different carbonyl compounds containing α-H atoms unite together in the presence of a dilute base such as NaOH, $Ba(OH)_2$ or K_2CO_3 etc., to form a new product which combines the properties of alcohol and aldehyde or ketone, is called **aldol condensation.**
- **Characteristics of aldol condensation**

  (i) This reaction may take place between (a) same or different aldehydes, (b) an aldehyde and a ketone, (c) same or different ketones.

  (ii) The carbonyl compound must contain hydrogen atom at α-carbon to the $>C{=}O$ group which is involved in aldol condensation. However, formaldehyde though contains no α-H atom yet undergoes abnormal aldol condensation in presence of lime water.

  (iii) New C—C linkage is formed (an irreversible process).

  (iv) The condensation product (*i.e.*, aldol) loses a molecule of water to give α, β-unsaturated $>C{=}O$ compounds.

Reactions in which aldehydes and ketones differ

- **Oxidation of aldehydes :** Aldehydes are easily oxidised to corresponding carboxylic acids and thus acts as strong **reducing agents.** Oxidising agents may be strong (such as acidified $K_2Cr_2O_7$ or acidified $Na_2Cr_2O_7$ or acidified $KMnO_4$ or hot conc. HNO_3) or mild (such as Tollens' reagent or Fehling's solution or Benedict's solution).
- **Reduction of Tollens' reagent :** It is ammoniacal $AgNO_3$. Aldehydes reduce weak (mild) oxidising agents like ammoniacal $AgNO_3$ (Tollens' reagent) to metallic silver which deposits as mirror **(Reducing character of aldehydes).** This reaction is known as **silver mirror test.**
- **Reduction of Fehling's solution :** It is an alkaline solution of cupric ion complexed with sodium potassium tartrate. Aldehydes on heating with Fehling's solution give a reddish brown precipitate of cuprous oxide (Cu_2O).

- **Reduction of Benedict's solution :** It is a solution of copper sulphate, sodium citrate and sodium carbonate. When heated with an aldehyde, a reddish brown precipitate of Cu_2O appears (similar to Fehling's test).
- Ketones do not reduce Tollens' reagent, Fehling's solution and Benedict's solution **(Distinction between aldehydes and ketones).**
- **Oxidation of ketones :** Ketones are oxidised with difficulty. They are oxidised only on heating with a strong oxidising agent to a mixture of carboxylic acids with lesser number of carbon atoms.
- Oxidation of mixed ketones is governed by **Popoff's rule** according to which, the $>C{=}O$ group remains with the smaller alkyl group.
- **Baeyer-Villiger oxidation :** Aliphatic ketones undergo oxidation with per acids such as Caro's acid (H_2SO_5) or per benzoic acid ($C_6H_5CO_3H$) or per acetic acid (CH_3CO_3H), etc., to form esters or their hydrolysed products (carboxylic acids and alcohols).
- **Schiff's test of aldehydes :** Schiff's reagent is a dilute solution of *p*-rosaniline hydrochloride whose pink (red) colour has been discharged by passing SO_2 gas. Aldehydes when treated with Schiff's reagent (magenta solution in H_2SO_3) restore its pink colour. Ketones do not give this test.
- **Reaction with NH_3 :** Except formaldehyde, other aldehydes form addition product with NH_3 (aldehyde ammonia).
- Formaldehyde on reaction with NH_3 gives hexamethylene tetramine **(urotropine)** which is used as an urinary antiseptic.
- Ketones on treatment with NH_3 form complex ketonic amine.
- **Reaction with alkali :** Aldehydes having α-hydrogen atom on heating with conc. alkali (except HCHO) gives a brown resinous mass (resinification). Ketones do not give this reaction.
- **Cannizzaro's reaction :** HCHO, C_6H_5CHO and other aldehydes containing **no α-hydrogen atoms** on heating with conc. alkali solution undergo oxidation reduction reaction. In this reaction, one molecule of aldehyde is oxidised to carboxylic acid and the other is reduced to 1° alcohol (disproportionation). This is known as **Cannizzaro's reaction.**
- When an aldehyde (having no α-H atom) is treated with HCHO and aqueous base, it is the formaldehyde that undergo oxidation (rather than other aldehyde) and this reaction is known as **crossed Cannizzaro's reaction.**
- Compounds containing two carbonyl groups undergo **intramolecular** or **internal Cannizzaro's reaction.**
- **Tischenko's reaction :** All aldehydes (with or without α-H atoms) undergo Cannizzaro's reaction in presence of aluminium ethoxide $(C_2H_5O)_3Al$. The acid and alcohol so formed react together to give an ester. This is known as **Tischenko's reaction** (a modified Cannizzaro's reaction).
- **Formation of sodio derivative :** Ketones yield sodio derivatives when treated with sodium or sodamide ($NaNH_2$) in ether solution. Aldehydes do not yield sodio derivatives.
- **Reaction with HNO_2 :** Ketones when treated with nitrous acid (HNO_2) form isonitroso derivative. This reaction is not observed in aldehydes.
- **Reduction in neutral or alkaline medium :** When ketones are reduced with Mg-Hg and water, pinacols (dihydric alcohols) are the main product which on heating with dil. H_2SO_4 give pinacolone. It is called **Pinacol-pinacolone** rearrangement.
- **Reformatsky reaction :** This reaction involves the treatment of carbonyl compounds with α-bromo acid ester in presence of metallic zinc to form β-hydroxy ester, which can be easily dehydrated into α, β-unsaturated ester.
- **Claisen-Schmidt reaction (Claisen reaction) :** This condensation reaction is between an aliphatic aldehyde or ketone containing α-hydrogen with benzaldehyde in presence of dilute alkali to form an α,β-unsaturated compound (similar to aldol condensation).
- **Reaction with diazomethane (CH_2N_2) :** In this reaction, aldehydes can be converted to ketones and lower ketones can be converted to higher ketones.
- **Pyrolysis of ketones :** Pyrolysis of ketones at 700°C gives ketene ($CH_2{=}C{=}O$).
- **Knoevenagel reaction :** A reaction between aldehydes and compounds with active methylene group (such as malonic ester, acetoacetic ester and cyanoethyl acetate, etc.) in presence of a base (pyridine) catalyst to give α, β-unsaturated acid is called **Knoevenagel reaction.**
- **Schmidt reaction :** This is a reaction between a carbonyl compound and hydrazoic acid (N_3H) on heating in presence of conc. H_2SO_4 to form N-alkyl acidamide.
- **Condensation with $CHCl_3$:** Acetone condenses with $CHCl_3/CHBr_3$ in presence of KOH to form chloretone/brometone respectively.
- **Condensation with aniline :** Aldehyde condenses with aniline and forms Schiff's base.

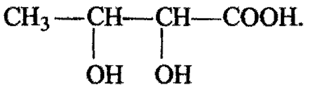
$$RCHO + H_2NC_6H_5 \xrightarrow{\Delta} \underset{\text{(Schiff's base)}}{RCH{=}NC_6H_5} + H_2O$$

- **Polymerisation :** Lower aldehydes show a marked tendency to polymerise forming compounds in which several molecules are linked together through oxygen.
- ***Para*-formaldehyde :** When an aqueous solution of formaldehyde (formalin) is evaporated to dryness, it polymerises to a white crystalline solid, *para*-formaldehyde $(HCHO)_n$ where $n = 6$ to 50. It is a long chain polymer.

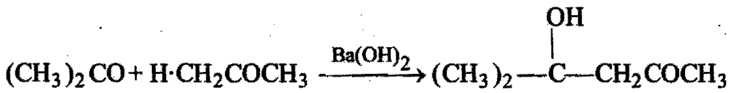
- ☐ ***Meta*-formaldehyde :** On allowing gaseous HCHO to stand at room temperature, a white crystalline solid *meta*-formaldehyde $(CH_2O)_3$ or trioxymethylene is formed.
- ☐ **Paraldehyde :** It is formed, when anhydrous acetaldehyde is treated with a few drops of conc. H_2SO_4. It is a cyclic trimer $(CH_3CHO)_3$ and has no properties of —CHO group and finds use as hypnotic and soporific.
- ☐ **Metaldehyde :** Acetaldehyde on treatment with dry HCl gas or conc. H_2SO_4 at 0°C, is converted into a solid tetramer, metaldehyde $(CH_3CHO)_4$. It is used as a **solid fuel** in spirit lamps and also used for killing slugs and snails.
- ☐ **Uses of formaldehyde:**
  - (i) The 40% solution of HCHO **(formalin)** is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens.
  - (ii) In the preparation of **urotropine** which is used as antiseptic and germicide.
  - (iii) Phenol —HCHO condensed product is used as synthetic plastic named **Bakelite.**
  - (iv) In the manufacture of **synthetic dyes** such as *para*-rosaniline and indigo.
- ☐ **Uses of acetaldehyde:**
  - (i) In the preparation of paraldehyde used as (hypnotic and sleep producing).
  - (ii) In the preparation of metaldehyde (used as a solid fuel).
  - (iii) In the preparation of buta-1,3-diene (used in rubbers).
- ☐ **Uses of acetone:**
  - (i) As a good solvent for cellulose acetate, cellulose nitrate and resins etc.
  - (ii) In the manufacture of cordite (a smokeless powder explosive).
  - (iii) As a nail polish remover.
  - (iv) In the preparation of an artificial scent, plexiglass and synthetic rubber.

QUESTIONS

❖ Very Short Answer Type

1. Fill in the blanks:
    - (a) To prepare a secondary alcohol using Grignard reagent, the other reagent required is ....
    - (b) A 40% aqueous solution of formaldehyde is called ....
    - (c) Formalin is used for the preservation of .... specimens.
    - (d) Urotropine is formed by the action of .... with ....
    - (e) Aldehydes and ketones have .... as general formula.
    - (f) Aldehydes undergo polymerisation while ketones undergo ....
    - (g) The conversion of acid chlorides into aldehydes by reduction is termed ....
    - (h) The conversion of aldehydes into alkanes by reduction is termed as ....
    - (i) Schiff's reagent gives .... colour with acetaldehyde.
    - (j) Acetone when distilled with a little conc. H_2SO_4 forms ....
    - (k) Ethanol vapour is passed over heated copper and the product is treated with aqueous NaOH. The final product is ....
    - (l) Aldehydes show reducing properties due to their ready conversion into ....
    - (m) The structure of the enol form of $CH_3COCH_2COCH_3$ with intramolecular hydrogen bonding is ....
    - (n) The carbon atom of the carbonyl group is .... hybridized.
    - (o) The carbonyl group in aldehydes and ketones undergoes .... addition reactions.
    - (p) Trimer of acetaldehyde has a structure ....
    - (q) Iodoform test is used to detect .... linked to alkyl group or hydrogen.
    - (r) Hydrazone of an aldehyde when heated with sodium ethoxide forms .... This is known as .... reaction.
    - (s) Cannizzaro's reaction is followed by those aldehydes which .... α-hydrogen atom.
    - (t) Two separate solutions, Fehling's solution *A*(......) and Fehling's solution *B*(NaOH + ...) are at first mixed up together and is then heated with the aldehyde. *A*...........precipitate is formed.
    - (u) Tollens' reagent gives .... with acetaldehyde.
    - (v) A plastic bakelite is a compound of HCHO with ....
    - (w) Acetyl chloride is reduced to acetaldehyde by ....
    - (x) Aldehydes have boiling points lower than those of .... and higher than those of .... of comparable molecular masses.
    - (y) When calcium acetate is distilled alone .... is formed.
    - (z) Pentan-2-one can be differentiated from 3-pentanone by ....
2. State whether the following statements are **True** or **False:**
    - (a) The reaction of methyl magnesium bromide with acetone followed by hydrolysis gives secondary alcohol.
    - (b) Aldehydes other than formaldehyde can be purified with ammonia.
    - (c) Aldehydes are more reactive than ketones.
    - (d) Formaldehyde is used for making polymer, bakelite.
    - (e) The yield of ketone, when a secondary alcohol is oxidised, is more than the yield of aldehyde when primary alcohol is oxidised.
    - (f) Both aldehydes and ketones reduce Tollens' reagent.
    - (g) Aldol condensation is given by all carbonyl compounds.
    - (h) Cannizzaro's reaction is shown by all aldehydes.
    - (i) Aldehydes and ketones are functional isomers.
    - (j) Acetaldehyde and acetone can be distinguished by iodoform test.
    - (k) Carbonyl compounds undergo nucleophilic addition.
    - (l) $LiAlH_4$ converts ketones into secondary alcohols.
    - (m) Methanol can be distinguished from ethanol by haloform reaction.
    - (n) Trimethyl acetaldehyde undergoes Cannizzaro's reaction.
    - (o) Propanone does not show tautomerism.
    - (p) Calcium formate on heating gives acetaldehyde.
    - (q) Formaldehyde reacts with ammonia to form hexamethylene tetramine.
    - (r) 2-Pentanone and 3-pentanone are position isomers.
    - (s) Ketones restore pink colour of Schiff's reagent.
    - (t) Aldehydes can act as strong oxidising agents since they themselves can be oxidised easily.
    - (u) The class of compounds that get reduced to primary alcohols and also respond to Fehling's test is known as aldehydes.
    - (v) Aldehydes are sweet smelling while ketones have pungent smell.
    - (w) Acetaldehyde reacts with both nucleophiles and electrophiles.
    - (x) A brown resinous product is formed when acetaldehyde is heated with conc. KOH.
    - (y) Acetaldehyde is more reactive than chloral.
    - (z) Tollens' reagent converts $CH_3CH{=}CHCHO$ to  $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH$. **[Roorkee 2001]**

3. Match the following:

(i)	(A) Formaldehyde	(1) Iodoform test
	(B) Acetone	(2) Test of aldehydes
	(C) Acetaldehyde	(3) Ammoniacal silver nitrate
	(D) Haloform reaction	(4) Polymer of phenol and formaldehyde
	(E) Schiff's reagent	(5) Calcium acetate
	(F) Clemmensen's reduction	(6) Urotropine
	(G) Bakelite	(7) Boiling point 21°C
	(H) Tollens' reagent	(8) Zinc amalgam and conc. HCl
(ii)	(A) Cannizzaro's reaction	(1) $H_2C{=}CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3CHO + Pd + 2HCl$
	(B) Rosenmund's reaction	(2)  $(CH_3)_2CO + H{\cdot}CH_2COCH_3 \xrightarrow{Ba(OH)_2} (CH_3)_2{-}\overset{OH}{\overset{\vert}{C}}{-}CH_2COCH_3$
	(C) Oxo process	(3) Zn/Hg + Conc. HCl
	(D) Wacker process	(4) $2HCHO \xrightarrow{NaOH} HCOONa + CH_3OH$
	(E) Clemmensen's reduction	(5) $H_2/Pd{-}BaSO_4$
	(F) Aldol condensation	(6) $(C_2H_5O)_3Al$
	(G) Tischenko's reaction	(7) Alkene + CO + $H_2 \xrightarrow{CO_2(CO)_8}$ Aldehyde
	(H) Fehling's solution	(8) Red ppt. of Cu_2O

4. Complete the following equations and write down the names of the products:

(i) $CH_3CHO \xrightarrow{H_2SO_4(conc.)} ?$

(ii) $HCHO + K_2Cr_2O_7 + H_2SO_4 \longrightarrow ?$

(iii) $HCHO + NaOH(conc.) \longrightarrow ?$

(iv) $HCHO + NH_3 \longrightarrow ?$

(v) $CH_3COCH_3 \xrightarrow[Distil.]{H_2SO_4(conc.)} ?$

(vi) $2(CH_3)_2CO + NH_3 \longrightarrow ?$

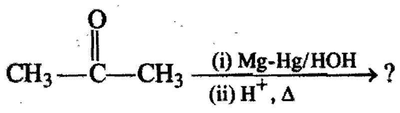
(vii) $CH_3COCH_3 \xrightarrow[NaOH]{I_2} ?$

(viii) $CH_3CHO + NaHSO_3 \longrightarrow ?$

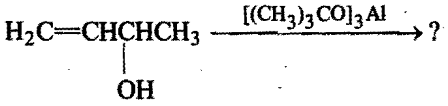
(ix) $CH_3CHO + Ag_2O \longrightarrow ?$

(x) $CH_3CHO + H_2NOH \longrightarrow ?$

(xi) $R{-}COCl + H_2 \xrightarrow{Pd\text{-}BaSO_4} ?$

(xii) 

$CH_3{-}\overset{O}{\overset{\Vert}{C}}{-}CH_3 \xrightarrow[(ii)\ H^+,\ \Delta]{(i)\ Mg\text{-}Hg/HOH} ?$

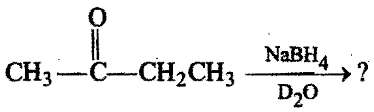
(xiii) 

$H_2C{=}CH\underset{\overset{\vert}{OH}}{C}HCH_3 \xrightarrow{[(CH_3)_3CO]_3Al} ?$

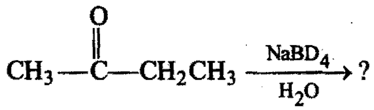
(xiv) $CH_3CH_2C{\equiv}CH \xrightarrow[(ii)\ H_2O_2/NaOH]{(i)\ Sia_2BH/THF} ?$

(xv) $CH_3CH_2C{\equiv}CH \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ BD_3,\ THF} ?$

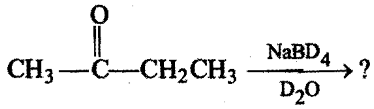
(xvi) $CH_3CH_2CH_2{-}C{\equiv}C{-}CH_3 \xrightarrow[HgSO_4]{H_2SO_4} ?$

(xvii) 

$CH_3{-}\overset{O}{\overset{\Vert}{C}}{-}CH_2CH_3 \xrightarrow[D_2O]{NaBH_4} ?$

(xviii) 

$CH_3{-}\overset{O}{\overset{\Vert}{C}}{-}CH_2CH_3 \xrightarrow[H_2O]{NaBD_4} ?$

(xix) 

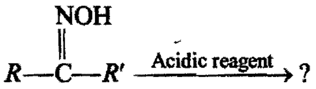
$CH_3{-}\overset{O}{\overset{\Vert}{C}}{-}CH_2CH_3 \xrightarrow[D_2O]{NaBD_4} ?$

(xx) $H_2C{=}CH_2 + O_2 \xrightarrow[H_2O]{PdCl_2,\ CuCl_2} ?$

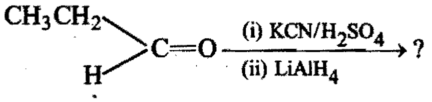
(xxi) $CH_3COCH_3 + CH_3MgBr \xrightarrow[HOH]{NH_4Cl} ?$

(xxii) $CH_3CH_2CHCl_2 \xrightarrow{Boil,\ alkali} ?$

(xxiii) $CH_3CHO \xrightarrow{NaOH(dil.)} ?$

(xxiv) 

$R{-}\overset{NOH}{\overset{\Vert}{C}}{-}R' \xrightarrow{Acidic\ reagent} ?$

(xxv) 

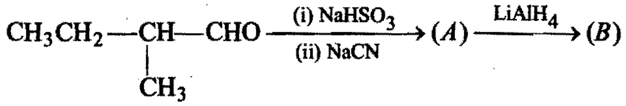
5. Identify the (*A*), (*B*), (*C*) and (*D*) in the following reactions sequence:

(i) $HC{\equiv}CH \xrightarrow[Hg^{2+}]{H_2SO_4(dil.)} (A) \xrightarrow[H_2O/H^+]{CH_3MgBr} (B) \xrightarrow[H_2SO_4]{K_2Cr_2O_7} (C)$

(ii) $CH_3CH_2OH \xrightarrow[300°C]{Cu} (A) \xrightarrow{HCN} (B) \xrightarrow[Heat]{H_2O/H^+} (C)$

(iii) $CH_3COCH_3 \xrightarrow{LiAlH_4} (A) \xrightarrow{HBr} (B) \xrightarrow{Alc.\ KOH} (C)$

(iv) $CH_3COCH_3 \xrightarrow[Heat]{I_2+NaOH} (A) \xrightarrow[Heat]{Ag} (B) \xrightarrow[HgSO_4]{H_2SO_4(dil.)} (C)$

(v) 
$CH_3CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CHO \xrightarrow[(ii)\ NaCN]{(i)\ NaHSO_3} (A) \xrightarrow{LiAlH_4} (B)$

(vi) $(HCOO)_2Ca + (CH_3COO)_2Ca \xrightarrow{Heat} (A) \xrightarrow{NaHSO_3} (B) \xrightarrow{Na_2CO_3} (C)$

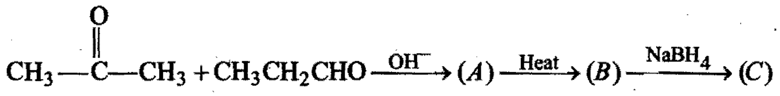
(vii) $CH_3{-}CH{=}CH{-}CHO \xrightarrow{NaBH_4} (A) \xrightarrow[ZnCl_2]{HCl} (B) \xrightarrow[H^+]{KCN} (C)$

(viii) $CH_3CH_2CH_2Br \xrightarrow{KOH(alc.)} (A) \xrightarrow{Br_2} (B) \xrightarrow[\text{followed by } NaNH_2]{KOH(alc.)} (C) \xrightarrow[H_2SO_4(dil.)]{Hg^{2+}} (D)$

(ix) $(CH_3)_2CO + HCN \longrightarrow (A) \xrightarrow{H_3O^+} (B) \xrightarrow[Heat]{H_2SO_4} (C) \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ BH_3} (D)$

(x) $CH_3CH_2CH_2CHO + BrCH_2COOC_2H_5 \xrightarrow[(H^+)]{Zn} (A) \xrightarrow{CrO_3/Py} (B) \xrightarrow{HOCH_2{-}CH_2OH} (C) \xrightarrow{LiAlH_4} (D) \xrightarrow{H_3O^+} (E)$

(xi) $CH_3CHO \xrightarrow{Ag_2O} (A) \xrightarrow{PCl_5} (B) \xrightarrow[Pd/BaSO_4]{H_2} (C) \xrightarrow[H_2O/H^+]{CH_3MgBr} (D)$

(xii) 
$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + CH_3CH_2CHO \xrightarrow{OH^-} (A) \xrightarrow{Heat} (B) \xrightarrow{NaBH_4} (C)$

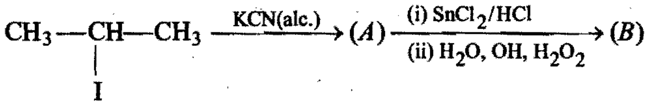
(xiii) $CH_3CH_2CHO \xrightarrow{NaOH} (A) \xrightarrow[Heat]{NaHSO_4} (B) \xrightarrow{H_2/Ni} (C)$

(xiv) $3(CH_3)_2C{=}O \xrightarrow{(A)} (B)$ (in condensation reaction)

(xv) $(A) \xrightarrow[C_2H_5ONa]{NH_2NH_2} CH_3CH_2CH_3$

(xvi) $H_2C{=}CHCH_2OH \xrightarrow[CH_2Cl_2]{CrO_3{\cdot}2C_5H_5N} (A) \xrightarrow{CH_3OH,\ H^+} C_5H_{10}O_2\,(B) \xrightarrow[(Cold,\ dilute)]{KMnO_4,\ OH^-} C_5H_{12}O_4\,(C) \xrightarrow{H_3O^+} (C_3H_6O_3)\,(D)$

[Roorkee 2000]

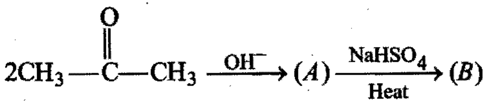
(xvii) 
$CH_3{-}\underset{\displaystyle I}{\underset{|}{C}H}{-}CH_3 \xrightarrow{KCN(alc.)} (A) \xrightarrow[(ii)\ H_2O,\ OH,\ H_2O_2]{(i)\ SnCl_2/HCl} (B)$

(xviii) $CH_3CH_2C{\equiv}CH \xrightarrow[Liq.\ NH_3]{NaNH_2\ in} (A) \xrightarrow{CH_3Br} (B) \xrightarrow[HgSO_4,\ 333K]{H_2SO_4} (C)$

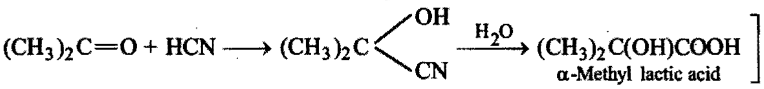
(xix) $(CH_3)_2C{=}O + C_6H_5NH_2 \xrightarrow{H^+} (A) \xrightarrow{H_2/Ni} (B)$

(xx) $(CH_3)_2C{=}O \xrightarrow[HCl]{NaCN} (A) \xrightarrow[Heat]{H_3^+O} (B)$

[CPMT 2000]

(xxi) 
$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{OH^-} (A) \xrightarrow[\text{Heat}]{NaHSO_4} (B)$ **[Roorkee 2000]**

6. What happens when (Give equations only)?
   - (i) Calcium acetate is heated.
   - (ii) Acetaldehyde is heated with aqueous sodium hydroxide solution.
   - (iii) Formaldehyde reacts with sodium hydroxide.
   - (iv) Acetone is treated with HCN and the product is boiled with an acid.

Hint: 
$\left[(CH_3)_2C{=}O + HCN \longrightarrow (CH_3)_2C\begin{matrix}\diagup OH\\ \diagdown CN\end{matrix} \xrightarrow{H_2O} \underset{\alpha\text{-Methyl lactic acid}}{(CH_3)_2C(OH)COOH}\right]$

   - (v) Formaldehyde is treated with methyl magnesium bromide and the product is then hydrolysed.
   - (vi) Ammonia reacts with formaldehyde.
   - (vii) Ammonia reacts with acetone.
   - (viii) Chloral is heated with aqueous sodium hydroxide.

[**Hint :** $CCl_3CHO + NaOH \longrightarrow CHCl_3 + HCOONa$]

   - (ix) Acetaldehyde reacts with Fehling's solution.

[**Hint :** $CH_3CHO + 2CuO \longrightarrow CH_3COOH + Cu_2O$ (Red ppt)]

   - (x) Acetone is distilled with conc. H_2SO_4.

❖ Short Answer Type

7. (i) Give an industrial preparation of (a) formaldehyde, (b) acetaldehyde and (c) acetone.

[**Hint:** (a) $CH_3OH + O_2 \xrightarrow[Cu]{600°C} HCHO$

(b) $HC{\equiv}CH \xrightarrow[H_2SO_4]{HgSO_4} CH_3CHO$ or $H_2C{=}CH_2 + O_2 \xrightarrow[H_2O]{PdCl_2,\ CuCl_2} CH_3CHO$ (Wacker's process)

(c) $CH_3CH{=}CH_2 + O_2 \xrightarrow[H_2O]{PdCl_2,\ CuCl_2} CH_3COCH_3$ (Wacker's process) or $2HC{\equiv}CH + 3H_2O \xrightarrow[420°C]{\text{Zinc vanadate}} CH_3COCH_3 + CO_2 + 2H_2$]

(ii) Give the methods by which ethyl alcohol may be converted into acetaldehyde.

[**Hint :** (a) By oxidation with acidified $K_2Cr_2O_7$ or acidified $KMnO_4$.

(b) By catalytic dehydrogenation-vapours are passed over heated copper at 300°C.]

(iii) How is an aldehyde obtained from an acid chloride?

[**Hint :** By Rosenmund's reduction, $RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$]

(iv) Write an equation for making aldehydes by the oxo process.

$\left[\textbf{Hint: } R{-}CH{=}CH_2 + CO + H_2 \xrightarrow{CO_2(CO)_8} RCH_2CH_2CHO\right]$

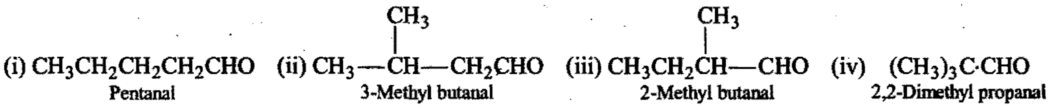
(v) How is impure acetaldehyde purified?

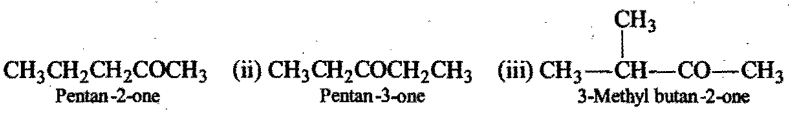
$\left[\textbf{Hint: } \underset{\text{Impure}}{CH_3CHO} + NH_3 \longrightarrow CH_3CH(OH)NH_2 \xrightarrow{H_2SO_4} \underset{\text{Pure}}{CH_3CHO} + NH_4HSO_4\right]$

(vi) How is impure acetone purified?

$\left[\textbf{Hint: } \underset{\text{Impure}}{(CH_3)_2CO} + NaHSO_3 \longrightarrow (CH_3)_2C(OH)SO_2ONa \xrightarrow{Na_2CO_3} \underset{\text{Pure}}{(CH_3)_2CO}\right]$

8. (a) Write the structural formulae and give the IUPAC names for all the aldehydes and ketones of molecular formula, $C_5H_{10}O$.

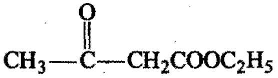
Hint: Aldehydes : 
(i) $\underset{\text{Pentanal}}{CH_3CH_2CH_2CH_2CHO}$ (ii) $\underset{\text{3-Methyl butanal}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2CHO}$ (iii) $\underset{\text{2-Methyl butanal}}{CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{CH}-CHO}$ (iv) $\underset{\text{2,2-Dimethyl propanal}}{(CH_3)_3C{\cdot}CHO}$

Ketones : 
(i) $\underset{\text{Pentan-2-one}}{CH_3CH_2CH_2COCH_3}$ (ii) $\underset{\text{Pentan-3-one}}{CH_3CH_2COCH_2CH_3}$ (iii) $\underset{\text{3-Methyl butan-2-one}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CO-CH_3}$]

(b) Write the functional isomers of $C_5H_{10}O$, that can give Cannizzaro's reaction.

[**Hint :** $(CH_3)_3C-CHO$ (2,2-Dimethyl propanal)]

(c) A keto ester, $C_6H_{10}O_3$ that forms oxime and by iodoform test (with I_2 and NaOH) forms $CH_2(COONa)_2$ and CHI_3. Give its structure.



[**Hint :** $CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOC_2H_5$ (Ethyl-3-ketobutanoate)]

9. How will you differentiate between?

(i) Acetaldehyde and acetone.

[**Hint :** Acetaldehyde responds to following tests while acetone does not give any of them:

(a) Acetaldehyde + Schiff's reagent solution ⟶ Pink colour.

(b) Acetaldehyde + Tollens' reagent ⟶ Silver mirror.

(c) Acetaldehyde + Fehling's solution ⟶ Red precipitate.

(d) Acetaldehyde + Sodium hydroxide (conc.) ⟶ Brown resinous mass.]

(ii) Aldehydes and ketones with (i) Tollens' reagent (ii) Fehling's solution.

[**Hint :** Same tests as in (i)]

(iii) Acetone and diethyl ether.

[**Hint :** Acetone forms yellow coloured iodoform when heated with I_2 and NaOH, *i.e.,* it gives iodoform test. Diethyl ether does not give this test.]

(iv) Formaldehyde and acetaldehyde.

[**Hint :** Acetaldehyde forms yellow precipitate of iodoform with an alkaline solution of iodine, *i.e.,* gives iodoform test. Formaldehyde does not give this test.]

(v) Ethyl alcohol and acetone.

[**Hint :** Ethyl alcohol gives pink colour with ceric ammonium nitrate while acetone does not. Acetone gives pink colour with an alkaline solution of sodium nitroprusside while ethyl alcohol does not.]

(vi) Formaldehyde and ethyl alcohol.

[**Hint :** Formaldehyde responds to following tests while ethyl alcohol does not give any of them:

(a) HCHO + Schiff's reagent ⟶ Pink colour

(b) HCHO + Tollens' reagent ⟶ Silver mirror

(c) HCHO + Fehling's solution ⟶ Red precipitate

Ethyl alcohol gives iodoform test while HCHO does not.]

(vii) Pentan-2-one and pentan-3-one.

[**Hint :** Pentan-2-one having $-COCH_3$ group forms a yellow precipitate of iodoform with an alkaline solution of iodine, *i.e.,* gives iodoform test while pentan-3-one does not.]

10. How would you bring the following conversions?

(a) Acetone from acetaldehyde.

[**Hint:** $\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\text{Heat}} \underset{\text{Acetone}}{CH_3COCH_3}$]

(b) Methanal to ethanal (not more than 3 steps).

[**Hint:** $HCHO \xrightarrow{CH_3MgBr} \underset{\text{Addition product}}{CH_3CH_2OMgBr} \xrightarrow{H_2O} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \underset{\text{Ethanal}}{CH_3CHO}$]

(c) Acetaldehyde from acetyl chloride.

[**Hint :** Rosenmund's reaction.]

(d) Ethyl acetate from acetaldehyde.

[**Hint :** Tischenko's reaction.]

(e) Acetaldehyde to ethylene.

[**Hint:** $CH_3CHO \xrightarrow[Na/C_2H_5OH]{[H]} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[170°C]{\text{Conc. } H_2SO_4} \underset{\text{Ethylene}}{C_2H_4}$]

(f) Formaldehyde to *n*-butane.

[**Hint :** HCHO to CH_3CH_2OH as in (b).

$C_2H_5OH \xrightarrow{PCl_5} \underset{\text{Ethyl chloride}}{C_2H_5Cl} \xrightarrow[\text{Wurtz reaction}]{Na} \underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3}$]

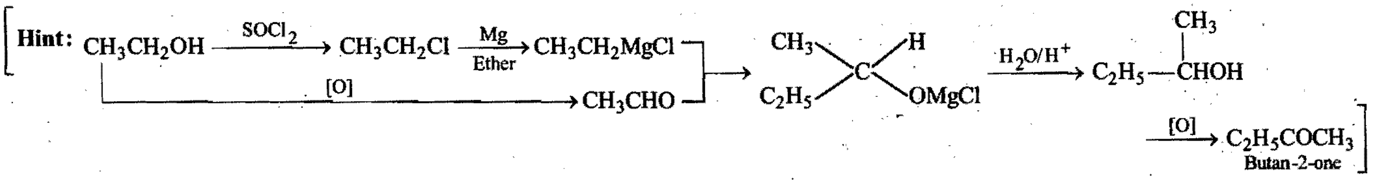
(g) Ethanol to acetone.

[**Hint:** $C_2H_5OH \xrightarrow{[O]} CH_3CHO$, then follow (a)]

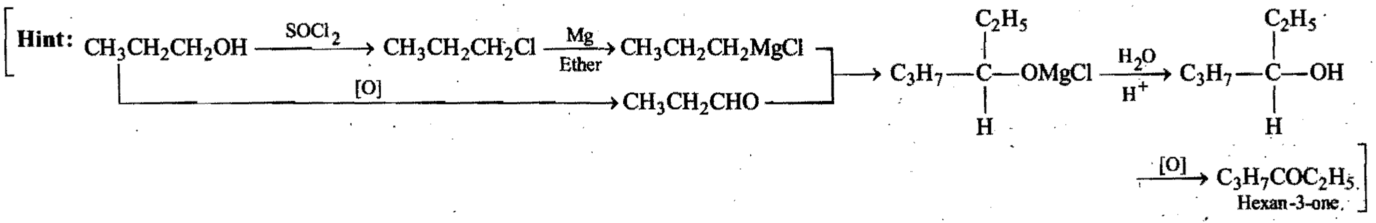
(h) Acetone from methane.

[**Hint:** $CH_4 \xrightarrow[h\nu]{Cl_2} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow[\text{Wurtz reaction}]{Na} \underset{\text{Ethane}}{CH_3—CH_3} \xrightarrow[h\nu]{Cl_2} \underset{\text{Ethyl chloride}}{CH_3 \cdot CH_2Cl} \xrightarrow{NaOH(aq.)} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$, then follow (g)]

(i) Butan-2-one from ethyl alcohol.



(j) Hexan-3-one from *n*-propyl alcohol.



(k) Ethanal to 2-hydroxy but-3-en-l-oic acid.

[**Hint:** $CH_3CHO \xrightarrow[\text{Sod. silicate}]{HCHO} CH_3CHOHCHO \xrightarrow{-H_2O} H_2C{=}CHCHO \xrightarrow{HCN} H_2C{=}CHCH(OH)CN \xrightarrow{H_2O/H^+} H_2C{=}CHCH(OH)COOH$]

(l) Propanal to propyne.

[**Hint:** $CH_3CH_2CHO \xrightarrow{PCl_5} CH_3CH_2CHCl_2 \xrightarrow{\text{Alc. KOH}} CH_3C{\equiv}CH$]

(m) Ethanal to crotonaldehyde.

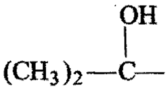
[**Hint:** Aldol condensation followed by dehydration,

$$2CH_3CHO \xrightarrow{\text{Dil. NaOH}} \underset{\text{3-Hydroxy butanal}}{CH_3CH(OH)CH_2CHO} \xrightarrow[-H_2O]{\text{Dehydration}} \underset{\text{But-2-en-1-al}}{CH_3CH{=}CHCHO}$$]

(n) Acetoacetic ester from acetaldehyde.

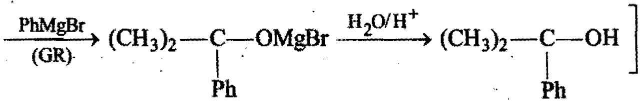
[**Hint:** $\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{C_2H_5OH} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$

$$\underset{\text{Ethyl acetate (2 moles)}}{CH_3COOC_2H_5 + HCH_2COOC_2H_5} \xrightarrow[\text{Claisen condensation}]{C_2H_5ONa} \underset{\text{Acetoacetic ester}}{CH_3COCH_2COOC_2H_5}$$]



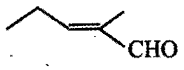
(o) $(CH_3)_2—\overset{\overset{\Large OH}{|}}{C}—Ph$ from acetaldehyde.

[**Hint:** $\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\text{Dry distillation}} \underset{\text{Acetone}}{(CH_3)_2C{=}O}$

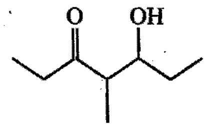


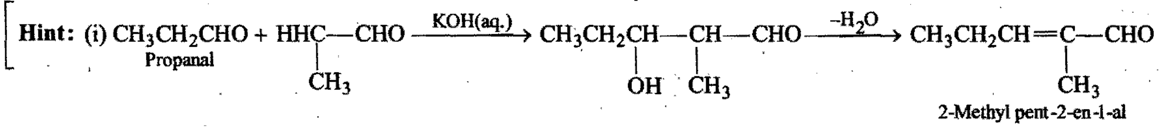
$$\xrightarrow[(GR)]{PhMgBr} (CH_3)_2—\underset{\underset{Ph}{|}}{C}—OMgBr \xrightarrow{H_2O/H^+} (CH_3)_2—\underset{\underset{Ph}{|}}{C}—OH$$]

(p) Propanal to (i)

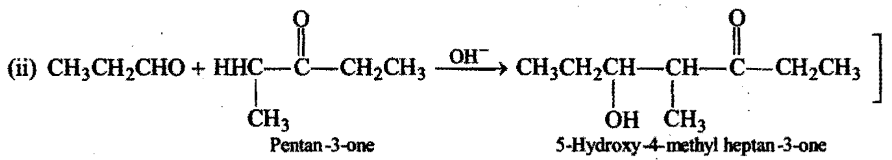


(ii)

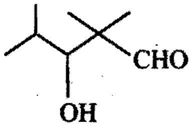


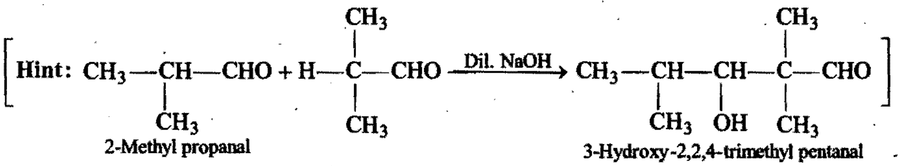


[**Hint:** (i) $\underset{\text{Propanal}}{CH_3CH_2CHO} + HH\underset{\underset{CH_3}{|}}{C}—CHO \xrightarrow{KOH(aq.)} CH_3CH_2\underset{\underset{OH}{|}}{CH}—\underset{\underset{CH_3}{|}}{CH}—CHO \xrightarrow{-H_2O} \underset{\text{2-Methyl pent-2-en-1-al}}{CH_3CH_2CH{=}\underset{\underset{CH_3}{|}}{C}—CHO}$



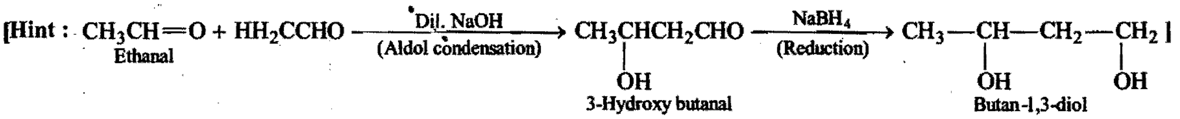
$$\text{(ii) } CH_3CH_2CHO + \underset{\text{Pentan-3-one}}{\underset{CH_3}{HHC}—\overset{O}{\overset{\|}{C}}—CH_2CH_3} \xrightarrow{OH^-} \underset{\text{5-Hydroxy-4-methyl heptan-3-one}}{CH_3CH_2\underset{OH}{CH}—\underset{CH_3}{CH}—\overset{O}{\overset{\|}{C}}—CH_2CH_3} \;]$$

(q) 2-Methyl propanal to 



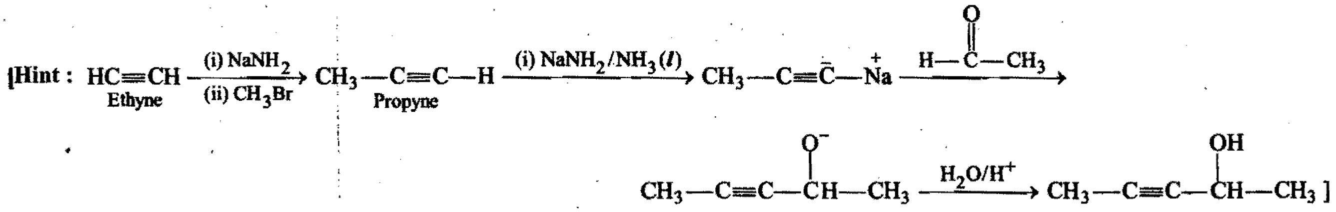
$$\left[\text{Hint: } \underset{\text{2-Methyl propanal}}{CH_3—\underset{CH_3}{CH}—CHO} + H—\overset{CH_3}{\underset{CH_3}{C}}—CHO \xrightarrow{\text{Dil. NaOH}} \underset{\text{3-Hydroxy-2,2,4-trimethyl pentanal}}{CH_3—\underset{CH_3}{CH}—\underset{OH}{CH}—\overset{CH_3}{\underset{CH_3}{C}}—CHO}\right]$$

(r) Ethanal to 3-hydroxy butanal to butan-1,3-diol.



$$[\text{Hint : } \underset{\text{Ethanal}}{CH_3CH{=}O} + HH_2CCHO \xrightarrow[\text{(Aldol condensation)}]{\text{Dil. NaOH}} \underset{\text{3-Hydroxy butanal}}{CH_3\underset{OH}{CH}CH_2CHO} \xrightarrow[\text{(Reduction)}]{NaBH_4} \underset{\text{Butan-1,3-diol}}{CH_3—\underset{OH}{CH}—CH_2—\underset{OH}{CH_2}} \,]$$

(s) Ethyne or propyne to pent-3-yn-2-ol.



$$[\text{Hint : } \underset{\text{Ethyne}}{HC{\equiv}CH} \xrightarrow[\text{(ii) }CH_3Br]{\text{(i) }NaNH_2} \underset{\text{Propyne}}{CH_3—C{\equiv}C—H} \xrightarrow{\text{(i) }NaNH_2/NH_3(l)} CH_3—C{\equiv}\bar{C}—\overset{+}{Na} \xrightarrow{H—\overset{O}{\overset{\|}{C}}—CH_3}$$

$$CH_3—C{\equiv}C—\overset{O^-}{CH}—CH_3 \xrightarrow{H_2O/H^+} CH_3—C{\equiv}C—\overset{OH}{CH}—CH_3 \,]$$

11. Acetaldehyde undergoes a reaction to form a product which exhibits properties of aldehydes and alcohols.
    (i) Name the reaction and give equation.
    (ii) Write the structural formula of the product formed.
    (iii) What are the reagents other than acetaldehyde required for the reaction to take place?
12. Which of the following compounds would undergo aldol condensation, which the Cannizzaro's reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro's reaction.
    (i) Methanal
    (ii) 2-Methylpentanal
    (iii) Benzaldehyde
    (iv) Benzophenone
    (v) Cyclohexanone
    (vi) 1-Phenyl propanone
    (vii) Phenyl ethanal
    (viii) Butan-1-ol
    (ix) 2,2-Dimethyl butanal
13. (a) Four different bottles containing methyl alcohol, ethyl alcohol, acetic acid and acetone have lost their labels. What chemical tests would be performed to identify them?
    (b) Four different bottles containing isopropyl iodide, acetone, propionaldehyde and heptane have lost their labels. What chemical tests would be performed to identify them?
14. How will you obtain the pure products from the following mixtures?
    (a) Acetaldehyde and ethyl alcohol.
    (b) Acetone, acetic acid and methyl alcohol.
    (c) Ethyl alcohol, propanone and acetic acid.
15. Explain the following with one example:
    (a) Aldol condensation
    (b) Cannizzaro's reaction
    (c) Wolff-Kishner reduction
    (d) Rosenmund's reduction
    (e) Clemmensen's reduction
    (f) Polymerisation
    (g) Haloform reaction
    (h) Tischenko's reaction
    (i) Beckmann rearrangement
    (j) Meerwein-Ponndorf-Verley reduction
    (k) Pinacol-Pinacolone rearrangement
    (l) Reformatsky reaction
    (m) Oppenauer oxidation
    (n) Claisen-Schmidt reaction
16. How do you account for the following?
    (a) Boiling points of aldehydes lie between parent alkanes and corresponding alcohols.
    (b) Aldehydes and ketones have high dipole moments.
    (c) $NaHSO_3$ is used for the purification of aldehydes and ketones.
    (d) Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide.

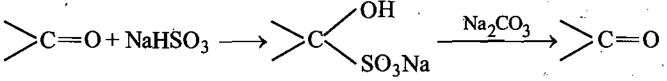
(e) Hydrazones of aldehydes and ketones are not prepared in highly acidic medium.

[**Hint:** (a) Alkanes have low boiling points as no hydrogen bonding and no dipole-dipole attractive forces are present. Alcohols have high boiling points as intermolecular hydrogen bonding is present. In aldehydes, dipole-dipole forces are present due to polar nature of carbonyl group. Thus, boiling points of aldehydes lie between alkanes and alcohols.

(b) The large dipole moment is due to the large contribution of the polar structure (resonance) to the hybrid.

$$>C=O \longleftrightarrow >\overset{+}{C}-\overset{-}{O}$$

(c) Aldehydes and ketones form insoluble crystalline compound with $NaHSO_3$ which can be filtered. These on distillation with saturated solution of Na_2CO_3 again give the aldehyde or ketone.



$$>C=O + NaHSO_3 \longrightarrow >C\begin{matrix}OH\\SO_3Na\end{matrix} \xrightarrow{Na_2CO_3} >C=O$$

(d) The reaction is initiated by the replacement of methyl protons (H^+) by I^+.

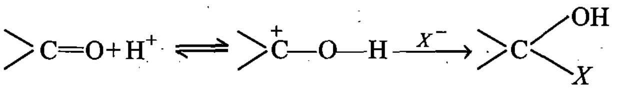
$$CH_3COCH_3 + 3IO^- \longrightarrow CI_3COCH_3 + 3OH^-$$

(e) In highly acidic medium, the protonation of hydrazine decreases its nucleophilic character.]

17. Explain the following with proper reasoning:

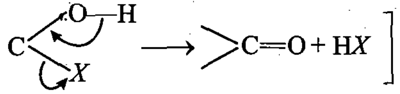
(i) Why do halogen acids which are easily added to $>C=C<$ grouping, fail to give addition products with $>C=O$ grouping?

[**Solution :** Halogen acids readily combine to the polarised $>C=O$ bond.



$$>C=O + H^+ \rightleftharpoons >\overset{+}{C}-O-H \xrightarrow{X^-} >C\begin{matrix}OH\\X\end{matrix}$$

The addition product being similar to gem-dihydroxyl compound decomposes into the original substance.



$$\longrightarrow >C=O + HX$$]

(ii) Pure HCN fails to react with aldehydes.

[**Solution :** HCN is a covalent compound and does not furnish CN^- ions. However, in the presence of bases, it furnishes sufficient concentration of CN^- ions and the reaction proceeds.

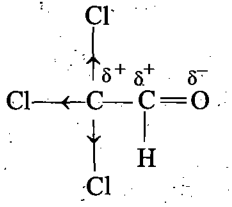
$$HCN + OH^- \longrightarrow H_2O + CN^-$$]

(iii) Why only RCHO, RCOCH$_3$ and cyclic ketones react with $NaHSO_3$?

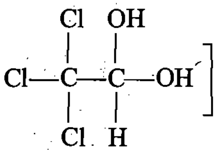
[**Solution :** SO_3^{2-} is a large ion. Its addition is possible only under the condition that $>C=O$ grouping is not sterically hindered as is the case for RCHO, RCOCH$_3$ and cyclic ketones.]

(iv) Chloral hydrate is a stable compound even it is a gem-diol.

[**Solution :** In chloral, the $-I$ effect of three chlorine atoms destabilise the $>C=O$ structure as it puts δ^+ charge on the carbon adjacent to the carbonyl $\overset{\delta^+}{C}$. In the chloral hydrate, adjacent positive charges are not present. As a result, weak nucleophiles like water readily add to the $>C=O$ group forming chloral hydrate there by shifting the equilibrium almost entirely towards right. Besides this, the intramolecular H-bonding between Cl and H atoms of the —OH group further stabilises the chloral hydrate molecule. The hydrogen bonding in the molecule also increases its stability.



Chloral



Chloral hydrate]

(v) Formation of oximes and other ammonia derivatives from carbonyl compounds require slightly acidic media for maximum rate.

[**Solution :** In weakly acidic medium, carbonyl group is protonated,

$$>C=O + \overset{+}{H} \longrightarrow >\overset{+}{C}-OH$$

This facilitates the addition of Lewis bases. However, in strongly acidic media, the nitrogen of the reagent is protonated through the unshared pair of electrons and thus the reagent cannot attack the carbonyl group. In basic media, there is no protonation of carbonyl group.]

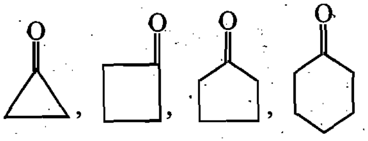
18. Arrange the following:

(i) —CHO, —COCH$_3$, —COOH, —COCl, —CONH$_2$, —COOCH$_3$, —COO$^-$ in decreasing order of nucleophilic addition.

(ii) CH_3CHO, CH_3COCH_3, HCHO, $C_2H_5COCH_3$ in decreasing order of nucleophilic addition.

(iii) CH_3COCH_2CHO, CH_3COCH_3, CH_3CHO, $CH_3COCH_2COCH_3$ in increasing order of expected enol content.

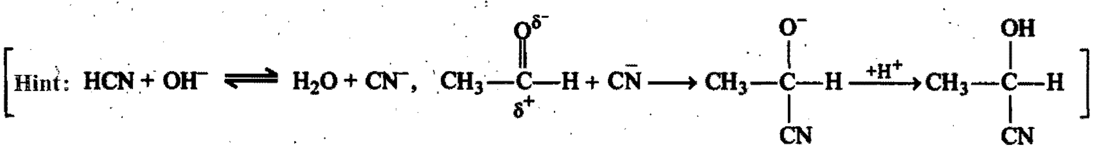
(iv) CH_3CHO, C_6H_5CHO, $(CH_3)_2CO$, FCH_2CHO in decreasing order of reactivity.

(v) 

in decreasing order of reactivity.

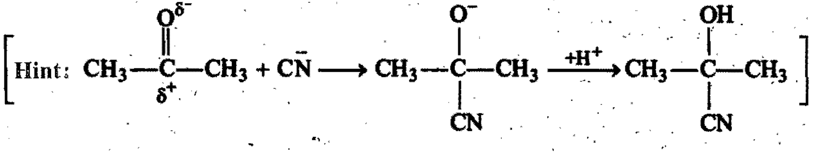
19. Give the mechanism of:

(i) Addition of HCN to acetaldehyde.



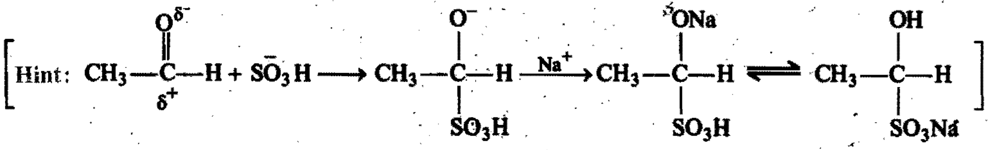
$$\left[\text{Hint: } HCN + OH^- \rightleftharpoons H_2O + CN^-,\ CH_3-\underset{\delta^+}{\overset{O^{\delta-}}{\overset{\|}{C}}}-H + \bar{C}N \longrightarrow CH_3-\underset{CN}{\overset{O^-}{C}}-H \xrightarrow{+H^+} CH_3-\underset{CN}{\overset{OH}{C}}-H\right]$$

(ii) Addition of HCN to acetone.



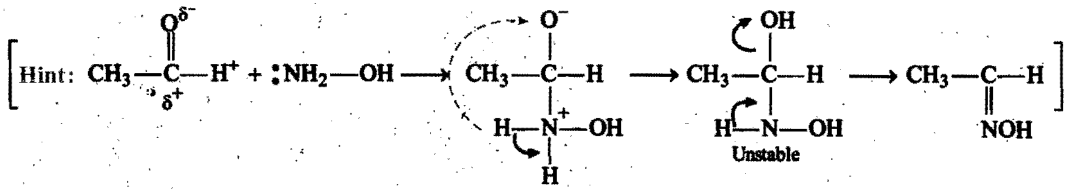
$$\left[\text{Hint: } CH_3-\underset{\delta^+}{\overset{O^{\delta-}}{\overset{\|}{C}}}-CH_3 + \bar{C}N \longrightarrow CH_3-\underset{CN}{\overset{O^-}{C}}-CH_3 \xrightarrow{+H^+} CH_3-\underset{CN}{\overset{OH}{C}}-CH_3\right]$$

(iii) Addition of $NaHSO_3$ to acetaldehyde.



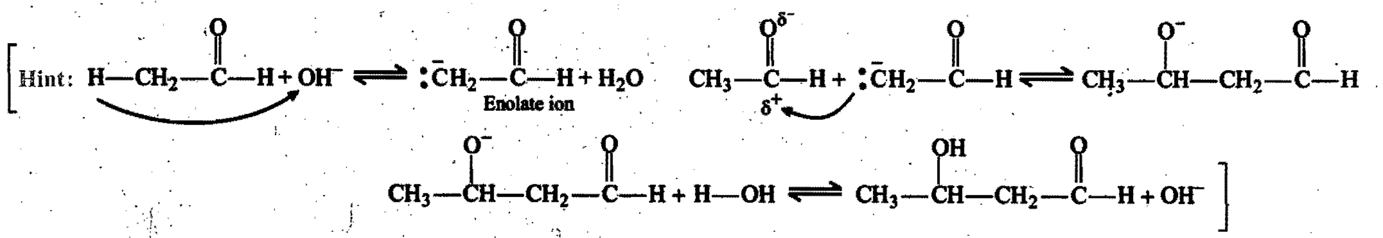
$$\left[\text{Hint: } CH_3-\underset{\delta^+}{\overset{O^{\delta-}}{\overset{\|}{C}}}-H + \bar{S}O_3H \longrightarrow CH_3-\underset{SO_3H}{\overset{O^-}{C}}-H \xrightarrow{Na^+} CH_3-\underset{SO_3H}{\overset{ONa}{C}}-H \rightleftharpoons CH_3-\underset{SO_3Na}{\overset{OH}{C}}-H\right]$$

(iv) The reaction of acetaldehyde with hydroxylamine.



$$\left[\text{Hint: } CH_3-\underset{\delta^+}{\overset{O^{\delta-}}{\overset{\|}{C}}}-H^+ + :NH_2-OH \longrightarrow CH_3-\underset{H-\underset{H}{\overset{+}{N}}-OH}{\overset{O^-}{C}}-H \longrightarrow CH_3-\underset{\underset{\text{Unstable}}{H-N-OH}}{\overset{OH}{C}}-H \longrightarrow CH_3-\underset{NOH}{\underset{\|}{C}}-H\right]$$

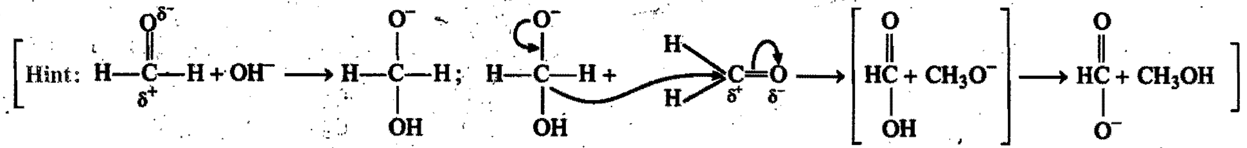
(v) Aldol condensation.



$$\left[\text{Hint: } H-CH_2-\overset{O}{\overset{\|}{C}}-H + OH^- \rightleftharpoons \underset{\text{Enolate ion}}{:\bar{C}H_2-\overset{O}{\overset{\|}{C}}-H} + H_2O \quad CH_3-\underset{\delta^+}{\overset{O^{\delta-}}{\overset{\|}{C}}}-H + :\bar{C}H_2-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons CH_3-\overset{O^-}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H\right.$$

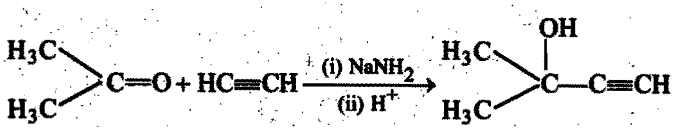
$$\left.CH_3-\overset{O^-}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H + H-OH \rightleftharpoons CH_3-\overset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H + OH^-\right]$$

(vi) Cannizzaro's reaction.

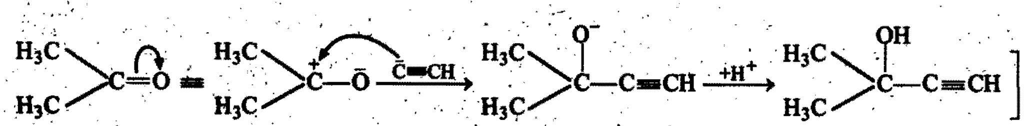


$$\left[\text{Hint: } H-\underset{\delta^+}{\overset{O^{\delta-}}{\overset{\|}{C}}}-H + OH^- \longrightarrow H-\underset{OH}{\overset{O^-}{C}}-H;\ H-\underset{OH}{\overset{O^-}{C}}-H + \underset{H}{\overset{H}{>}}\underset{\delta^+}{C}=\underset{\delta^-}{O} \longrightarrow \left[\underset{OH}{\overset{O}{\overset{\|}{HC}}} + CH_3O^-\right] \longrightarrow \underset{O^-}{\overset{O}{\overset{\|}{HC}}} + CH_3OH\right]$$

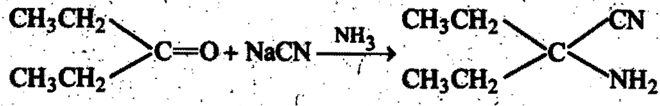
(vii)



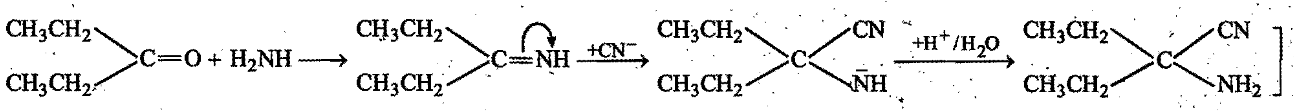
[Hint: $HC\equiv CH + NaNH_2 \longrightarrow HC\equiv\bar{C} + \overset{+}{Na} + NH_3$



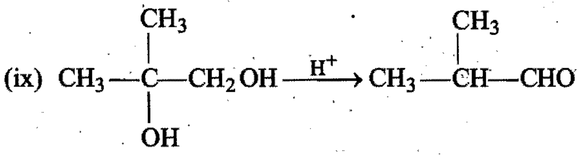
(viii)



Hint:

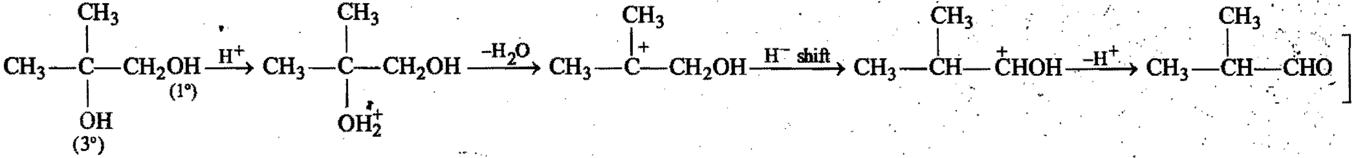


(ix)



$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH \xrightarrow{H^+} CH_3-\overset{\overset{CH_3}{|}}{CH}-CHO$$

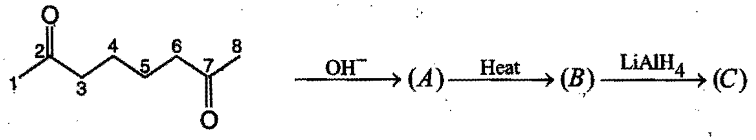
Hint:



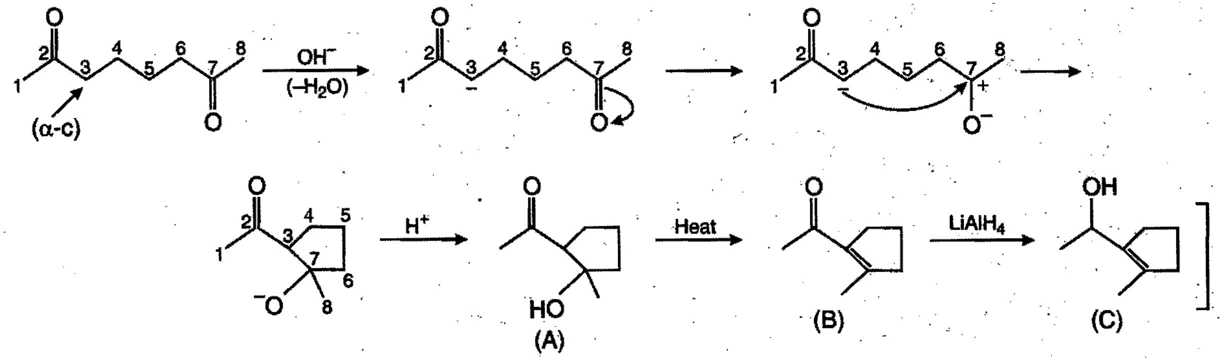
$$CH_3-\underset{\underset{\underset{(3^\circ)}{OH}}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{(1^\circ)}{CH_2OH} \xrightarrow{H^+} CH_3-\underset{\underset{OH_2^+}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH \xrightarrow{-H_2O} CH_3-\overset{\overset{CH_3}{|}}{\overset{+}{C}}-CH_2OH \xrightarrow{H^-\text{ shift}} CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{+}{C}HOH \xrightarrow{-H^+} CH_3-\overset{\overset{CH_3}{|}}{CH}-CHO$$

(3° is more basic than 1°)

(x) Identify *A*, *B* and *C* in the following:



Hint: Di-ketone can undergo internal aldol condensation reaction to form (*A*).

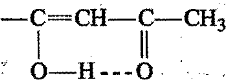


20. Write the structural formulae and names of the four possible aldol condensation products from propanal and butanal. In each case indicate which aldehyde acts as nucleophile and which as electrophile.

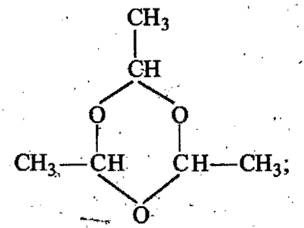
21. (a) Give two typical reactions of an aldehyde.
(b) Give two typical reactions of a ketone.
(c) What is the product formed when acetaldehyde acts as a reducing agent?
(d) Give one use of the following reagents:
(i) Schiff's reagent, (ii) Tollens' reagent, (iii) Fehling's solution, (iv) 2,4-dinitrophenylhydrazine.
(e) What product is obtained when acetone is distilled with conc. H_2SO_4?
(f) How is *meta*-formaldehyde obtained from formaldehyde?

ANSWERS

1. (a) aldehyde (except HCHO); (b) formalin; (c) biological and anatomical; (d) HCHO, NH_3; (e) $C_nH_{2n}O$; (f) condensation; (g) Rosenmund's reaction; (h) Clemmensen's reaction; (i) pink; (j) mesitylene; (k) aldol; (l) carboxylic acids; (m)



$CH_3-\underset{O-H---O}{C=CH-\overset{\|}{C}}-CH_3$; (n) sp^2; (o) nucleophilic; (p)



(Paraldehyde)

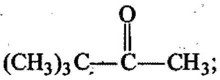
(q) CH_3CO-; (r) alkanes, Wolff-Kishner reduction; (s) do not possess; (t) $CuSO_4$ solution, sodium potassium tartrate or Rochelle salt, red-brown; (u) silver mirror; (v) phenol; (w) $H_2/Pd-BaSO_4$; (x) alcohols, alkanes; (y) acetone; (z) iodoform test.

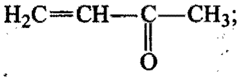
2. (a) False—gives tertiary alcohol; (b) True; (c) True; (d) True; (e) True; (f) False—only aldehydes reduce Tollens' reagent; (g) False—only by those which have α-hydrogen atom; (h) False—only by those which do not have α-hydrogen; (i) True; (j) False—both give iodoform test; (k) True; (l) True; (m) True; (n) True; (o) False—shows tautomerism; (p) False—gives formaldehyde; (q) True; (r) False—metamers; (s)

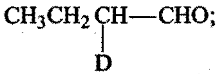
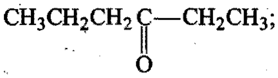
False—do not restore pink colour; (t) False—act as reducing agents since they themselves can be oxidised; (u) True; (v) False; (w) True; (x) True; (y) False—chloral is more reactive than acetaldehyde; (z) False—converts into $CH_3CH{=}CHCOOH$.

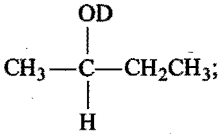
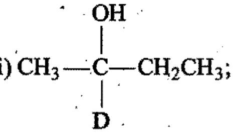
3. (i) (A—6); (B—5); (C—7); (D—1); (E—2); (F—8); (G—4); (H—3).
(ii) (A—4); (B—5); (C—7); (D—1); (E—3); (F—2); (G—6); (H—8)

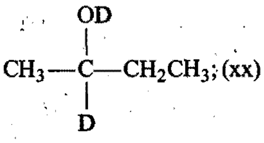
4. (i) $(CH_3CHO)_3$, Paraldehyde; (ii) HCOOH, Formic acid;
(iii) HCOONa (sodium formate) and CH_3OH (methyl alcohol);
(iv) $(CH_2)_6N_4$, Hexamethylene tetramine; (v) $C_6H_3(CH_3)_3$, Mesitylene; (vi) $(CH_3)_2C(NH_2)CH_2COCH_3$, diacetone amine;
(vii) CHI_3 (iodoform), CH_3COONa (sodium acetate);
(viii) $CH_3CH(OH)OSO_2Na$, bisulphite addition compound of acetaldehyde; (ix) CH_3COOH (acetic acid) and Ag (silver);
(x) $CH_3CH{=}NOH$, oxime; (xi) R—CHO + HCl;

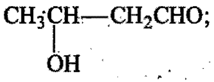
(xii) 
$(CH_3)_3C-\overset{\overset{O}{\|}}{C}-CH_3$;

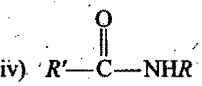
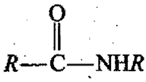
(xiii) 
$H_2C{=}CH-\underset{\underset{O}{\|}}{C}-CH_3$; (xiv) $CH_3CH_2CH_2CHO$;

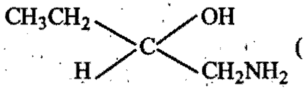
(xv) 
$CH_3CH_2\underset{\underset{D}{|}}{CH}-CHO$; (xvi) 
$CH_3CH_2CH_2\underset{\underset{O}{\|}}{C}-CH_2CH_3$;

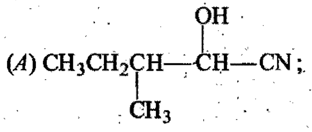
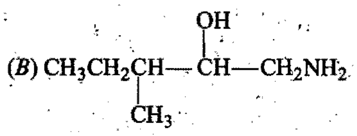
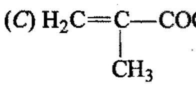
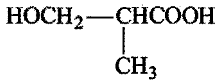
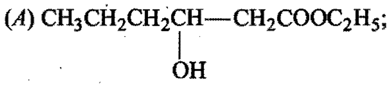
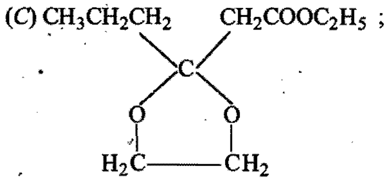
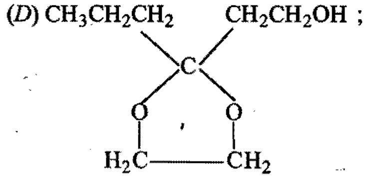
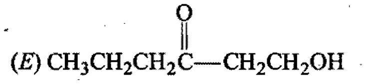
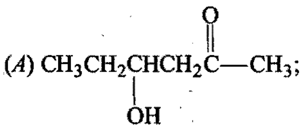
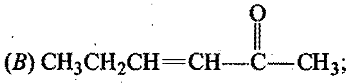
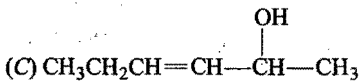
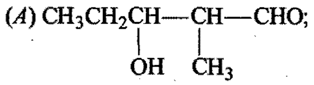
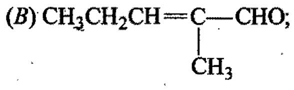
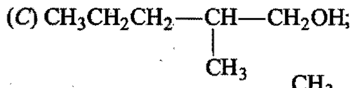
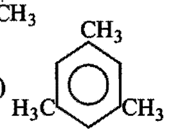
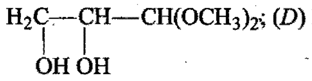
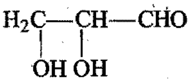
(xvii) 
$CH_3-\overset{\overset{OD}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CH_3$; (xviii) 
$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{D}{|}}{C}}-CH_2CH_3$;

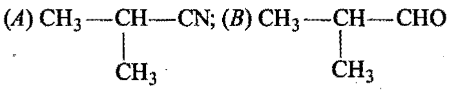
(xix) 
$CH_3-\overset{\overset{OD}{|}}{\underset{\underset{D}{|}}{C}}-CH_2CH_3$; (xx) CH_3CHO; (xxi) $(CH_3)_3C$—OH;

(xxii) CH_3CH_2CHO ; (xxiii) 
$CH_3\underset{\underset{OH}{|}}{CH}-CH_2CHO$;

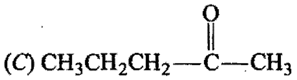
(xxiv) 
$R'-\overset{\overset{O}{\|}}{C}-NHR$ or 
$R-\overset{\overset{O}{\|}}{C}-NHR'$ (depending upon whether R or R' is *trans* to —OH of the =N—OH);

(xxv) 
(1-Aminobutan-2-ol)

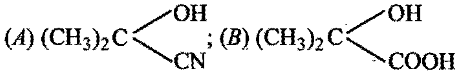
5. (i) (*A*) CH_3CHO; (*B*) $CH_3CHOHCH_3$; (*C*) CH_3COCH_3
(ii) (*A*) CH_3CHO; (*B*) $CH_3CH(OH)CN$; (*C*) $CH_3CH(OH)COOH$
(iii) (*A*) $CH_3CHOHCH_3$; (*B*) $CH_3CHBrCH_3$; (*C*) $CH_3-CH{=}CH_2$
(iv) (*A*) CHI_3; (*B*) $HC{\equiv}CH$; (*C*) CH_3CHO
(v) (*A*) 
$CH_3CH_2\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{OH}{|}}{CH}-CN$;
(*B*) 
$CH_3CH_2\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{OH}{|}}{CH}-CH_2NH_2$
(vi) (*A*) CH_3CHO; (*B*) $CH_3CH(OH)OSO_2Na$; (*C*) CH_3CHO
(vii) (*A*) $CH_3CH{=}CHCH_2OH$; (*B*) $CH_3CH{=}CHCH_2Cl$; (*C*) $CH_3CH{=}CHCH_2COOH$
(viii) (*A*) $CH_3CH{=}CH_2$; (*B*) $CH_3CHBr-CH_2Br$; (*C*) $CH_3C{\equiv}CH$; (*D*) CH_3COCH_3
(ix) (*A*) $(CH_3)_2C(OH)CN$; (*B*) $(CH_3)_2C(OH)COOH$; (*C*) 
$H_2C{=}\underset{\underset{CH_3}{|}}{C}-COOH$; (*D*) 
$HOCH_2-\underset{\underset{CH_3}{|}}{CH}COOH$
(x) (*A*) 
$CH_3CH_2CH_2\underset{\underset{OH}{|}}{CH}-CH_2COOC_2H_5$;
(*B*) $CH_3CH_2CH_2COCH_2COOC_2H_5$;
(*C*) 
(*D*) 
(*E*) 
$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}-CH_2CH_2OH$
(xi) (*A*) CH_3COOH; (*B*) CH_3COCl; (*C*) CH_3CHO; (*D*) $CH_3CHOHCH_3$
(xii) (*A*) 
$CH_3CH_2\underset{\underset{OH}{|}}{CH}CH_2\overset{\overset{O}{\|}}{C}-CH_3$;
(*B*) 
$CH_3CH_2CH{=}CH-\overset{\overset{O}{\|}}{C}-CH_3$;
(*C*) 
$CH_3CH_2CH{=}CH-\overset{\overset{OH}{|}}{CH}-CH_3$
(xiii) (*A*) 
$CH_3CH_2\underset{\underset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CHO$;
(*B*) 
$CH_3CH_2CH{=}\underset{\underset{CH_3}{|}}{C}-CHO$;
(*C*) 
$CH_3CH_2CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$;
(xiv) (*A*) Conc. H_2SO_4; (*B*) 
(Mesitylene)
or (*A*) Dry HCl; (*B*) 
$(CH_3)_2C{=}CH-\overset{\overset{O}{\|}}{C}-CH{=}C(CH_3)_2$
(Phorone)
(xv) (*A*) CH_3COCH_3 (in Wolff-Kishner reduction)
(xvi) (*A*) $H_2C{=}CH-CHO$; (*B*) $H_2C{=}CHCH(OCH_3)_2$;
(*C*) 
$\underset{\underset{OH}{|}}{H_2C}-\underset{\underset{OH}{|}}{CH}-CH(OCH_3)_2$; (*D*) 
$\underset{\underset{OH}{|}}{H_2C}-\underset{\underset{OH}{|}}{CH}-CHO$

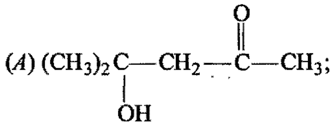
(xvii)

$(A)\ CH_3-\underset{CH_3}{\underset{|}{CH}}-CN$; $(B)\ CH_3-\underset{CH_3}{\underset{|}{CH}}-CHO$

(xviii) (*A*) $CH_3CH_2C\equiv C-Na$; (*B*) $CH_3CH_2C\equiv C-CH_3$;

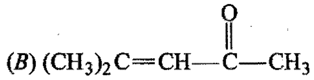

(*C*) $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(xix) (*A*) $(CH_3)_2C=N-C_6H_5$; (*B*) $(CH_3)_2CH-NH-C_6H_5$

(xx)

(*A*) $(CH_3)_2C{<}^{OH}_{CN}$; (*B*) $(CH_3)_2C{<}^{OH}_{COOH}$

(xxi)

(*A*) $(CH_3)_2\underset{OH}{\underset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$;

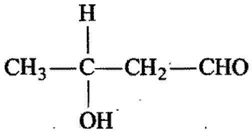
Diacetone alcohol


(*B*) $(CH_3)_2C=CH-\overset{O}{\overset{\|}{C}}-CH_3$

Mesityloxide

11. (i) Aldol condensation

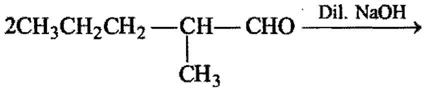
$CH_3CHO + HCH_2CHO \longrightarrow CH_3CH(OH)CH_2CHO$

(ii) Structure

$CH_3-\overset{H}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2-CHO$

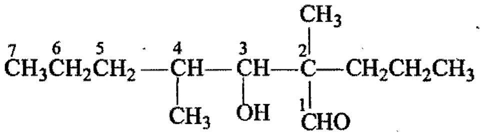
(iii) Other reagent required is dilute NaOH or mild alkali.

12. **(A) Aldol condensation**

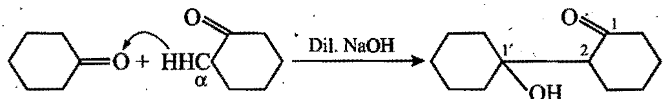
(ii) 2-Methylpentanal, (v) Cyclohexanone, (vi) 1-phenyl propanone, and (vii) phenyl ethanal, have one or more α-hydrogen atoms and hence undergo aldol condensation. For example,

(ii)

$2CH_3CH_2CH_2-\underset{CH_3}{\underset{|}{CH}}-CHO \xrightarrow{\text{Dil. NaOH}}$

2-Methylpentanal

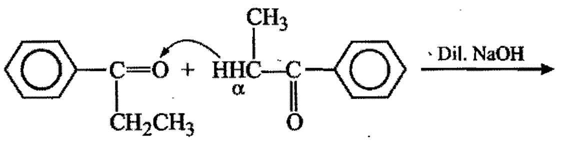

$\overset{7}{C}H_3\overset{6}{C}H_2\overset{5}{C}H_2-\underset{CH_3}{\underset{|}{\overset{4}{C}H}}-\underset{OH}{\underset{|}{\overset{3}{C}H}}-\overset{CH_3}{\overset{|}{\underset{\overset{1}{C}HO}{\underset{|}{\overset{2}{C}}}}}-CH_2CH_2CH_3$

3-Hydroxy-2,4-dimethyl-2-propyl heptanal

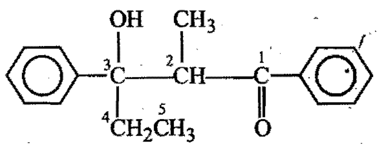
(v)


Cyclohexanone (2 mols)

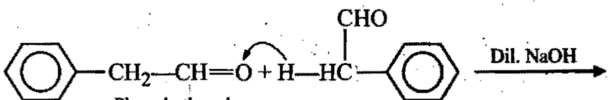
2(1′-Hydroxy-1′-cyclohexyl) cyclohexan-1-one

(vi)


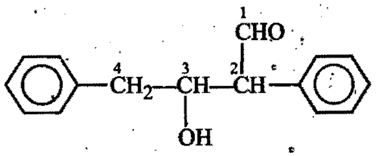
1-Phenylpropanone (2 mols)



3-Hydroxy-2-methyl-1,3- diphenyl pentan-1-one

(vii)


Phenyl ethanal

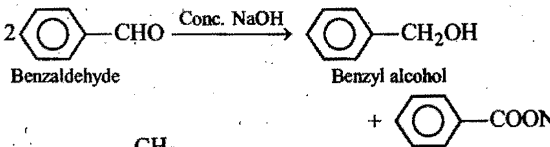


3-Hydroxy-2,4-diphenyl butanal

(B) Cannizzaro's reaction

(i) Methanal, (iii) benzaldehyde, and (ix) 2,2-dimethylbutanal, do not contain α-hydrogen and hence undergo Cannizzaro's reaction. For example,

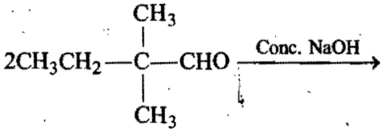
(i) $\underset{\text{Methanal}}{2HCHO} \xrightarrow{\text{Conc. NaOH}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Sod. methanoate}}{HCOONa}$

(iii)


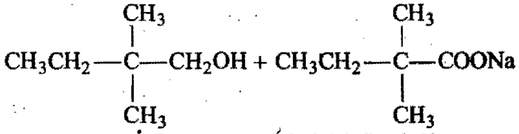
Benzaldehyde

Benzyl alcohol

Sod. benzoate

(ix)

$2CH_3CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CHO \xrightarrow{\text{Conc. NaOH}}$

2,2-Dimethyl butanal


$CH_3CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2OH + CH_3CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-COONa$

2,2-Dimethyl butan-1-ol Sod. 2,2-dimethyl butanoate

(C) (iv) Benzophenone is a ketone having no α-hydrogen atom, while

(viii) butan-1-ol is an alcohol. Both of these neither undergo aldol condensation nor Cannizzaro's reaction.

13. (a) (i) Add $NaHCO_3$. The one which evolves brisk effervescences contains **acetic acid.**

(ii) Add $NaHSO_3$. The one which forms a white crystalline precipitate contains **acetone.**

(iii) Perform iodoform test in remaining two bottles. The one which forms a yellow product with I_2 and NaOH contains **ethyl alcohol.**

(b) **Isopropyl iodide** with alcoholic $AgNO_3$ gives yellow precipitate. **Propionaldehyde** gives pink colour with Schiff's reagent. **Acetone** responds to iodoform test.

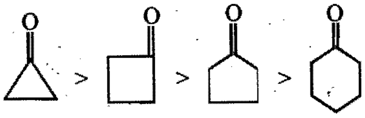
18. (i) The tendency of nucleophilic addition increases with increase of positive partial charge on the carbonyl carbon atom.

$-COCl > -CHO > -COCH_3 > -COOCH_3 >$
$-CONH_2 > -COOH > -COO^-$

(ii) $HCHO > CH_3CHO > CH_3COCH_3 > CH_3COC_2H_5$

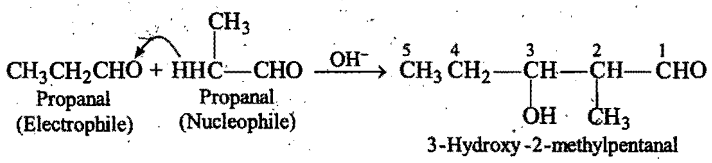
(iii) $CH_3CHO < CH_3COCH_3 < CH_3COCH_2CHO$
$< CH_3COCH_2COCH_3$

(iv) $FCH_2CHO > CH_3CHO > C_6H_5CHO > (CH_3)_2CO$

(v)


[**Hint :** More is the angle strain in cyclic ketones, more is its reactivity for nucleophilic addition reactions.]

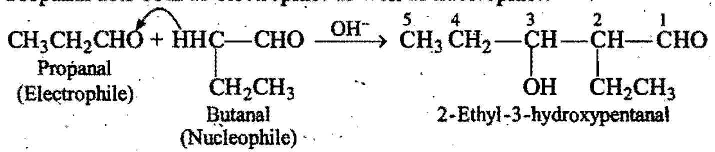
20\. (i)



$$\underset{\substack{\text{Propanal}\\ \text{(Electrophile)}}}{\mathrm{CH_3CH_2CHO}} + \underset{\substack{\text{Propanal}\\ \text{(Nucleophile)}}}{\mathrm{H}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{HC}}}\mathrm{{-}CHO}} \xrightarrow{OH^-} \underset{\text{3-Hydroxy-2-methylpentanal}}{\overset{5}{\mathrm{CH_3}}\,\overset{4}{\mathrm{CH_2}}\mathrm{{-}}\underset{\mathrm{OH}}{\underset{|}{\overset{3}{\mathrm{CH}}}}\mathrm{{-}}\underset{\mathrm{CH_3}}{\underset{|}{\overset{2}{\mathrm{CH}}}}\mathrm{{-}}\overset{1}{\mathrm{CHO}}}$$

Propanal acts both as electrophile as well as nucleophile.

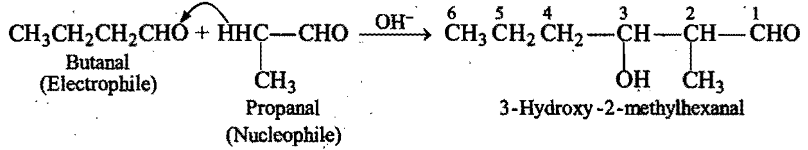
(ii)



$$\underset{\substack{\text{Propanal}\\ \text{(Electrophile)}}}{\mathrm{CH_3CH_2CHO}} + \underset{\substack{\text{Butanal}\\ \text{(Nucleophile)}}}{\mathrm{H}\underset{\mathrm{CH_2CH_3}}{\underset{|}{\mathrm{HC}}}\mathrm{{-}CHO}} \xrightarrow{OH^-} \underset{\text{2-Ethyl-3-hydroxypentanal}}{\overset{5}{\mathrm{CH_3}}\,\overset{4}{\mathrm{CH_2}}\mathrm{{-}}\underset{\mathrm{OH}}{\underset{|}{\overset{3}{\mathrm{CH}}}}\mathrm{{-}}\underset{\mathrm{CH_2CH_3}}{\underset{|}{\overset{2}{\mathrm{CH}}}}\mathrm{{-}}\overset{1}{\mathrm{CHO}}}$$

Propanal as electrophile and butanal as nucleophile.

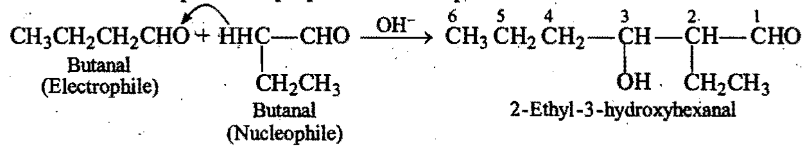
(iii)



$$\underset{\substack{\text{Butanal}\\ \text{(Electrophile)}}}{\mathrm{CH_3CH_2CH_2CHO}} + \underset{\substack{\text{Propanal}\\ \text{(Nucleophile)}}}{\mathrm{H}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{HC}}}\mathrm{{-}CHO}} \xrightarrow{OH^-} \underset{\text{3-Hydroxy-2-methylhexanal}}{\overset{6}{\mathrm{CH_3}}\,\overset{5}{\mathrm{CH_2}}\,\overset{4}{\mathrm{CH_2}}\mathrm{{-}}\underset{\mathrm{OH}}{\underset{|}{\overset{3}{\mathrm{CH}}}}\mathrm{{-}}\underset{\mathrm{CH_3}}{\underset{|}{\overset{2}{\mathrm{CH}}}}\mathrm{{-}}\overset{1}{\mathrm{CHO}}}$$

Butanal as electrophile and propanal as nucleophile.

(iv)



$$\underset{\substack{\text{Butanal}\\ \text{(Electrophile)}}}{\mathrm{CH_3CH_2CH_2CHO}} + \underset{\substack{\text{Butanal}\\ \text{(Nucleophile)}}}{\mathrm{H}\underset{\mathrm{CH_2CH_3}}{\underset{|}{\mathrm{HC}}}\mathrm{{-}CHO}} \xrightarrow{OH^-} \underset{\text{2-Ethyl-3-hydroxyhexanal}}{\overset{6}{\mathrm{CH_3}}\,\overset{5}{\mathrm{CH_2}}\,\overset{4}{\mathrm{CH_2}}\mathrm{{-}}\underset{\mathrm{OH}}{\underset{|}{\overset{3}{\mathrm{CH}}}}\mathrm{{-}}\underset{\mathrm{CH_2CH_3}}{\underset{|}{\overset{2}{\mathrm{CH}}}}\mathrm{{-}}\overset{1}{\mathrm{CHO}}}$$

Butanal acts both as electrophile as well as nucleophile.

PROBLEMS BASED ON STRUCTURE AND PROPERTIES

1. Compound (*A*), $C_5H_{10}O$ forms phenylhydrazone, gives negative Tollens' and iodoform tests and reduces to pentane. What is the structure of the compound (*A*)?
[**Ans.** Pentan-3-one, $CH_3CH_2COCH_2CH_3$]

2. A ketone (*A*) gives iodoform on reacting with iodine and sodium hydroxide. (*A*) on reduction gives (*B*) which on heating with sulphuric acid gives (*C*). (*C*) on ozonolysis gives acetaldehyde and acetone. Identify (*A*), (*B*) and (*C*).
[**Ans.** (*A*) $CH_3COCH(CH_3)_2$; (*B*) $CH_3CHOHCH(CH_3)_2$; (*C*) $CH_3CH{=}C(CH_3)_2$]

3. An organic compound (*A*) adds Br_2 to give $C_5H_8Br_2O$. It does not react with Tollens' reagent but enters into reaction with phenyl hydrazine. Ozonolysis of (*A*) gives an acetaldehyde and $C_3H_4O_2$ which readily loses CO to form acetaldehyde. What is (*A*)?
[**Hint:** The compound reacts with Br_2 and adds one molecule of bromine. Thus, it consists one double bond. The compound is a ketone as it reacts with phenylhydrazine but does not react with Tollens' reagent. The ozonolysis of (*A*) gives acetaldehyde and $C_3H_4O_2$.
Thus, the compound (*A*) is,

$$\underset{(A)}{CH_3CH{=}CHCOCH_3} \xrightarrow{\text{Ozonolysis}} CH_3CHO + CH_3COCHO \xrightarrow{-CO} CH_3CHO$$

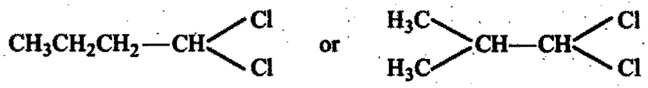
α-ketoaldehydes lose CO readily to form aldehydes.]

4. Two organic compounds (*A*) and (*B*) with molecular formula, C_3H_6O, react with HCN in different manner to produce (*C*) and (*D*) respectively. On subsequent hydrolysis of (*C*) and (*D*) gives optically active substances (*E*) and (*F*). Both (*E*) and (*F*) on decarboxylation give propanol-1. What are (*A*), (*B*), (*C*), (*D*), (*E*) and (*F*)?
[**Ans.** (*A*) CH_3CH_2CHO; (*B*) $H_2C{=}CH{\cdot}CH_2OH$; (*C*) $CH_3CH_2CH(OH)CN$; (*D*) $CH_3{-}CH(CN)CH_2OH$;
(*E*) $\underset{\text{Optically active}}{CH_3CH_2\overset{*}{C}H(OH)COOH}$; (*F*) $\underset{\text{Optically active}}{CH_3{-}\overset{*}{C}H(COOH){\cdot}CH_2OH}$]

5. An organic compound having molecular formula, $C_6H_{12}O$ does not reduce Tollens' reagent, but gives a crystalline derivative with 2,4-dinitrophenyl hydrazine. It also gives iodoform test and produces 2-methyl pentane on Clemmensen's reduction. Assign a structural formula to the organic compound.
[**Ans.** $(CH_3)_2CHCH_2COCH_3$ (4-Methyl pentan-2-one)]

6. An organic compound (*A*) obtained by the hydrolysis of dichlorobutane, gives a positive test with Schiff's reagent and forms an oxime. Compound (*A*) on oxidation yields (*B*) which gives propane with soda lime. Suggest the structural formulae of various compounds.

[Hint : Dichlorobutane is,



Thus, (*A*) is

$$\begin{array}{ccc} CH_3CH_2CH_2CHO & \text{or} & (CH_3)_2CHCHO \\ \downarrow \text{Oxidation} & & \downarrow \text{Oxidation} \\ CH_3CH_2CH_2COOH & & (CH_3)_2CHCOOH \\ \downarrow NaOH/CaO & & \downarrow NaOH/CaO \\ CH_3CH_2CH_3 & & CH_3CH_2CH_3\ ] \end{array}$$

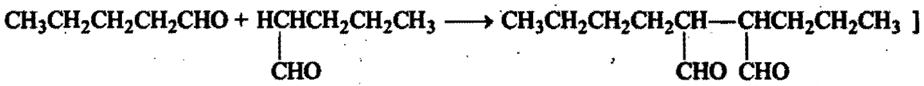
7. An organic compound having molecular formula $C_5H_{10}O$ exists in two chain isomers, (*A*) and (*B*). Isomer (*A*) undergoes the Cannizzaro's reaction to give 2,2-dimethyl propanoic acid and 2,2-dimethyl propan-1-ol. Compound (*B*) in the presence of dilute alkali undergoes aldol condensation to form 3-hydroxy-2-propyl heptanal. Give graphic representations of (*A*) and (*B*).

[Hint : Isomers have formula C_4H_9CHO.

(*A*) undergoes Cannizzaro's reaction, thus it does not have α-hydrogen. The structure of (*A*) is $(CH_3)_3CCHO$.

$$(CH_3)_3CCHO \xrightarrow{NaOH} \underset{\text{2,2-Dimethyl propanoic acid}}{(CH_3)_3C\cdot COOH} + \underset{\text{2,2-Dimethyl propan-1-ol}}{(CH_3)_3CCH_2OH}$$

(*B*) undergoes aldol condensation, it possesses α-hydrogen atom. The structure of (*B*) is $CH_3CH_2CH_2CH_2CHO$.

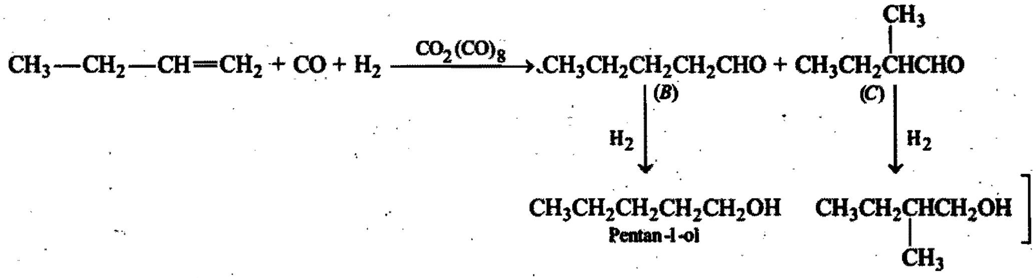


$$CH_3CH_2CH_2CH_2CHO + H\underset{\underset{CHO}{|}}{C}HCH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2\underset{\underset{CHO}{|}}{C}H-\underset{\underset{CHO}{|}}{C}HCH_2CH_2CH_3\ ]$$

3-Hydroxy-2-propyl heptanal

8. An organic compound (*A*) having molecular formula C_4H_8, decolourises bromine water. (*A*) when treated with carbon monoxide and hydrogen in the presence of a suitable catalyst undergoes oxo-reaction, to give aldehydes (*B*) and (*C*). (*B*) on reduction forms pentan-1-ol, while 2-methyl butan-1-ol is obtained by the reduction of (*C*). Give the structural formulae of (*A*), (*B*) and (*C*).

[Hint : (*A*) is an alkene having a double bond between carbon 1 and carbon 2.

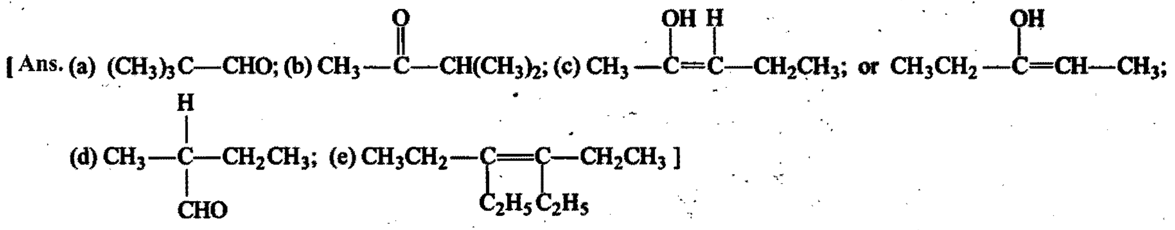


$$CH_3-CH_2-CH=CH_2 + CO + H_2 \xrightarrow{CO_2(CO)_8} \underset{(B)}{CH_3CH_2CH_2CH_2CHO} + \underset{(C)}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCHO}$$

$$\begin{array}{cc} \downarrow H_2 & \downarrow H_2 \\ \underset{\text{Pentan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH} & CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2OH\ ] \end{array}$$

2-Methyl butan-1-ol

9. An organic compound (*A*) having molecular formula $C_5H_{10}O$ can show various properties depending on structures. Draw them if it:
   (a) shows Cannizzaro's reaction.
   (b) gives iodoform test and converted into isobutyric acid.
   (c) reacts with Na and decolourises Br_2 water. It can also show geometrical isomerism.
   (d) reduces Tollens' reagent and has chiral carbon.
   (e) is obtained by ozonolysis of 3,4-diethyl-3-hexene.



[Ans. (a) $(CH_3)_3C-CHO$; (b) $CH_3-\overset{\overset{O}{\|}}{C}-CH(CH_3)_2$; (c) $CH_3-\overset{\overset{OH}{|}}{C}=\overset{\overset{H}{|}}{C}-CH_2CH_3$; or $CH_3CH_2-\overset{\overset{OH}{|}}{C}=CH-CH_3$;

(d) $CH_3-\overset{\overset{H}{|}}{\underset{\underset{CHO}{|}}{C}}-CH_2CH_3$; (e) $CH_3CH_2-\underset{\underset{C_2H_5}{|}}{C}=\underset{\underset{C_2H_5}{|}}{C}-CH_2CH_3$]

OBJECTIVE QUESTIONS

SET I : This set contains questions with single correct answer.

1. The general formula of both aldehydes and ketones is:
(a) $C_nH_{2n+2}O$ ☐ (b) $C_nH_{2n}O$ ☐
(c) $C_nH_{2n-2}O$ ☐ (d) $C_nH_{2n+4}O$ ☐

2. The grouping $>CO$ is present in:
(a) ethers ☐ (b) alcohols ☐
(c) ketones ☐ (d) none of these ☐

3. Aldehydic group can occur:
(a) anywhere in the carbon chain ☐
(b) in the middle of carbon chain ☐
(c) only at the second carbon atom of the chain ☐
(d) only at the end carbon atom of the carbon chain ☐

4. The carbon atom of the carbonyl group is:
(a) *sp*-hybridized ☐ (b) sp^2-hybridized ☐
(c) sp^3-hybridized ☐ (d) dsp^2-hybridized ☐

5. When acetylene is passed through dil. H_2SO_4 in the presence of $HgSO_4$, the compound formed is:
(a) C_2H_5OH ☐ (b) acetone ☐
(c) CH_3CHO ☐ (d) carbide of Hg ☐

6. Aldehydes are first oxidation products of:
(a) primary alcohols ☐ (b) secondary alcohols ☐
(c) tertiary alcohols ☐ (d) monohydric alcohols ☐

7. Isopropyl alcohol on oxidation forms:
(a) acetone ☐ (b) ether ☐
(c) acetaldehyde ☐ (d) ethylene ☐

8. Dry heating of calcium acetate will give:
[AFMC 2007; CMC Ludhiana (Med.) 2008]
(a) CH_3COOH ☐ (b) CH_3CHO ☐
(c) C_2H_6 ☐ (d) CH_3COCH_3 ☐

9. When a mixture of calcium acetate and calcium formate is heated. It yields:
(a) acetone ☐ (b) acetaldehyde ☐
(c) formic acid ☐ (d) acetic acid ☐

10. When propyne is treated with aqueous sulphuric acid in presence of mercuric sulphate, the major product is:
(a) propanal ☐
(b) propyl hydrogen sulphate ☐
(c) propanol ☐
(d) acetone ☐

11. Which of the following compounds is oxidised to prepare ethyl methyl ketone?
(a) Propan-2-ol ☐ (b) Butan-1-ol ☐
(c) Butan-2-ol ☐ (d) *Tert.* butyl alcohol ☐

12. When but-2-yne is treated with dil. $H_2SO_4/HgSO_4$, the product formed is:
(a) butan-1-ol ☐ (b) butan-2-ol ☐
(c) acetone ☐ (d) butanone ☐

13. The reaction,

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

is called:
(a) Cannizzaro's reaction ☐
(b) Rosenmund's reaction ☐
(c) Haloform reaction ☐
(d) Clemmensen's reaction ☐

14. At room temperature, formaldehyde is:
(a) a gas ☐ (b) a liquid ☐
(c) a solid ☐ (d) not known ☐

15. Formalin is the commercial name of:
[MHCET (Med.) 2007]
(a) formic acid ☐
(b) fluoroform ☐
(c) 40% aqueous solution of methanal ☐
(d) paraformaldehyde ☐

16. The reagent with which both acetaldehyde and acetone react easily is:
(a) Fehling's solution ☐ (b) Grignard reagent ☐
(c) Schiff's reagent ☐ (d) Tollens' reagent ☐

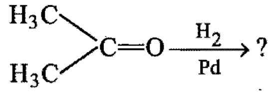
17. A compound that gives a positive iodoform test is:
(a) pentan-1-ol ☐ (b) pentan-2-one ☐
(c) pentan-3-one ☐ (d) pentanal ☐

18. $2HCHO + NaOH \longrightarrow CH_3OH + HCOONa$
The above reaction is known as:
(a) Wurtz reaction ☐ (b) Rosenmund's reaction ☐
(c) Frankland reaction ☐ (d) Cannizzaro's reaction ☐

19. An aldehyde on oxidation gives:
(a) an alcohol ☐ (b) an acetone ☐
(c) an ether ☐ (d) an acid ☐

20. The compound that will not give iodoform test on treatment with alkali and iodine, is:
(a) acetone ☐ (b) ethanol ☐
(c) diethyl ketone ☐ (d) isopropyl alcohol ☐

21. Main product(s) of the reaction is/are:



(a) $CH_3COOH + H_2$ ☐ (b) CH_3CH_2COOH ☐
(c) $CH_3CH(OH)CH_3$ ☐ (d) CH_3CH_2OH ☐

22. Tollens' reagent is:
(a) alkaline mercuric chloride ☐
(b) alkaline potassium permanganate ☐
(c) ammoniacal silver nitrate ☐
(d) ammonium citrate ☐

23. When dihydroxy acetone reacts with HIO_4, the product is/are: **[JIPMER (Med.) 2008]**
(a) HCHO ☐ (b) HCHO and HCOOH ☐
(c) HCHO and CO_2 ☐ (d) HCOOH ☐

24. Schiff's reagent is:
(a) magenta solution decolourised with sulphurous acid ☐
(b) magenta solution decolourised with chlorine ☐
(c) ammoniacal cobalt chloride solution ☐
(d) ammoniacal manganese sulphate solution ☐

25. Fehling's solution is:
(a) acidified copper sulphate solution ☐
(b) ammoniacal cuprous chloride solution ☐
(c) copper sulphate and Rochelle salt + NaOH ☐
(d) none of the above ☐

26. Which one of the following reagents can distinguish aldehydes and ketones?
(a) Fehling's solution ☐ (b) H_2SO_4 solution ☐
(c) $NaHSO_3$ ☐ (d) NH_3 ☐

27. When acetaldehyde is heated with Fehling's solution, it gives a red precipitate of: **[EAMCET (Engg.) 2006; AFMC 2010]**
(a) Cu ☐ (b) CuO ☐
(c) $CuSO_4$ ☐ (d) Cu_2O ☐

28. Which statement is incorrect in the case of acetaldehyde and acetone?
(a) Both react with hydroxylamine ☐
(b) Both react with $NaHSO_3$ ☐
(c) Both react with hydrazine ☐
(d) Both reduce ammoniacal silver nitrate ☐

29. Which statement is incorrect in the case of acetaldehyde and acetone?
(a) Both react with HCN ☐
(b) Both give iodoform test ☐
(c) Both react with NaOH to form polymer ☐
(d) Both can be reduced into alcohols ☐

30. Acetyl chloride is reduced to acetaldehyde by:
(a) Na/C_2H_5OH ☐ (b) $LiAlH_4$ ☐
(c) H_2/Ni ☐ (d) $H_2/Pd—BaSO_4$ ☐

31. Acetaldehyde is:
(a) oxidising agent ☐
(b) reducing agent ☐
(c) both oxidising as well as reducing agent ☐
(d) none of the above ☐

32. When formaldehyde is treated with ammonia, the compound formed is:
(a) formaldehyde ammonia ☐
(b) hexamethylene tetramine ☐
(c) formalin ☐
(d) methylamine ☐

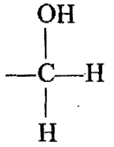
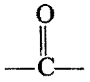
33. When acetaldehyde is treated with ammoniacal silver nitrate solution, we get:
(a) silver mirror ☐ (b) a brown precipitate ☐
(c) red colouration ☐ (d) no precipitate ☐

34. A plastic bakelite is a compound of phenol with: **[BHU (Screening) 2008]**
(a) CH_3CHO ☐ (b) HCHO ☐
(c) acetal ☐ (d) chlorobenzene ☐

35. Compound '*A*' undergoes formation of cyanohydrin which on hydrolysis gives lactic acid [$CH_3CH(OH)COOH$]. Therefore, compound '*A*' is: **[DUMET 2010]**
(a) acetone ☐ (b) benzaldehyde ☐
(c) formaldehyde ☐ (d) acetaldehyde ☐

36. An unknown compound gives a positive haloform test and a positive Fehling's test. The compound is:
(a) acetaldehyde ☐ (b) acetone ☐
(c) diethyl ketone ☐ (d) formaldehyde ☐

37. When acetone is treated with conc. H_2SO_4, we get: **[PET (Raj.) 2003; JEE (WB) 2008]**
(a) mesitylene ☐ (b) benzene ☐
(c) phorone ☐ (d) mesityl oxide ☐

38. In bakelite, the rings are joined to each other through: **[AMU (Engg.) 2010]**
(a) $—CH_2—$ ☐ (b) $—O—$ ☐
(c) 
$—C(OH)(H)—$ ☐ (d) 
$—C(=O)—$ ☐

39. The composition of urotropine is:
(a) $(CH_2)_4N_6$ ☐ (b) $(CH_2)_5N_5$ ☐
(c) $(CH_2)_6N_6$ ☐ (d) $(CH_2)_6N_4$ ☐

40. Urotropine is formed by the action of ammonia on: **[BHU 2002]**
(a) acetaldehyde ☐ (b) formaldehyde ☐
(c) acetone ☐ (d) phenol ☐

41. Hydrocarbons are formed when aldehydes and ketones are reduced with amalgamated zinc and conc. HCl. The reaction is called: **[CBSE (Med.) 2007]**
(a) Dow reduction ☐
(b) Clemmensen's reduction ☐
(c) Cope reduction ☐
(d) Wolff-Kishner reduction ☐

42. The catalyst in Tischenko reaction is:
(a) C_2H_5ONa ☐ (b) H_2SO_4 ☐
(c) $(C_2H_5O)_3Al$ ☐ (d) NaOH ☐

43. When acetaldehyde is treated with aluminium ethoxide, it forms:
(a) ethyl acetate ☐ (b) ethyl alcohol ☐
(c) acetic acid ☐ (d) methyl propionate ☐

44. Chloretone is formed when chloroform reacts with:
(a) formaldehyde ☐ (b) acetaldehyde ☐
(c) acetone ☐ (d) benzaldehyde ☐

45. Which of the following reagents reacts differently with HCHO, CH_3CHO and CH_3COCH_3?
(a) HCN ☐ (b) NH_2OH ☐
(c) $C_6H_5NHNH_2$ ☐ (d) NH_3 ☐

46. In the following sequence of reactions, the end product is:

$$CaC_2 \xrightarrow{H_2O} (A) \xrightarrow{Hg^{2+}/H_2SO_4} (B) \xrightarrow{[O]} (C) \xrightarrow{Ca(OH)_2} (D) \xrightarrow{Heat} (E)$$

(a) acetaldehyde ☐ (b) formaldehyde ☐
(c) acetic acid ☐ (d) acetone ☐

47. In the following sequence of reactions, the end product is:

$$HC\equiv CH \xrightarrow{Hg^{2+}/H_2SO_4} (A) \xrightarrow[{[H_2O]}]{CH_3MgX} (B) \xrightarrow{[O]} (C)$$

(a) acetaldehyde ☐ (b) isopropyl alcohol ☐
(c) acetone ☐ (d) ethyl alcohol ☐

48. In the following sequence of reactions, the end product is:

$$CH_3CHO \xrightarrow{HCN} (A) \xrightarrow{H_2O} (B)$$

(a) CH_3COOH ☐ (b) $CH_3CHOHCOOH$ ☐
(c) $CH_3CH_2NH_2$ ☐ (d) CH_3CONH_2 ☐

49. In the following sequence of reactions, the end product is:

$$CH_3CHO \xrightarrow[\text{Mild alkali}]{\text{Condensation}} (A) \xrightarrow[\text{Heat}]{\text{Dehydrating agent}} (B)$$

(a) aldol ☐ (b) crotonaldehyde ☐
(c) paraldehyde ☐ (d) metaldehyde ☐

50. Which of the following is an example of aldol condensation?

(a) $2CH_3CHO \xrightarrow{NaOH(dil.)} CH_3CHOHCH_2CHO$ ☐
(b) $HCHO \xrightarrow{NaOH(dil.)} CH_3OH$ ☐
(c) $C_6H_5CHO + HCHO \xrightarrow{NaOH(dil.)} C_6H_5CH_2OH$ ☐
(d) $C_6H_5CHO \xrightarrow{NaOH(conc.)} C_6H_5CH_2OH$ ☐

51. Formaldehyde can be distinguished from acetaldehyde by the use of: [UPSEAT 2004]

(a) Schiff's reagent ☐
(b) Tollens' reagent ☐
(c) Fehling's solution ☐
(d) Iodine in presence of base ☐

52. Which compound does not react with PCl_5?

(a) CH_3CHO ☐ (b) CH_3COCH_3 ☐
(c) $HCHO$ ☐ (d) C_2H_5OH ☐

53. Diacetone alcohol is obtained from acetone by the use of:

(a) conc. H_2SO_4 ☐ (b) $Ba(OH)_2$ ☐
(c) dil. H_2SO_4 ☐ (d) dil. NaOH ☐

54. Which of the following reactions is a condensation reaction?

(a) $HCHO \longrightarrow$ Paraformaldehyde ☐
(b) $CH_3CHO \longrightarrow$ Paraldehyde ☐
(c) $CH_3COCH_3 \longrightarrow$ Mesityl oxide ☐
(d) $H_2C{=}CH_2 \longrightarrow$ Polyethylene ☐

55. Which of the following would undergo aldol condensation?

(a) CH_3CHO ☐ (b) CCl_3CHO ☐
(c) $HCHO$ ☐ (d) $(CH_3)_3CCHO$ ☐

56. Methyl ketones are characterized through the:

(a) Tollens' reagent ☐ (b) iodoform test ☐
(c) Schiff's test ☐ (d) Benedict's reagent ☐

57. Treatment of propionaldehyde with dil. NaOH gives:

(a) $CH_3CH_2COOCH_2CH_2CH_3$ ☐
(b) $CH_3CH_2CHOHCH_2CH_2CHO$ ☐
(c) $CH_3CH_2CHOHCH(CH_3)CHO$ ☐
(d) $CH_3CH_2COCH_2CH_2CHO$ ☐

58. Formaldehyde gives an additive product with methyl magnesium iodide which on aqueous hydrolysis yields: [BHU 2005]

(a) ethyl iodide ☐ (b) ethyl alcohol ☐
(c) methyl alcohol ☐ (d) methyl iodide ☐

59. Paraldehyde is formed by the polymerisation of: [CPMT 2004]

(a) CH_3CHO ☐ (b) HCHO ☐
(c) CH_3OH ☐ (d) $(CH_3)_2CO$ ☐

60. Which of the following is used as a hypnotic? [AFMC 2005]

(a) Paraldehyde ☐ (b) Metaldehyde ☐
(c) Acetaldehyde ☐ (d) Formaldehyde ☐

61. The enolic form of acetone contains:

(a) 9 sigma bonds, 1 pi bond and 2 lone pairs ☐
(b) 8 sigma bonds, 2 pi bonds and 2 lone pairs ☐
(c) 10 sigma bonds, 1 pi bond and 1 lone pair ☐
(d) 9 sigma bonds, 2 pi bonds and 1 lone pair ☐

62. The formation of cyanohydrin from a ketone is an example of: [CET (J&K) 2007; JEE (WB) 2008]

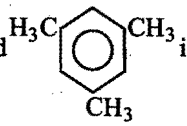
(a) electrophilic addition ☐
(b) nucleophilic addition ☐
(c) nucleophilic substitution ☐
(d) electrophilic substitution ☐

63. Paraldehyde is used as a:

(a) medicine ☐ (b) poison ☐
(c) polymer ☐ (d) dye ☐

64. A compound (*A*) has molecular formula C_2Cl_3OH. It reduces Fehling's solution and on oxidation gives a monocarboxylic acid. (*A*) is obtained by the action of Cl_2 on ethyl alcohol. The compound (*A*) is:

(a) chloroform ☐ (b) chloral ☐
(c) trichloro ethanol ☐ (d) trichloro acetic acid ☐

65. The compound 

is a condensation product. It is obtained either by treating 3 molecules of acetone with conc. H_2SO_4 or passing propyne through a red-hot tube. The product is:

(a) phorone ☐ (b) diacetonyl alcohol ☐
(c) mesityl oxide ☐ (d) mesitylene ☐

66. A compound (*A*), $C_5H_{10}O$, forms a phenyl hydrazone and gives negative Tollens' and iodoform tests. The compound on reduction gives *n*-pentane. The compound (*A*) is: [AMU 2002]

(a) pentanal ☐ (b) pentan-2-one ☐
(c) pentan-3-one ☐ (d) amyl alcohol ☐

67. The product *Z* in the series is:

$$H_2C{=}CH_2 \xrightarrow{HBr} X \xrightarrow{\text{Hydrolysis}} Y \xrightarrow[I_2(\text{excess})]{Na_2CO_3} Z$$

(a) C_2H_5I ☐ (b) C_2H_5OH ☐
(c) CHI_3 ☐ (d) CH_3CHO ☐

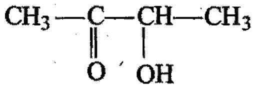
68. If formaldehyde and KOH are treated together, we get:

(a) methane ☐ (b) methanol ☐
(c) ethyl acetate ☐ (d) acetylene ☐

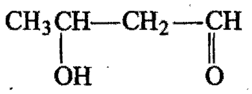
69. Wolff-Kishner reduction is:
(a) reduction of carbonyl compounds into hydrocarbons ☐
(b) reduction of carbonyl compounds into alcohols ☐
(c) reduction of nitrobenzene into aniline ☐
(d) reduction of carbohydrates into alcohols ☐

70. In which of the following reactions, aldehydes and ketones are distinguished?
(a) Reaction with phenyl hydrazine ☐
(b) Reaction with hydroxylamine ☐
(c) Reaction with semicarbazide ☐
(d) Reaction with silver nitrate mixed with ammonia ☐

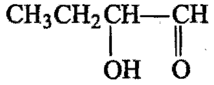
71. The aldol condensation of acetaldehyde results in the formation of: **[CPMT 2004; DCE 2008]**

(a)  ☐

$CH_3-C(=O)-CH(OH)-CH_3$

(b)  ☐

$CH_3CH(OH)-CH_2-CH(=O)$

(c)  ☐

$CH_3CH_2CH(OH)-CH(=O)$

(d) $CH_3CH_2CH_2CHO$ ☐

72. Match the following lists:

(A) Grignard reagent	(1) H_2/Pd-$BaSO_4$
(B) Clemmensen's reduction	(2) N_2H_4/KOH/ CH_2OH-CH_2OH
(C) Rosenmund's reduction	(3) CH_3MgX
(D) Wolff-Kishner reduction	(4) Zn-Hg/conc. HCl
	(5) H_2/Ni

the correct answer is: **[EAMCET (Engg.) 2006]**
(a) A-3, B-4, C-1, D-2 ☐ (b) A-3, B-4, C-2, D-1 ☐
(c) A-2, B-1, C-4, D-5 ☐ (d) A-5, B-3, C-2, D-1 ☐

73. Ethanal reacts with alkali to give 3-hydroxy butanal. The reaction is:
(a) polymerisation ☐ (b) Claisen condensation ☐
(c) aldol condensation ☐ (d) none of these ☐

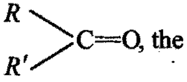
74. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions : **[JEE (WB) 2010]**
Ethanal (I), Propanal (II),
Propanone (III), Butanone (IV)
(a) I < II < III < IV ☐ (b) IV < III < II < I ☐
(c) III < II < I < IV ☐ (d) II < I < III < IV ☐

75. Clemmensen's reduction will convert cyclohexanone into:
(a) *n*-hexane ☐ (b) benzene ☐
(c) cyclohexane ☐ (d) cyclohexanol ☐

76. For obtaining butan-2-one from acetyl chloride which of the following reagents can be used?
(a) Grignard reagent ☐ (b) HI ☐
(c) H_2, Pd—$BaSO_4$ ☐ (d) Diethyl cadmium ☐

77. To distinguish between 2-pentanone and 3-pentanone which reagent can be used? **[JEE (WB) 2009]**
(a) NaOH/I_2 ☐ (b) SeO_2 ☐
(c) $K_2Cr_2O_7/H^+$ ☐ (d) Zn—Hg, HCl ☐

78. Which of the following reagents can help in separating a mixture of acetone and isopropyl alcohol?
(a) NaOH ☐ (b) NaCl ☐
(c) $NaHSO_3$ ☐ (d) None of these ☐

79. In the group  C=O, the carbonyl carbon is joined to other atoms by:
(a) two sigma and one pi bond ☐
(b) three sigma and one pi bond ☐
(c) two sigma and two pi bonds ☐
(d) three sigma and two pi bonds ☐

80. Acetaldehyde cannot show:
(a) Iodoform test ☐ (b) Benedict's test ☐
(c) Tollens' test ☐ (d) Lucas test ☐

81. Which one of the following statements is wrong?
(a) Aldehydes and ketones are good reducing agents ☐
(b) Aldehydes and ketones are polar compounds ☐
(c) Aldehydes are more reactive than ketones ☐
(d) Aldehydes and ketones are reduced to alcohols ☐

82. Dialkyl cadmium reacts with a compound to form a ketone. The compound is:
(a) an acid ☐ (b) an acid chloride ☐
(c) an ester ☐ (d) carbon monoxide ☐

83. Out of butane, butan-1-ol, butanal and butanone, the decreasing order of their boiling point is:
(a) butane > butanol > butanal > butanone ☐
(b) butanol > butane > butanal > butanone ☐
(c) butanone > butanal > butanol > butane ☐
(d) butanol > butanal > butanone > butane ☐

84. Acetaldehyde is converted to ethane by Wolff-Kishner reduction. Acetaldehyde is treated with:
(a) $LiAlH_4$ ☐
(b) $NaBH_4$ ☐
(c) NH_2NH_2 and $NaOC_2H_5$ ☐
(d) H_2 with Pd/$BaSO_4$ ☐

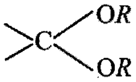
85. Acetone is mixed with bleaching powder to give: **[AFMC 2004]**
(a) ethanol ☐ (b) acetaldehyde ☐
(c) chloroform ☐ (d) phosgene ☐

86. Ketones react with Mg-Hg over water gives: **[AFMC 2005]**
(a) alcohols ☐ (b) pinacols ☐
(c) pinacolones ☐ (d) none of these ☐

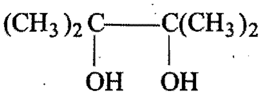
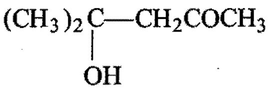
87. Cyanohydrin of which of the following gives lactic acid on hydrolysis? **[PMT (MP) 2000]**
(a) CH_3COCH_3 ☐ (b) CH_3CHO ☐
(c) $C_6H_5CH_2CHO$ ☐ (d) HCHO ☐

88. Aldol condensation between which of the following compounds followed by dehydration gives mesityl oxide?
(a) Two molecules of CH_3COCH_3 ☐
(b) Two molecules of CH_3CHO ☐
(c) CH_3CHO and HCHO ☐
(d) CH_3CHO and CH_3COCH_3 ☐

89. A natural compound (*X*), $C_4H_8O_2$, reduces Fehling's solution, liberates hydrogen when treated with sodium metal and gives a positive iodoform test. The structure of (*X*) is:
(a) $CH_3CHOHCH_2CHO$ ☐
(b) $HOCH_2CH_2CHO$ ☐
(c) CH_3COCH_2CHO ☐
(d) $CH_3COCH_2CH_2OH$ ☐

90. Compounds of general formula,  $>C<^{OR}_{OR}$ are called:
(a) diesters ☐ (b) acid anhydrides ☐
(c) hemiacetals ☐ (d) acetals ☐

91. In the reaction,
$(CH_3)_2C{=}O + X \rightarrow (CH_3)_2C(OC_2H_5)_2 + HCOOC_2H_5$,
X is:
(a) ethyl oxalate ☐ (b) propan-2-ol ☐
(c) ethyl *ortho* formate ☐ (d) none of these ☐

92. Major product obtained when acetone is reduced with Mg/Hg, H^+ in neutral or alkaline solution:
[PET (Raj.) 2003]
(a)  $(CH_3)_2\underset{OH}{C}—\underset{OH}{C}(CH_3)_2$ ☐
(b) $CH_3CH_2CH_3$ ☐
(c) $CH_3CHOHCH_3$ ☐
(d)  $(CH_3)_2\underset{OH}{C}—CH_2COCH_3$ ☐

93. During reduction of aldehydes with hydrazine and potassium hydroxide, the first is the formation of:
[CBSE (Med.) 2002]
(a) $RCH{=}NNH_2$ ☐ (b) $RCONH_2$ ☐
(c) $RCH{=}NH$ ☐ (d) $R—C{\equiv}N$ ☐

94. Acetaldehyde and ethyl alcohol reacts in presence of dry HCl gas. The product obtained is:
(a) $CH_3CH_2CH_2OH$ ☐
(b) $CH_3—CH(OH)—CH_3$ ☐
(c) $CH_3—CH(OH)—C_2H_5$ ☐
(d) $CH_3CH(OC_2H_5)_2$ ☐

95. A bad smelling yellow insoluble resin is obtained by boiling NaOH solution with:
(a) HCHO ☐ (b) CH_3CHO ☐
(c) CH_3COCH_3 ☐ (d) $C_2H_5COCH_3$ ☐

96. Acetals are:
(a) aldehydes ☐ (b) ketones ☐
(c) diethers ☐ (d) hydroxy aldehydes ☐

97. Which of the following compounds give a ketone with Grignard reagent?
(a) HCHO ☐ (b) CH_3CH_2OH ☐
(c) CH_3CN ☐ (d) CH_3I ☐

98. Reduction of acetonitrile in presence of $SnCl_2/HCl$, followed by hydrolysis gives:
(a) HCHO ☐ (b) CH_3CHO ☐
(c) CH_3CH_2CHO ☐ (d) CH_3COCH_3 ☐

99. If pentan-2-one is reacted with $NaBH_4$, followed by hydrolysis with D_2O, the product will be :
(a) $CH_3CD(OD)CH_2CH_2CH_3$ ☐
(b) $CH_3CD(OH)CH_2CH_2CH_3$ ☐
(c) $CH_3CH(OH)CH_2CH_2CH_3$ ☐
(d) $CH_3CH(OD)CH_2CH_2CH_3$ ☐

100. Aldol condensation between following compounds, followed by dehydration gives methyl vinyl ketone:
(a) formaldehyde and acetone ☐
(b) formaldehyde and acetaldehyde ☐
(c) two molecules of acetaldehyde ☐
(d) two molecules of acetone ☐

101. Aldol condensation will not take place in:
(a) HCHO ☐ (b) CH_3CH_2CHO ☐
(c) CH_3CHO ☐ (d) CH_3COCH_3 ☐

102. In the reaction, $CH_3CHO + HCN \longrightarrow CH_3CHOHCN$, a chiral centre is produced. The product is:
(a) meso compound ☐ (b) laevorotatory ☐
(c) dextrorotatory ☐ (d) racemic mixture ☐

103. Which of the given compounds will give positive test with Tollens' reagent?
(a) Acetamide ☐ (b) Acetaldehyde ☐
(c) Acetic acid ☐ (d) Acetone ☐

104. The haloform reaction of acetone with sodium hypobromite yields:
(a) acetic acid ☐ (b) propionic acid ☐
(c) acetaldehyde ☐ (d) isopropyl alcohol ☐

105. Which is the best solvent?
(a) HCHO ☐ (b) CH_3CHO ☐
(c) CH_3COCH_3 ☐ (d) CH_3COOH ☐

106. When formaldehyde is treated with ethylamine, it gives:
(a) ethyl alcohol ☐ (b) propionaldehyde ☐
(c) dimethylamine ☐ (d) ethyl methylamine ☐

107. When formaldehyde is treated with methanol in presence of dry HCl gas or fused $CaCl_2$, it yields:
(a) acetaldehyde ☐ (b) mercaptal ☐
(c) methylal ☐ (d) dimethyl ether ☐

108. Formaldehyde is used:
(a) as antiseptic and germicide ☐
(b) for making synthetic plastics and resins ☐
(c) for the preservation of biological specimens ☐
(d) all of the above ☐

109. Polarization of electrons in acrolein may be written as:
[CBSE (Med.) 2002]
(a) $H_2\overset{\delta^-}{C}{=}\overset{\delta^+}{C}H—CH{=}O$ ☐
(b) $H_2\overset{\delta^+}{C}{=}CH—CH{=}\overset{\delta^-}{O}$ ☐
(c) $H_2\overset{\delta^-}{C}{=}CH—\overset{\delta^+}{C}H{=}O$ ☐
(d) $H_2\overset{\delta^-}{C}{=}CH—CH{=}\overset{\delta^+}{O}$ ☐

110. Acetoacetic ester on hydrolysis by boiling with dil. acid yields:

(a) acetic acid ☐ (b) acetaldehyde ☐
(c) propanal ☐ (d) propanone ☐

111. Grignard reagent reacts with (*X*) to give aldehyde, (*X*) may be:
(a) acetyl chloride ☐ (b) acetic anhydride ☐
(c) ethyl formate ☐ (d) water ☐

112. Acetone on condensation gives:
(a) mesitylene ☐ (b) phorone ☐
(c) mesityl oxide ☐ (d) all of these ☐

113. A carbonyl compound with molecular weight 86, does not reduce Fehling's solution but forms crystalline bisulphite derivatives and gives iodoform test. The possible compound can be:
(a) pentan-2-one and pentan-3-one ☐
(b) pentan-2-one and methyl butan-2-one ☐
(c) pentanone and pentanal ☐
(d) pentan-3-one and 3-methyl butan-2-one ☐

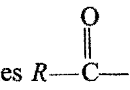
114. Which has minimum reactivity towards nucleophiles?
(a) Butanone ☐ (b) Propanone ☐
(c) Ethanal ☐ (d) Methanal ☐

115. $CH_3CH{=}CHCHO$ is oxidised to $CH_3{-}CH{=}CHCOOH$, using oxidising agent as:
(a) alkaline $KMnO_4$ ☐
(b) $K_2Cr_2O_7$/conc. H_2SO_4 ☐
(c) ammoniacal $AgNO_3$ ☐
(d) dilute HNO_3 ☐

116. Propanal on aldol condensation with aqueous K_2CO_3 gives mainly:
(a) 3-hydroxy butanal ☐
(b) 3-hydroxy-2-methyl pentanal ☐
(c) 3-hydroxy propanal ☐
(d) 4-hydroxy-4-methyl pentan-2-one ☐

117. Which will give a yellow precipitate with iodine and alkali?
(a) Ethyl methyl ketone ☐ (b) Acetophenone ☐
(c) 2-Hydroxy propane ☐ (d) All of these ☐

118. The product(s) obtained *via* oxymercuration $(HgSO_4 + H_2SO_4)$ of but-l-yne would be:
(a) $CH_3CH_2CH_2CHO$ ☐
(b) $CH_3CH_2COCH_3$ ☐
(c) $CH_3CH_2CHO + HCHO$ ☐
(d) $CH_3CH_2COOH + HCOOH$ ☐


$R-\overset{\displaystyle O}{\overset{\|}{C}}-R'$

119. Ketones $R-\overset{O}{\overset{\|}{C}}-R'$. Where, $R{=}R'{=}$alkyl group can be obtained in one step by:
(a) oxidation of primary alcohols ☐
(b) hydrolysis of esters ☐
(c) oxidation of tertiary alcohols ☐
(d) reduction of acid chloride with alcohol ☐

120. Among the given compounds, the most-susceptible to nucleophilic attack at the carbonyl group is:
(a) MeCOCl ☐ (b) MeCHO ☐
(c) MeCOOMe ☐ (d) MeCOOCOMe ☐

121. In the Cannizzaro's reaction given below,

$$2Ph-CHO \xrightarrow{OH^-} PhCH_2OH + PhCOO^-$$

the slowest step is: **[AIEEE 2009]**
(a) the attack of OH^- at the carbonyl group ☐
(b) the transfer of hydride to the carbonyl group ☐
(c) the abstraction of proton from the carboxylic acid ☐
(d) the deprotonation of $Ph-CH_2OH$ ☐

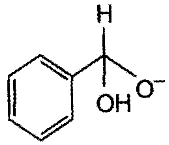
122. In the following sequence of reactions, the alkene affords the compound *B*. The compound '*B*' is: **[AIEEE 2008]**

$$CH_3CH{=}CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B$$

(a) CH_3CHO ☐ (b) CH_3CH_2CHO ☐
(c) CH_3COCH_3 ☐ (d) $CH_3CH_2COCH_3$ ☐

123. Among the following compounds, which will react with acetone to give a product containing $>C{=}N-$?
(a) $C_6H_5NH_2$ ☐ (b) $(CH_3)_3N$ ☐
(c) $C_6H_5NHC_6H_5$ ☐ (d) $C_6H_5NHNH_2$ ☐

124. In a Cannizzaro's reaction, the intermediate that will be the best hydride donor is:

(a) 

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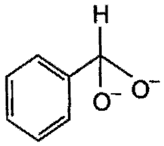
(b) 

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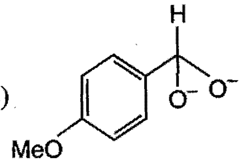
(c) 

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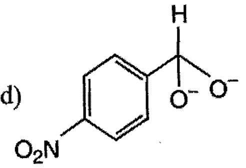
(d) 

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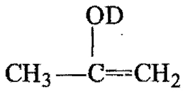
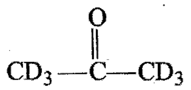
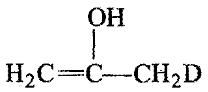
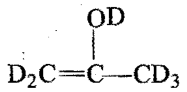
125. The reagent of choice for the selective reduction of a ketone in the presence of an ester is:
(a) $LiAlH_4$ ☐ (b) $NaBH_4$ ☐
(c) $H_2/Pd-C$ ☐ (d) $Na-C_2H_5OH$ ☐

126. The 'enol' form of acetone after treatment with D_2O, gives: **[PET (Kerala) 2006]**

(a) 
$CH_3-\overset{OD}{\overset{|}{C}}{=}CH_2$ ☐

(b) 
$CD_3-\overset{O}{\overset{\|}{C}}-CD_3$ ☐

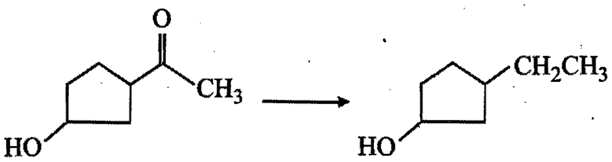
(c) 
$H_2C{=}\overset{OH}{\overset{|}{C}}-CH_2D$ ☐

(d) 
$D_2C{=}\overset{OD}{\overset{|}{C}}-CD_3$ ☐

127. Oxidation of acetaldehyde with selenium dioxide produces:
(a) ethanoic acid ☐ (b) methanoic acid ☐
(c) glyoxal ☐ (d) oxalic acid ☐

128. Which of the following does not give formaldehyde on heating or distillation? **[PMT (MP) 2000]**
(a) Formalin ☐ (b) Trioxan ☐
(c) Paraldehyde ☐ (d) Paraformaldehyde ☐

129. The appropriate reagent for the following transformation **[IIT(S) 2000]**



is:

(a) Zn(Hg), HCl ☐ (b) NH_2NH_2, OH^- ☐
(c) H_2/Ni ☐ (d) $NaBH_4$ ☐

130. Which of the following has the most acidic hydrogen? **[IIT(S) 2000]**

(a) Hexan-3-one ☐ (b) Hexan-2,4-dione ☐
(c) Hexan-2-one ☐ (d) Hexan-2,3-dione ☐

131. Which of the following is correct? **[CBSE (Med.) 2001]**

(a) Reduction of any aldehyde gives secondary alcohol ☐
(b) Reduction of vegetable oil with H_2SO_4 gives glycerine ☐
(c) Alcoholic iodine with NaOH gives iodoform ☐
(d) Sucrose on reaction with NaCl gives invert sugar ☐

132. Which of the following is the industrial method of preparation of acetaldehyde? **[AMU (PMT) 2009]**

(a) $H_2C{=}CH_2 + H_2O \xrightarrow{Pd^{++}} CH_3CHO$ ☐
(b) $CH_3COCl + H_2 \xrightarrow[BaSO_4]{Pd} CH_3CHO + HCl$ ☐
(c) $CH_3CN \xrightarrow[HCl]{SnCl_2} CH_3CH{=}NH \xrightarrow{H_3O^+} CH_3CHO$ ☐
(d) None of the above ☐

133. Acetone, formaldehyde and acetaldehyde can be distinguished when treated with: **[CPMT 2002]**

(a) H_2NNH_2 ☐ (b) NH_3 ☐
(c) NH_2OH ☐ (d) $C_6H_5NHNH_2$ ☐

134. When three molecules of acetone condense in presence of dry HCl, the product formed is: **[MGIMS (Wardha) 2003]**

(a) mesityl oxide ☐ (b) glyoxal ☐
(c) mesitylene ☐ (d) phorone ☐

135. Ozonolysis of C_7H_{14} gave 2-methyl pentan-3-one. The alkene is: **[DPMT 2000]**

(a) 2-ethyl-3-methyl but-l-ene ☐
(b) 2-methyl-3-ethyl but-3-ene ☐
(c) 2,5-dimethyl-3,4-diethyl hex-3-ene ☐
(d) 2-methyl-3-ethyl but-l-ene ☐

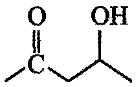
136. In the reaction,

$$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN \xrightarrow{HOH} CH_3CH(OH)COOH$$

an asymmetric centre is generated. The acid obtained will be: **[UPSEE (Engg.) 2007; JCECE (Med.) 2008]**

(a) (*L*)-isomer ☐
(b) (*D*)-isomer ☐
(c) 20% (*D*) + 80%(*L*)-isomer ☐
(d) 50% (*D*) + 50% (*L*)-isomer ☐

137. Which of the following will be most easily dehydrated in acidic conditions? **[IIT (S) 2000]**

(a)


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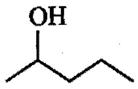
(b)


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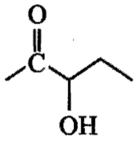
(c)


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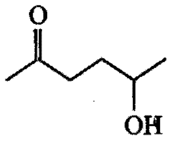
(d)


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138. A substance $C_4H_{10}O$ yields on oxidation, a compound C_4H_8O, which gives an oxime and positive iodoform test. The original substance on treatment with conc. H_2SO_4 gives C_4H_8. The structure of the compound is: **[SCRA 2000]**

(a) $CH_3CH_2CH_2CH_2OH$ ☐
(b) $CH_3\underset{}{\overset{OH}{\overset{|}{C}}}HCH_2CH_3$ ☐
(c) $(CH_3)_3C—OH$ ☐
(d) $CH_3CH_2—O—CH_2CH_3$ ☐

139. $(CH_3)_2CO \xrightarrow[HCl]{NaCN} (A) \xrightarrow[\Delta]{H_3\overset{+}{O}} (B)$

In the above sequence of reactions, (*A*) and (*B*) are: **[CPMT 2000]**

(a) $(CH_3)_2C(OH)CN$, $(CH_3)_2C(OH)COOH$ ☐
(b) $(CH_3)_2C(OH)CN$, $(CH_3)_2C(OH)_2$ ☐
(c) $(CH_3)_2C(OH)CN$, $(CH_3)_2CHCOOH$ ☐
(d) $(CH_3)_2C(OH)CN$, $(CH_3)_2CO$ ☐

140. Aldol condensation will not be observed in: **[GATE 2001]**

(a) chloral ☐ (b) phenyl acetaldehyde ☐
(c) hexanal ☐ (d) nitromethane ☐

141. The most reactive compound towards formation of cyanohydrin on treatment with KCN followed by acidification is: **[GATE 2001]**

(a) benzaldehyde ☐
(b) *p*-nitrobenzaldehyde ☐
(c) phenyl acetaldehyde ☐
(d) *p*-hydroxy benzaldehyde ☐

142. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH gives:. **[IIT (S) 2001]**

(a) benzyl alcohol and sodium formate ☐
(b) sodium benzoate and methyl alcohol ☐
(c) sodium benzoate and sodium formate ☐
(d) benzyl alcohol and methyl alcohol ☐

143. Which of the following reacts with NaOH to produce an acid and an alcohol? **[MGIMS (Wardha) 2001]**

(a) HCHO ☐ (b) CH_3COOH ☐
(c) CH_3CH_2COOH ☐ (d) C_6H_5COOH ☐

144. Which of the following is not correctly matched? **[SCRA 2001]**

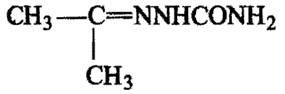
(a) $>C{=}O \xrightarrow[\text{Reduction}]{\text{Clemmensen's}} >CH_2$ ☐
(b) $>C{=}O \xrightarrow[\text{Reduction}]{\text{Wolff-Kishner}} >CHOH$ ☐

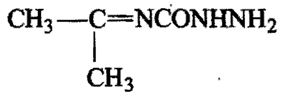
(c) $—COCl \xrightarrow[\text{Reduction}]{\text{Rosenmund's}} —CHO$ ☐

(d) $—C{\equiv}N \xrightarrow[\text{Reduction}]{\text{Stephen's}} —CHO$ ☐

145. Compound '*A*' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product '*B*' (molecular formula C_3H_6O). '*B*' forms a shining silver mirror on warming with ammoniacal silver nitrate. '*B*' when treated with an aqueous solution of $NH_2CONHNH_2{\cdot}HCl$ and sodium acetate gives a product '*C*'. Identify the structure of '*C*': **[IIT (S) 2002]**

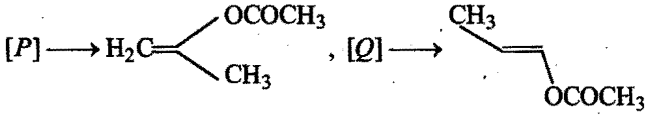
(a) $CH_3CH_2CH{=}NNHCONH_2$ ☐

(b) 
$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NNHCONH_2$ ☐

(c) 
$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NCONHNH_2$ ☐

(d) $CH_3CH_2CH{=}NCONHNH_2$ ☐

146. The product of acid hydrolysis of [*P*] and [*Q*] can be distinguished by: **[IIT (S) 2003]**



(a) Lucas reagent ☐ (b) 2,4-DNP ☐
(c) Fehling's solution ☐ (d) $NaHSO_3$ ☐

147. A compound does not react with 2,4-dinitrophenyl hydrazine, compound is: **[UPSEAT 2003]**

(a) acetone ☐ (b) acetaldehyde ☐
(c) CH_3OH ☐ (d) $CH_3CH_2COCH_3$ ☐

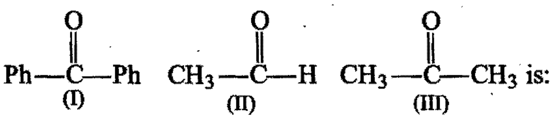
148. Which one of the following does not form sodium bisulphite addition product with sodium bisulphite solution? **[CET (J&K) 2009]**

(a) CH_2O ☐ (b) $C_6H_5COCH_3$ ☐
(c) C_6H_5CHO ☐ (d) CH_3CHO ☐

149. Acetone reacts with Grignard reagent to form: **[AFMC 2004]**

(a) 3° alcohol ☐ (b) 2° alcohol ☐
(c) ether ☐ (d) no reaction ☐

150. The correct order of reactivity of PhMgBr with,


$$\underset{(I)}{Ph—\overset{\displaystyle O}{\overset{\|}{C}}—Ph} \quad \underset{(II)}{CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—H} \quad \underset{(III)}{CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3} \text{ is:}$$

[IIT 2004]

(a) I > II > III ☐ (b) III > II > I ☐
(c) II > III > I ☐ (d) I > III > II ☐

151. Which one of the following can be oxidised to the corresponding carbonyl compounds? **[CBSE (Med.) 2004]**

(a) 2-Hydroxy propane ☐
(b) *Ortho* nitrophenol ☐
(c) Phenol ☐
(d) 2-Methyl-2-hydroxy propane ☐

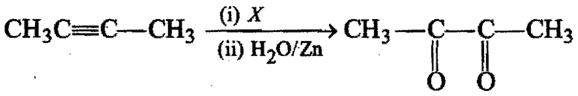
152. Acetone reacts with iodine to form iodoform in the presence of: **[BHU 2004]**

(a) $CaCO_3$ ☐ (b) $MgCO_3$ ☐
(c) KOH ☐ (d) NaOH ☐

153. Which one of the following gives positive haloform and positive Tollens' tests? **[PET (MP) 2004]**

(a) Formaldehyde ☐ (b) Acetone ☐
(c) Propionaldehyde ☐ (d) Acetaldehyde ☐

154. In the reaction,


$$CH_3C{\equiv}C—CH_3 \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) } X} CH_3—\underset{\displaystyle O}{\underset{\|}{C}}—\underset{\displaystyle O}{\underset{\|}{C}}—CH_3$$

X is: **[DCE 2005]**

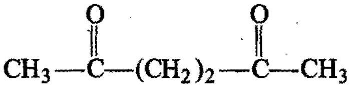
(a) HNO_3 ☐ (b) O_2 ☐
(c) O_3 ☐ (d) $KMnO_4$ ☐

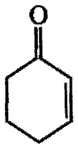
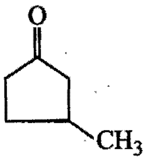
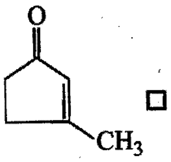
155. Which of the following reagents converts both acetaldehyde and acetone to alkanes? **[EAMCET (Med.) 2005]**

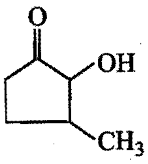
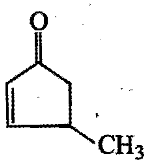
(a) Ni/H_2 ☐ (b) $LiAlH_4$ ☐
(c) $I_2/NaOH$ ☐ (d) Zn-Hg/conc. HCl ☐

156. Which reagent is used to convert 2-butanone into propanoic acid? **[IIT 2005]**

(a) NaOH, I_2/H^+ ☐ (b) Tollens' reagent ☐
(c) Fehling's solution ☐ (d) NaOH, NaI/H^+ ☐

157. The diketone 
$CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—(CH_2)_2—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3$ on intramolecular aldol condensation gives the final product: **[PMT (Kerala) 2006]**

(a)  ☐ (b)  ☐ (c)  ☐

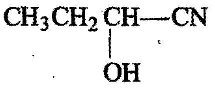
(d)  ☐ (e)  ☐

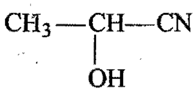
158. The increasing order of the rate of HCN addition to compounds *A–D* is: **[AIEEE 2006]**

(*A*) HCHO (*B*) CH_3COCH_3 (*C*) $PhCOCH_3$ (*D*) PhCOPh

(a) $A < B < C < D$ ☐ (b) $D < B < C < A$ ☐
(c) $D < C < B < A$ ☐ (d) $C < D < B < A$ ☐

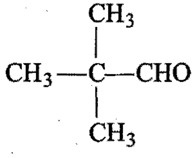
159. Which of the following compounds is obtained when acetone is reacted with HCN? **[CET (Gujarat) 2006]**

(a) $(CH_3)_2C(OH)NC$ ☐ (b) 
$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{CH}}—CN$ ☐

(c)  $CH_3—CH(OH)—CN$ ☐ (d) $(CH_3)_2C(OH)CN$ ☐

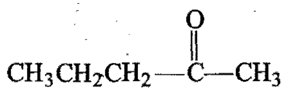
160. Aldol condensation is: **[PMT (HP) 2006]**
(a) self condensation of aldehydes only having atleast one alpha hydrogen ☐
(b) self condensation of ketones only having atleast one alpha hydrogen ☐
(c) self condensation of both aldehydes and ketones having atleast one alpha hydrogen ☐
(d) self condensation of both aldehydes and ketones having no alpha hydrogen ☐

161. Cannizzaro's reaction is not given by: **[BHU 2006]**
(a) CH_3CHO ☐ (b) HCHO ☐
(c) benzaldehyde ☐ (d) triethyl acetaldehyde ☐

162.  $CH_3—C(CH_3)_2—CHO$ does not show aldol condensation because: **[BHU 2006]**
(a) carbon is bounded by 3-heavy methyl groups ☐
(b) due to the absence of α-hydrogen ☐
(c) it is a neutral molecule ☐
(d) due to hindrance created by methyl group for carbanion ☐

163. What reagent is used in the Rosenmund's reduction? **[EAMCET (Med.) 2006]**
(a) $H_2/Pd\text{-}BaSO_4$ ☐
(b) $LiAlH_4$ ☐
(c) $NH_2NH_2/KOH/CH_2OH\text{-}CH_2OH$ ☐
(d) Zn-Hg/HCl ☐

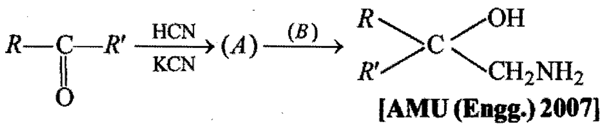
164. A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is: **[CBSE (Med.) 2006]**
(a) diethyl ketone ☐ (b) formaldehyde ☐
(c) acetaldehyde ☐ (d) acetone ☐

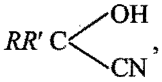
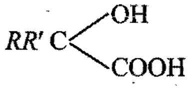
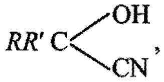
165. Nucleophilic addition reaction will be most favoured in: **[CBSE (Med.) 2006]**
(a) CH_3CH_2CHO ☐
(b) CH_3CHO ☐
(c)  $CH_3CH_2CH_2—C(=O)—CH_3$ ☐
(d) $(CH_3)_2C{=}O$ ☐

166. The smallest ketone and its next homologue are reacted with NH_2OH to form oxime: **[IIT 2006]**
(a) two different oximes are formed ☐
(b) three different oximes are formed ☐
(c) two oximes are optically active ☐
(d) all oximes are optically active ☐

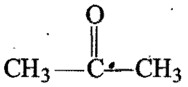
167. The product formed in aldol condensation is: **[CBSE (Med.) 2007]**
(a) an alpha-hydroxy aldehyde or ketone ☐
(b) an alpha beta unsaturated ester ☐
(c) a beta-hydroxy acid ☐
(d) a beta-hydroxy aldehyde or a beta-hydroxy ketone ☐

168. (*A*) and (*B*) in the following reactions are:



[AMU (Engg.) 2007]
(a) $(A) = $  $RR'C(OH)CN$, $(B) = LiAlH_4$ ☐
(b) $(A) = $  $RR'C(OH)COOH$, $(B) = NH_3$ ☐
(c) $(A) = $  $RR'C(OH)CN$, $(B) = H_3O^+$ ☐
(d) $(A) = RR'\,CH_2CN$, $(B) = NaOH$ ☐

169. Clemmensen's reduction of ketones is carried out in: **[BCECE (Med.) 2007]**
(a) $LiAlH_4$ in H_2O ☐ (b) glycol and KOH ☐
(c) Zn-Hg and HCl ☐ (d) H_2 and Pd catalyst ☐

170. Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid? **[CBSE (Med.) 2007]**
(a) $CH_3CH_2CH_2CHO$ ☐ (b)  $CH_3—C(=O)—CH_3$ ☐
(c) $C_6H_5CH_2CHO$ ☐ (d) C_6H_5CHO ☐

171. Which one of the following reactions is called Rosenmund reaction? **[EAMCET (Med.) 2007; CPMT 2008]**
(a) Aldehydes are reduced to alcohols ☐
(b) Acids are converted to acid chlorides ☐
(c) Alcohols are reduced to hydrocarbons ☐
(d) Acid chlorides are reduced to aldehydes ☐

172. Bakelite is prepared by the reaction between: **[BCECE (Med.) 2007]**
(a) phenol and formaldehyde ☐
(b) urea and formaldehyde ☐
(c) ethylene and glycol ☐
(d) tetramethylene and glycol ☐

173. CH_3COCH_3 and CH_3CH_2CHO can be distinguished by: **[DCE (Engg.) 2007]**
(a) $FeCl_3$ ☐ (b) Tollens' reagent ☐
(c) $NaHSO_3$ ☐ (d) 2,4-DNP ☐

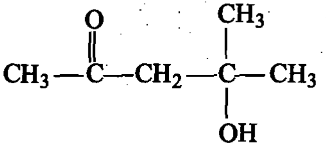
174. On reaction with hydroxylamine, aldehydes produce: **[CET (J & K) 2007]**
(a) ketoxime ☐ (b) hydrazone ☐
(c) semicarbazone ☐ (d) aldoxime ☐

175. Aldehyde with $NH_2 \cdot NH_2$ forms: **[BCECE (Med.) 2008]**
(a) aniline ☐ (b) hydrazones ☐
(c) nitrobenzene ☐ (d) none of these ☐

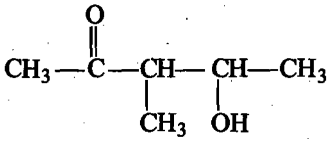
176. The most suitable reagent for the conversion of primary alcohol into aldehyde with the same number of carbon is: **[PET (Kerala) 2007]**

(a) acidified $K_2Cr_2O_7$ ☐
(b) acidified $KMnO_4$ ☐
(c) alkaline $KMnO_4$ ☐
(d) pyridinium chlorochromate ☐
(e) CrO_3 ☐

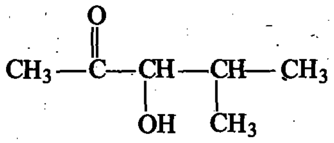
177. Which of the products is formed when acetone is reacted with barium hydroxide solution? **[AFMC 2008]**

(a)  ☐

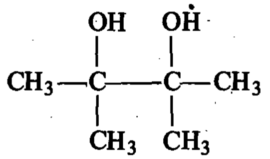
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\underset{OH}{\overset{CH_3}{C}}-CH_3$

(b)  ☐

$CH_3-\overset{\overset{O}{\|}}{C}-\underset{CH_3}{CH}-\underset{OH}{CH}-CH_3$

(c)  ☐

$CH_3-\overset{\overset{O}{\|}}{C}-\underset{OH}{CH}-\underset{CH_3}{CH}-CH_3$

(d)  ☐

$CH_3-\underset{CH_3}{\overset{OH}{C}}-\underset{CH_3}{\overset{OH}{C}}-CH_3$

178. $CH_3CH_2C\equiv N \xrightarrow{X} CH_3CH_2CHO$

the compound X is: **[AIIMS 2008]**

(a) $H_2/Pd\text{-}BaSO_4$ ☐ (b) $SnCl_2/HCl/H_2O$, boil ☐
(c) $LiAlH_4$/ether ☐ (d) $NaBH_4/ether/H_3O^+$ ☐

179. Reduction of aldehydes and ketones into hydrocarbons using hydrazine and sodium ethoxide is called: **[BHU (Mains) 2008]**

(a) Clemmensen reduction ☐
(b) Cope reduction ☐
(c) Dow reduction ☐
(d) Wolff-Kishner reduction ☐

180. 3-Hydroxy butanal is formed when X reacts with Y in dilute Z solution. What are X, Y and Z? **[AIIMS 2008]**

	X	Y	Z	
(a)	CH_3CHO	$(CH_3)_2CO$	NaOH	☐
(b)	CH_3CHO	CH_3CHO	NaCl	☐
(c)	$(CH_3)_2CO$	$(CH_3)_2CO$	HCl	☐
(d)	CH_3CHO	CH_3CHO	NaOH	☐

181. A Wittig reaction with an aldehyde gives: **[VITEEE 2008]**

(a) ketone ☐ (b) a long chain fatty acid ☐
(c) olefin compound ☐ (d) epoxide ☐

182. A strong base can abstract an α-hydrogen from: **[CBSE (Med.) 2008]**

(a) alkane ☐ (b) alkene ☐
(c) alkyne ☐ (d) ketone ☐

183. Which of the following pathways produces 2-hexanone? **[PMT (Kerala) 2008]**

(i) 1-Hexyne is treated with H_2SO_4, $HgSO_4$ and water
(ii) 3-Methyl-2-heptene is treated with O_3 followed by hydrolysis
(iii) *n*-Butyl magnesium bromide reacts with acetaldehyde followed by hydrolysis and then chromic acid oxidation
(iv) Hydroboration oxidation of 1-hexyne

(a) (i), (ii) and (iii) ☐ (b) (i) and (ii) only ☐
(c) (i) and (iii) only ☐ (d) (i), (ii) and (iv) ☐
(e) all the four methods ☐

184. In a reaction RCHO is reduced to RCH_3 using amalgamated zinc and concentrated HCl and warming the solution. The reaction is known as: **[DCE 2009]**

(a) Meerwein-Ponndorf reaction ☐
(b) Clemmensen's reduction ☐
(c) Wolff-Kishner reduction ☐
(d) Schiff's reaction ☐

185. $CH_3COOH \xrightarrow{LiAlH_4} (X) \xrightarrow[300°C]{Cu} (Y) \xrightarrow[NaOH]{dilute} (Z)$,

In the above reaction, (Z) is: **[CET (Karnataka) 2009]**

(a) aldol ☐ (b) ketol ☐
(c) acetol ☐ (d) butanol ☐

186. The synthesis of crotonaldehyde from acetaldehyde is an example of ...... reaction: **[EAMCET 2009]**

(a) nucleophilic addition ☐
(b) elimination ☐
(c) electrophilic addition ☐
(d) nucleophilic addition elimination ☐

187. In which of the following reactions new carbon-carbon bond is not formed? **[JEE (WB) 2009]**

(a) Cannizzaro reaction ☐ (b) Wurtz reaction ☐
(c) Aldol condensation ☐ (d) Friedel-Crafts reaction ☐

188. Compound (A) undergoes Cannizzaro reaction and (B) undergoes positive iodoform test. Therefore, **[DPMT 2009]**

(a) A = Acetaldehyde ; B = 1-Pentanal ☐
(b) A = $C_6H_5CH_2CHO$; B = 3-Pentanone ☐
(c) A = Formaldehyde ; B = 2-Pentanone ☐
(d) A = Propionaldehyde ; B = 1-Pentanol ☐

189. The compound which is not formed during the dry distillation of a mixture of calcium formate and calcium acetate is: **[CET (Karnataka) 2009]**

(a) propanal ☐ (b) propanone ☐
(c) ethanal ☐ (d) methanal ☐

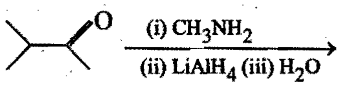
190. Aldol condensation does not occur between : **[DPMT 2009]**

(a) two different aldehydes ☐
(b) two different ketones ☐
(c) an aldehyde and ketone ☐
(d) an aldehyde and an ester ☐

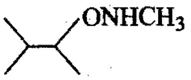
191. Which factor/s will increase the reactivity of $>C{=}O$ group? **[AMU (Engg.) 2009]**

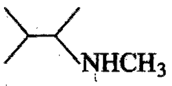
(i) Presence of a group with positive inductive effect
(ii) Presence of a group with negative inductive effect
(iii) Presence of large alkyl group
(a) only (i) ☐ (b) only (ii) ☐
(c) (i) and (ii) ☐ (d) (ii) and (iii) ☐

192. The major organic product formed from the following reaction

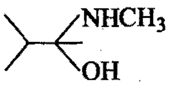


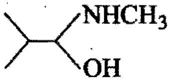
is : **[AFMC 2010]**

(a) 

☐ (b) 

☐

(c) 

☐ (d) 

☐

193. Which of the following reaction will not result in the formation of carbon-carbon bonds ? **[CBSE (Med.) Prelims] 2010**
(a) Reimer-Tiemann reaction ☐
(b) Cannizzaro reaction ☐
(c) Wurtz reaction ☐
(d) Friedel-Crafts acylation ☐

194. Which of the following statements is not correct ? **[DUMET 2010]**
(a) Aldehydes and ketones contain polar carbonyl group ☐
(b) Aldehydes and ketones undergo nucleophilic addition ☐
(c) Aldehydes and ketones undergo electrophilic substitution ☐
(d) Lower members of aldehydes and ketones are soluble in water due to hydrogen bonding ☐

SET II : This set contains the questions with two or more correct answers.

195. Which compounds undergo Cannizzaro's reaction?
(a) Methanal ☐ (b) Ethanal ☐
(c) Propanone ☐ (d) Benzaldehyde ☐

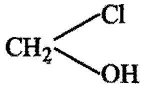
196. Reaction of Grignard reagent with ...... gives alcohol.
(a) carbon dioxide ☐ (b) formaldehyde ☐
(c) acetaldehyde ☐ (d) acetone ☐

197. Which of the following reagents react in a same manner with HCHO, CH_3CHO and CH_3COCH_3?
(a) HCN ☐ (b) NH_2OH ☐
(c) Schiff's reagent ☐ (d) NH_3 ☐

198. A plastic bakelite is obtained from:
(a) benzene ☐ (b) formaldehyde ☐
(c) ammonia ☐ (d) phenol ☐

199. Which statements are correct in the case of acetaldehyde and acetone?
(a) Both react with $NaHSO_3$ ☐
(b) Both give iodoform test ☐
(c) Both can be reduced into alcohols ☐
(d) Both undergo aldol condensation ☐

200. Which are mixed ketones?
(a) Propan-2-one ☐ (b) Butan-2-one ☐
(c) Pentan-3-one ☐ (d) Pentan-2-one ☐

201. CH_2Cl_2 on heating with NaOH solution gives:
(a) CH_3OH ☐ (b) HCOONa ☐
(c) HCHO ☐ (d) 
$CH_2\begin{matrix}Cl\\OH\end{matrix}$ ☐

202. Which gives nucleophilic addition reactions?
(a) Methanal ☐ (b) Ethanal ☐
(c) Propanone ☐ (d) None of these ☐

203. Gem dihalides on hydrolysis form:
(a) alkenes ☐ (b) aldehydes ☐
(c) ketones ☐ (d) alkynes ☐

204. Which of the following compounds will give positive iodoform test?
(a) $C_6H_5COCH_3$ ☐ (b) $CH_3COC_2H_5$ ☐
(c) $CH_3CHOHC_2H_5$ ☐ (d) $CH_3COOCOCH_3$ ☐

205. Grignard reagent can give aldehyde with:
(a) ethyl formate ☐ (b) ethyl *ortho* formate ☐
(c) methyl cyanide ☐ (d) hydrogen cyanide ☐

206. Which of the following reagents react in a same manner with HCHO and C_6H_5CHO?
(a) NaOH ☐ (b) NH_3 ☐
(c) HCN ☐ (d) Fehling's solution ☐

207. The names of the compound, $CH_3CH_2CH_2CH_2CHO$ are:
(a) butyraldehyde ☐ (b) 4-methyl butanal ☐
(c) valeraldehyde ☐ (d) pentanal ☐

208. Which of the following methods can be used to prepare aldehydes?
(a) By the reduction of acid chlorides in presence of Pd or Pt ☐
(b) By passing the vapours of fatty acids with formic acid ☐
(c) By interaction of formic ester with Grignard reagent ☐
(d) By the reduction of alkyl cyanide with $SnCl_2/HCl$ and hydrolysis ☐

209. Ketones can be prepared by:
(a) heating calcium propionate with calcium formate ☐
(b) dry distillation of fused calcium acetate ☐
(c) hydrolysis of propylidene chloride with alkali ☐
(d) action of dialkyl cadmium on acid chloride ☐

210. Which of the following compounds will give Fehling's solution test?
(a) Acetone ☐ (b) Benzaldehyde ☐
(c) Acetaldehyde ☐ (d) Propanal ☐

211. Which of the following compounds will undergo aldol condensation?
(a) Acetaldehyde ☐
(b) Benzaldehyde ☐

(c) Propionaldehyde ☐
(d) Trideutero acetaldehyde ☐

212. Which of the following compounds will not undergo aldol condensation when treated with an alkali?

(a) Acetone ☐ (b) Formaldehyde ☐
(c) Acetaldehyde ☐ (d) Benzaldehyde ☐

213. Acetone gives addition elimination reaction with:

(a) NH_2OH ☐ (b) $NaHSO_3$ ☐
(c) $NH_2NHCONH_2$ ☐ (d) $NH_2NHC_6H_5$ ☐

214. Aldol condensation takes place between:

(a) two moles of formaldehyde ☐
(b) two moles of acetaldehyde ☐
(c) two moles of acetone ☐
(d) one mole of acetaldehyde and one mole of acetone ☐

215. Acetone molecules on condensation can give:

(a) mesityl oxide ☐ (b) phorone ☐
(c) crotonaldehyde ☐ (d) mesitylene ☐

216. Acetone on condensation with chloroform in presence of caustic potash forms:

(a) chloretone ☐
(b) trichloro nitromethane ☐
(c) 1,1,1-trichloro-2-methyl propan-2-ol ☐
(d) chloropicrin ☐

217. Choose the correct statements:

(a) Acetaldehyde on polymerisation gives paraldehyde ☐
(b) Formaldehyde gas on polymerisation gives metaformaldehyde ☐
(c) Acetaldehyde forms Schiff's base with formaldehyde ☐
(d) Benzaldehyde does not polymerise ☐

218. An aldehyde can give nucleophilic addition reaction with:

(a) HCN ☐ (b) $NaHSO_3$ ☐
(c) $R—Mg—X$ ☐ (d) NH_2NH_2 ☐

ASSERTION-REASON TYPE QUESTIONS

Following questions consist of an **Assertion (A)** and the **Reason (R).** Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) Carbonyl compounds take part in nucleophilic addition reactions.
(R) These reactions are initiated by nucleophilic attack at the electron deficient carbon atom.

2. (A) Primary alcohols can be easily oxidised to aldehydes.
(R) Aldehydes are prone to further oxidation to carboxylic acids.

3. (A) The addition of ammonia derivatives on carbonyl compounds is carried in weakly acidic medium.
(R) In weakly acidic medium, attacking nucleophile is also protonated.

4. (A) Fehling's reagent is a test for all aliphatic aldehydes.
(R) Aliphatic aldehydes can be easily oxidised even with mild oxidising agents.

5. (A) 2-Methyl propanal undergoes Cannizzaro's reaction.
(R) It has an α-hydrogen atom.

6. (A) Formaldehyde is a planar molecule.
(R) Carbon atom in formaldehyde is sp^2-hybridized.

7. (A) Nitromethane can give aldol condensation.
(R) α-hydrogen of nitromethane is acidic.

8. (A) Chloral hydrate is stable.
(R) It is stable due to its high molecular weight.

9. (A) Acetaldehyde does not show aldol condensation.
(R) Compounds having atleast one α-hydrogen give aldol condensation.

10. (A) Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular mass increases.
(R) Distinction between aldehydes and ketones can be made by Tollens' reagent.

ANSWERS

OBJECTIVE QUESTIONS

1. (b)	2. (c)	3. (d)	4. (b)	5. (c)	6. (a)	7. (a)	8. (d)	9. (b)	10. (d)
11. (c)	12. (d)	13. (b)	14. (a)	15. (c)	16. (b)	17. (b)	18. (d)	19. (d)	20. (c)
21. (c)	22. (c)	23. (b)	24. (a)	25. (c)	26. (a)	27. (d)	28. (d)	29. (c)	30. (d)
31. (c)	32. (b)	33. (a)	34. (b)	35. (d)	36. (a)	37. (a)	38. (a)	39. (d)	40. (b)
41. (b)	42. (c)	43. (a)	44. (c)	45. (d)	46. (d)	47. (c)	48. (b)	49. (b)	50. (a)
51. (d)	52. (c)	53. (b)	54. (c)	55. (a)	56. (b)	57. (c)	58. (b)	59. (a)	60. (a)
61. (a)	62. (b)	63. (a)	64. (b)	65. (d)	66. (c)	67. (c)	68. (b)	69. (a)	70. (d)
71. (b)	72. (a)	73. (c)	74. (b)	75. (c)	76. (d)	77. (a)	78. (c)	79. (b)	80. (d)
81. (a)	82. (b)	83. (d)	84. (c)	85. (c)	86. (b)	87. (b)	88. (a)	89. (a)	90. (d)
91. (c)	92. (a)	93. (a)	94. (d)	95. (b)	96. (c)	97. (c)	98. (b)	99. (d)	100. (a)
101. (a)	102. (d)	103. (b)	104. (a)	105. (c)	106. (d)	107. (c)	108. (d)	109. (b)	110. (d)
111. (c)	112. (d)	113. (b)	114. (a)	115. (c)	116. (b)	117. (d)	118. (b)	119. (c)	120. (a)
121. (b)	122. (a)	123. (a,d)	124. (c)	125. (b)	126. (a)	127. (c)	128. (c)	129. (b)	130. (b)
131. (c)	132. (a)	133. (b)	134. (d)	135. (a)	136. (d)	137. (a)	138. (b)	139. (a)	140. (a)
141. (b)	142. (a)	143. (a)	144. (b)	145. (a)	146. (c)	147. (c)	148. (b)	149. (a)	150. (c)
151. (a)	152. (d)	153. (d)	154. (c)	155. (d)	156. (a)	157. (c)	158. (c)	159. (d)	160. (c)
161. (a)	162. (b)	163. (a)	164. (c)	165. (b)	166. (b)	167. (d)	168. (a)	169. (c)	170. (d)
171. (d)	172. (a)	173. (b)	174. (d)	175. (b)	176. (d)	177. (a)	178. (b)	179. (d)	180. (d)
181. (c)	182. (d)	183. (a)	184. (b)	185. (a)	186. (d)	187. (a)	188. (c)	189. (a)	190. (d)
191. (b)	192. (b)	193. (b)	194. (c)	195. (a,d)	196. (b,c,d)	197. (a,b)	198. (b,d)	199. (a,b,c,d)	200. (b,d)
201. (a,b,c)	202. (a,b,c)	203. (b,c)	204. (a,b,c)	205. (a,b,d)	206. (a,c)	207. (c,d)	208. (a,b,c,d)	209. (b,d)	210. (c,d)
211. (a,c,d)	212. (b,d)	213. (a,c,d)	214. (b,c,d)	215. (a,b,d)	216. (a,c)	217. (a,b,d)	218. (a,b,c)		

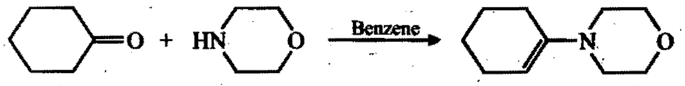
ASSERTION-REASON TYPE QUESTIONS

1. (a)	2. (d)	3. (c)	4. (a)	5. (d)	6. (a)	7. (a)	8. (c)	9. (d)	10. (b)

BRAIN STORMING PROBLEMS

1. What happens when?
   - (i) Cyclohexanone reacts with morpholine.
   - (ii) Acetaldehyde reacts with α-chloro ethylacetate in presence of Zn.
   - (iii) Acetaldehyde is heated with acetic anhydride.
   - (iv) 4,4-Dimethylpentan-2-one is treated with Br_2 in presence of NaOH.
   - (v) 2-Benzylcyclohexane-1,3-dione reacts with benzyl chloride in presence of potassium ethoxide and ethanol.

[Ans. (i)



Cyclohexanone   Morpholine   1-Morpholinecyclohexene

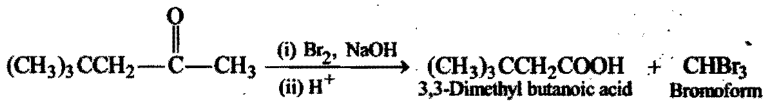
(ii) $CH_3CHO + Zn + ClCH_2COOC_2H_5 \xrightarrow{\Delta} CH_3-CH=CH-COOH$

(Reformatsky reaction)   Crotonic acid

(iii) $CH_3CHO + (CH_3CO)_2O \xrightarrow[H_2O]{\Delta} CH_3-CH=CH-COOH$

Crotonic acid

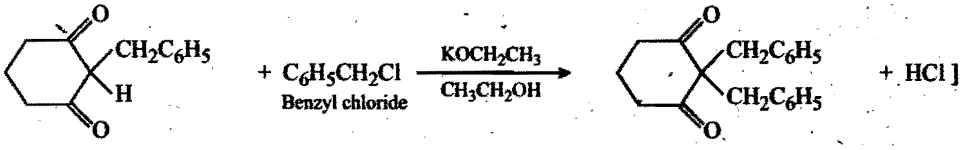
(iv)



$$(CH_3)_3CCH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow[(ii)\ H^+]{(i)\ Br_2,\ NaOH} (CH_3)_3CCH_2COOH + CHBr_3$$

3,3-Dimethyl butanoic acid   Bromoform

(v)



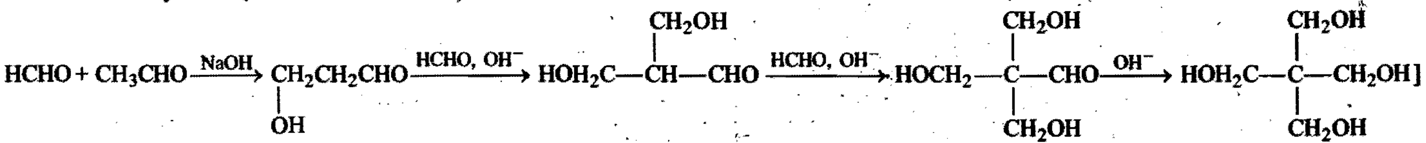
2-Benzyl cyclohexane-1,3-dione   2,2-Dibenzyl cyclohexane-1,3-dione

2. Give a reaction which involves both Claisen-Schmidt and Cannizzaro's reactions.

   OR

   How will you prepare penta erythritol?

[Ans. Formaldehyde and acetaldehyde combine to form trihydroxy aldehyde (Claisen-Schmidt reaction) which reacts with alkali to form penta erythritol (Cannizzaro's reaction)

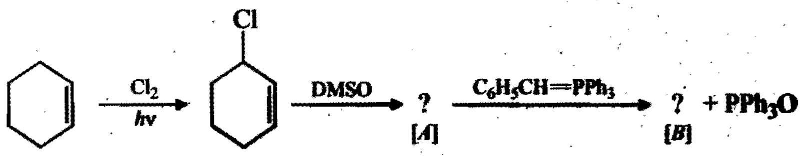


$$HCHO + CH_3CHO \xrightarrow{NaOH} \underset{\displaystyle OH}{\underset{|}{CH_2}}CH_2CHO \xrightarrow{HCHO,\ OH^-} HOH_2C-\overset{\displaystyle CH_2OH}{\overset{|}{CH}}-CHO \xrightarrow{HCHO,\ OH^-} HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{\overset{|}{\underset{|}{C}}}}-CHO \xrightarrow{OH^-} HOH_2C-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{\overset{|}{\underset{|}{C}}}}-CH_2OH]$$

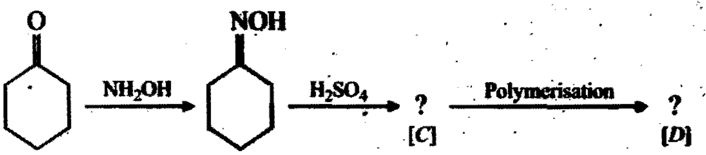
Penta erythritol

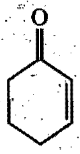
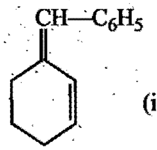
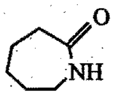
3. Complete the following reactions:

(i)



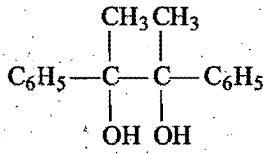
(ii)



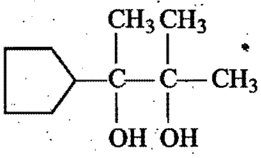
[Ans. (i) [A] ⟶ , [B] ⟶  (ii) [C] ⟶ , [D] ⟶ Nylon-6]

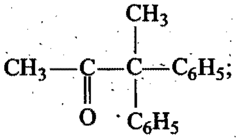
Caprolactum

4. Complete the following reactions:

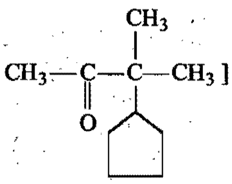
(i) 

$$C_6H_5-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-C_6H_5 \xrightarrow{H_2SO_4} (A)$$

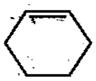
(ii)  $\xrightarrow{H_2SO_4} (B)$

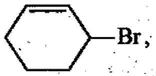
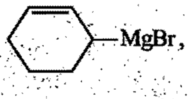
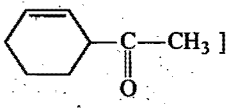
[Ans. (i) (A) 

$$CH_3-\underset{O}{\overset{\|}{C}}-\underset{C_6H_5}{\overset{CH_3}{C}}-C_6H_5;$$

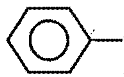
(ii) (B) ]

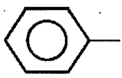
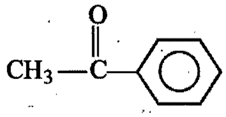
5. Identify (A), (B) and (C):

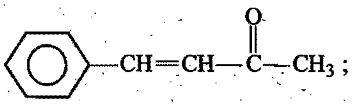
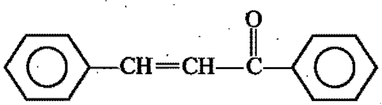
 $+ \text{NBS} \longrightarrow (A) \xrightarrow[\text{Ether}]{\text{Mg}} (B) \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3CN} (C)$

[Ans. (A) , (B) , (C) ]

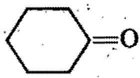
6. Complete the following reactions:

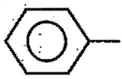
(a)  $-CHO + CH_3COCH_3 \xrightarrow{OH^-} (A)$

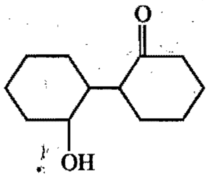
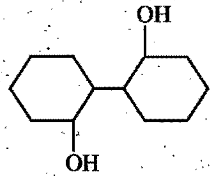
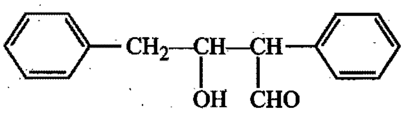
(b)  $-CHO +$  $\xrightarrow{OH^-} (B)$

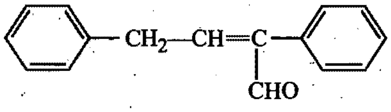
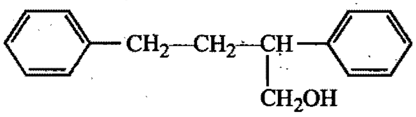
[Ans. (a) (A) ; (b) (B) ]

7. Identify (A), (B), (C), (D) and (E) in the following reactions:

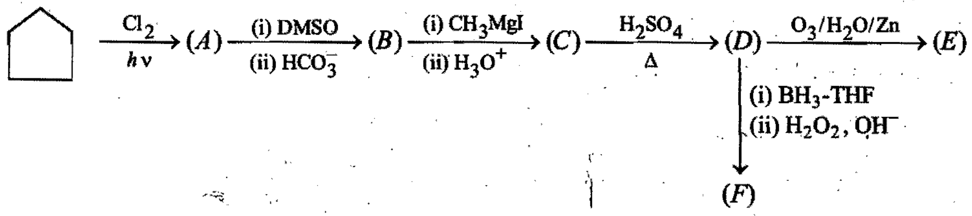
(a)  $\xrightarrow{\text{Dil. NaOH}} (A) \xrightarrow{\text{Sn(Hg) + Conc. HCl}} (B)$

(b)  $-CH_2CHO \xrightarrow{\text{NaOH}} (C) \xrightarrow{\Delta,\ NaHSO_4} (D) \xrightarrow{H_2/Ni} (E)$

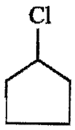
[Ans. (a) (A) ; (B) ; (b) (C) ;

(D) ; (E) ]

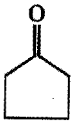
8. Identify (*A*) to (*F*) :



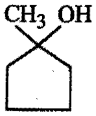
[**Ans.** (*A*)



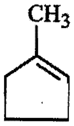
; (*B*)



; (*C*)

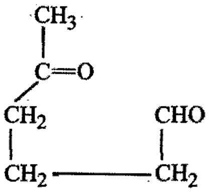


; (*D*)

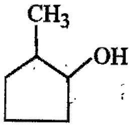


;

(*E*)

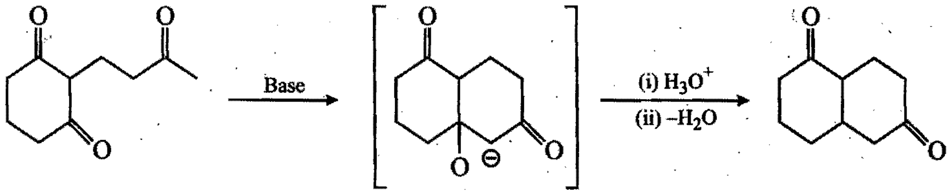


; (*F*)

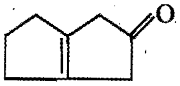


]

9. Provide a detailed reaction mechanism for the following:



10. What are the reduction products of the following:



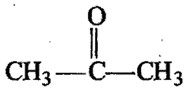
Using (i) 1 equivalent of H_2 with Pt, (ii) H_2 with Raney Ni, (iii) $NaBH_4/CH_3OH$?
[**Hint :** See the text for reduction.]

11. In the reaction,

$$H—C\equiv C—H \xrightarrow{NaNH_2} A \xrightarrow{CH_3I} B \xrightarrow[H_3O^+]{Hg^{2+}} C$$

the final product '*C*' is :

(a) CH_3CHO ☐ (b) CH_3CH_2CHO ☐

(c) 
$CH_3—\overset{\overset{\large O}{\|}}{C}—CH_3$ ☐ (d) CH_3CH_2COOH ☐

12. Match the **List I** with **List II** and select the correct answer from the given codes :

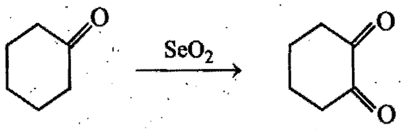
List I (Reaction)	**List II** (Reagent/catalyst)
A. Cannizzaro reaction	(i) $SnCl_2/HCl$
B. Stephen's reaction	(ii) NaOH
C. Clemmensen reduction	(iii) Zn/Hg-conc. HCl
D. Rosenmund's method	(iv) $\frac{Pd/BaSO_4}{\text{Boiling xylene}}$

Codes :

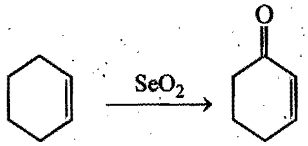
	A	B	C	D	
(a)	(i)	(ii)	(iii)	(iv)	☐
(b)	(ii)	(i)	(iii)	(iv)	☐
(c)	(iv)	(iii)	(ii)	(i)	☐
(d)	(i)	(iv)	(ii)	(iii)	☐

13. Which of the following reactions is not correct ?

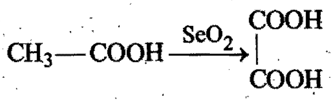
(a) $CH_3—CHO \xrightarrow{SeO_2} CHO—CHO$ (glyoxal) ☐

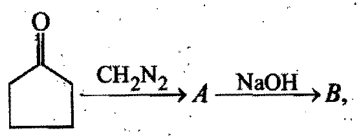
(b) 

Cyclohexan-1,2-dione ☐

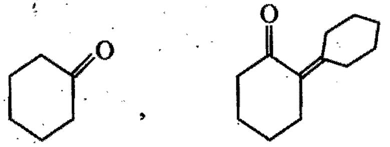
(c) 

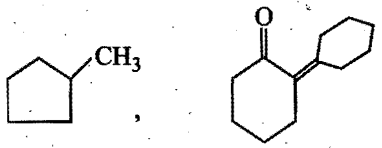
☐

(d) 
$CH_3—COOH \xrightarrow{SeO_2} \begin{matrix}COOH\\|\\COOH\end{matrix}$ ☐

14. 

'*A*' and '*B*' in above reaction are respectively:

(a)  ☐

(b) 

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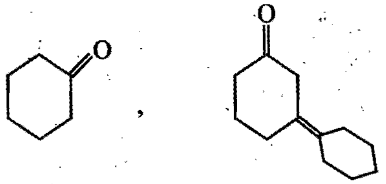
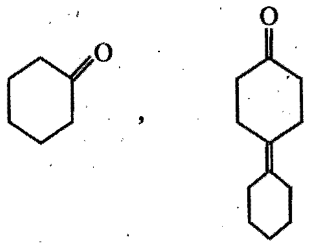
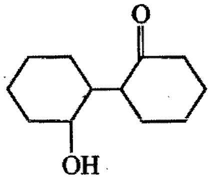
(c)  ☐

(d)  ☐

15. What is the product formed when cyclohexanone undergoes aldol condensation followed by heating ?

(a) 

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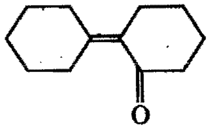
(b) 

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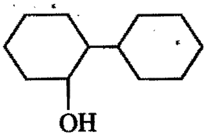
(c) 

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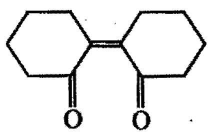
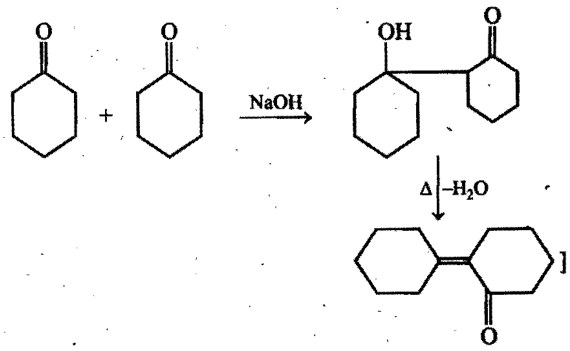
(d) 

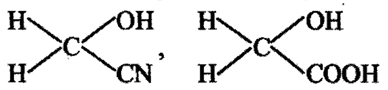
☐

[**Hint :**



]

16. A carbonyl compound '*A*' reacts with hydrogen cyanide to form a cyanohydrin '*B*' which on hydrolysis gives an optically active alpha hydroxy acid '*C*'. '*C*' gives positive iodoform test. *A*, *B* and *C* respectively are given by the set:

(a) HCHO, 

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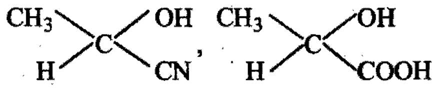
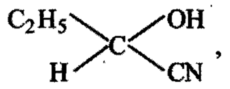
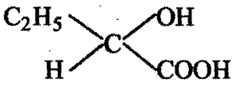
(b) CH_3CHO, 

☐

(c) CH_3CH_2CHO, 



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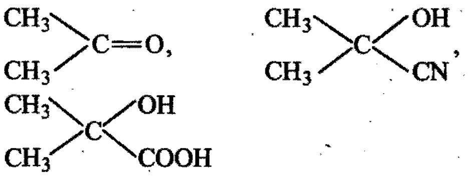
(d) 

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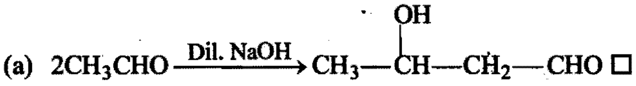
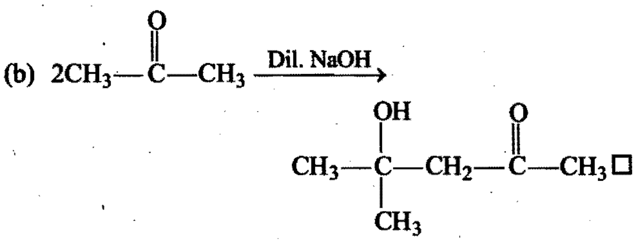
17. Acetone + $A \longrightarrow$ oxime of acetone
Acetone + $B \longrightarrow$ diacetone amine
Acetone + $C \longrightarrow$ mesitylene
Acetone + $D \longrightarrow$ isopropylidene chloride
A, B, C and D are :
(a) NH_2OH, NH_3, Conc. H_2SO_4, $SOCl_2$ ☐
(b) HNO_2, NH_3, Conc. H_2SO_4, PCl_5 ☐
(c) HNO_2, NH_3, Conc. H_2SO_4, Cl_2 ☐
(d) $NH_2OH, NH_3, H_2SO_4, Cl_2$ ☐

18. Which of the following is/are example(s) of aldol condensation?



(a) $2CH_3CHO \xrightarrow{\text{Dil. NaOH}} CH_3—\overset{OH}{\overset{|}{C}H}—CH_2—CHO$ ☐



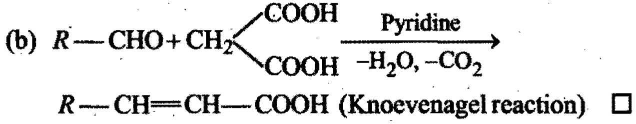
(b) $2CH_3—\overset{O}{\overset{\|}{C}}—CH_3 \xrightarrow{\text{Dil. NaOH}} CH_3—\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}—CH_2—\overset{O}{\overset{\|}{C}}—CH_3$ ☐

(c) $2HCHO \xrightarrow{\text{Dil. NaOH}} CH_3OH + HCOOH$ ☐

(d) $C_6H_5CHO + HCHO \xrightarrow{\text{Dil. NaOH}} C_6H_5CH_2OH$ ☐

19. Select the incorrectly matched options :

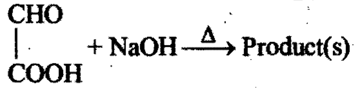
(a) $R—CO—CH_3 \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} R—CH_2—CH_3$ ☐
(Clemmensen reduction)



(b) $R—CHO + CH_2\begin{matrix}COOH\\COOH\end{matrix} \xrightarrow[-H_2O,\,-CO_2]{\text{Pyridine}}$
$R—CH═CH—COOH$ (Knoevenagel reaction) ☐

(c) $R—CHO + N_3H \xrightarrow[(330-340\text{ K})]{\text{Conc. } H_2SO_4}$
$R—CN + RNHCHO + N_2$ (Schmidt reaction) ☐

(d) $BrCH_2COOC_2H_5 + Zn \xrightarrow{\text{Dry ether}}$
$BrZn—CH_2COOC_2H_5$ (Perkin reaction) ☐

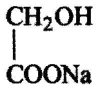
20. 

$\begin{matrix}CHO\\|\\COOH\end{matrix} + NaOH \xrightarrow{\Delta}$ Product(s)

Identify the product(s):

(a) 

$\begin{matrix}COONa\\|\\COONa\end{matrix}$ ☐

(b) 

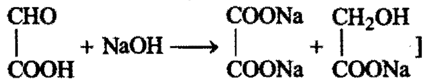
$\begin{matrix}CH_2OH\\|\\COONa\end{matrix}$ ☐

(c) both (a) and (b) ☐

(d) 

$\begin{matrix}CHO\\|\\COONa\end{matrix}$ ☐

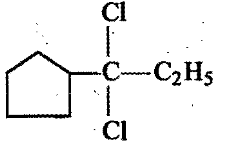
[Hint : This reaction involved Cannizzaro reaction hence, two products are obtained,

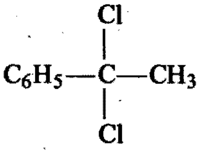


$\begin{matrix}CHO\\|\\COOH\end{matrix} + NaOH \longrightarrow \begin{matrix}COONa\\|\\COONa\end{matrix} + \begin{matrix}CH_2OH\\|\\COONa\end{matrix}$]

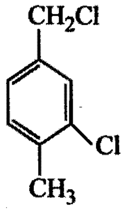
21. Methyl-*n*-propyl ketone on oxidation with $K_2Cr_2O_7$ and H_2SO_4 gives mainly :
(a) $CH_3CH_2COOH + CH_3COOH$ ☐
(b) $CH_3CH_2CH_2COOH + HCOOH$ ☐
(c) $CH_3COOH + HCOOH$ ☐
(d) $CH_3CH_2COOH + CO_2 + H_2O$ ☐

22. Structure of $C_8H_8Cl_2$, which on aqueous alkali hydrolysis gives a product which does not give positive iodoform test, but gives silver mirror test, is:

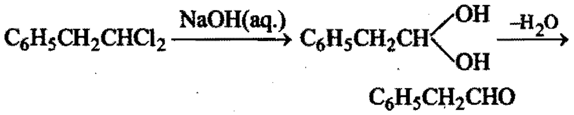
(a)  ☐

(b) 

$C_6H_5—\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}—CH_3$ ☐

(c)  ☐

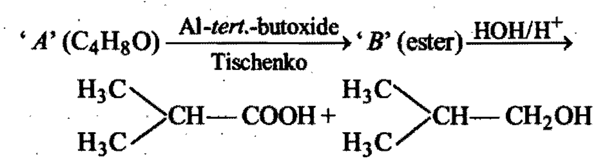
(d) $C_6H_5CH_2CHCl_2$ ☐



[Hint: $C_6H_5CH_2CHCl_2 \xrightarrow{\text{NaOH(aq.)}} C_6H_5CH_2CH\begin{matrix}OH\\OH\end{matrix} \xrightarrow{-H_2O} C_6H_5CH_2CHO$
Final product will give silver mirror test but not iodoform test.]

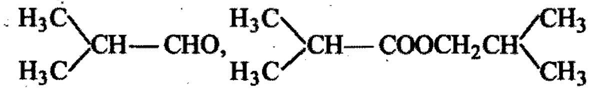
23. Which one of the following reagents is used to get sp^3-hybridised carbon atom from sp^2-hybridised carbon atom ?
(a) Zn/Hg and Conc. HCl ☐
(b) Red P/HI ☐
(c) $NH_2—NH_2$/KOH ☐
(d) All of the above ☐

24. Aldehyde

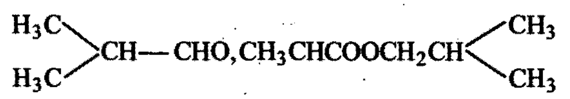


'A' $(C_4H_8O) \xrightarrow[\text{Tischenko}]{\text{Al-}tert\text{.-butoxide}}$ 'B' (ester) $\xrightarrow{HOH/H^+}$
$\begin{matrix}H_3C\\H_3C\end{matrix}\!>\!CH—COOH + \begin{matrix}H_3C\\H_3C\end{matrix}\!>\!CH—CH_2OH$

'A' and 'B' are :

(a) 

$\begin{matrix}H_3C\\H_3C\end{matrix}\!>\!CH—CHO, \begin{matrix}H_3C\\H_3C\end{matrix}\!>\!CH—COOCH_2CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$ ☐

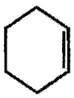
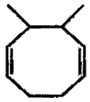
(b) 

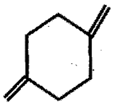
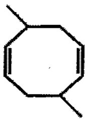
$\begin{matrix}H_3C\\H_3C\end{matrix}\!>\!CH—CHO, CH_3CHCOOCH_2CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$ ☐

(c) both (a) and (b) are correct ☐
(d) none is correct ☐

25. An alkene (A) on ozonolysis gives (B) as one of the product, (B) can perform Cannizzaro reaction. (A) is :
(a) but-2-ene ☐
(b) isobutene ☐
(c) $(CH_3)_2C═C(CH_3)_2$ ☐
(d) $C_6H_5CH_2CH═CH—CH_3$ ☐

26. One mole of a hydrocarbon (A) on ozonolysis gives two moles of dicarbonyl compound (A) is :

(a)  ☐ (b)  ☐

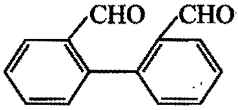
(c)  ☐ (d)  ☐

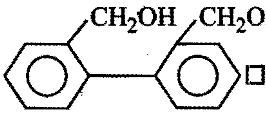
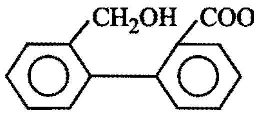
27. Which of the following alkanes cannot be prepared by the Clemmensen reduction of ketone?

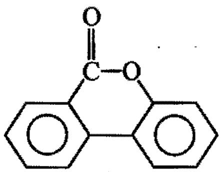
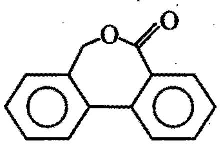
(a) Neopentane ☐ (b) Neohexane ☐
(c) Both of these ☐ (d) None of these ☐

28. Reaction of acetaldehyde with NH_2OH will be fastest at which of the following pH ?

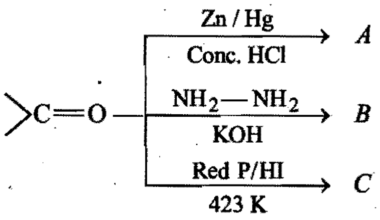
(a) 1 ☐ (b) 7 ☐
(c) 8 ☐ (d) 6 ☐

29. Tischenko reaction of  gives :

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

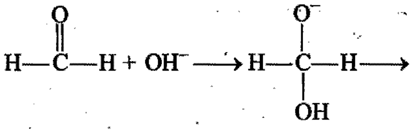
30. In the reactions :



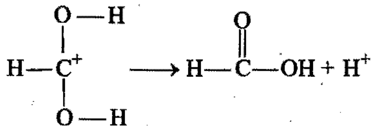
(a) A is an aldehyde; B is ketone and C is an alkene ☐
(b) A, B and C are alkenes ☐
(c) A, B and C are alkanes ☐
(d) A and B are alkenes while C is an alkane ☐

31. The Cannizzaro's reaction of formaldehyde involves an :

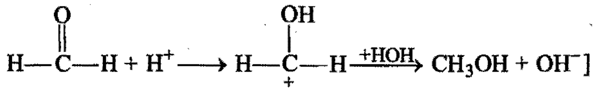
(a) intramolecular shift of proton ☐
(b) intramolecular shift of hydride ☐
(c) intermolecular shift of proton ☐
(d) intermolecular shift of hydride ☐

[Hint : 

$$\text{H—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—H} + \text{OH}^- \longrightarrow \text{H—}\overset{\text{O}^-}{\underset{\text{OH}}{\text{C}}}\text{—H} \longrightarrow$$



$$\text{H—}\overset{\text{O—H}}{\underset{\text{O—H}}{\text{C}^+}} \longrightarrow \text{H—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—OH} + \text{H}^+$$



$$\text{H—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—H} + \text{H}^+ \longrightarrow \text{H—}\overset{\text{OH}}{\underset{+}{\text{C}}}\text{—H} \xrightarrow{+\text{HOH}} \text{CH}_3\text{OH} + \text{OH}^-]$$

32. (I) $$R\text{—COCl} \xrightarrow[\text{Boiling xylene}]{\text{Pd/BaSO}_4} R\text{—CHO}$$

(II) $$R\text{—CN} \xrightarrow[\text{HOH}]{\text{SnCl}_2\text{/HCl}} R\text{—CHO}$$

Reaction (I) and (II) are ...... and ...... respectively.

(a) Oxo-process, Wacker's process ☐
(b) Rosenmund's reaction, Stephen's reaction ☐
(c) Gattermann's synthesis, Stephen's reaction ☐
(d) Reimer-Tiemann's reaction, Wacker's process ☐

33. Consider two aldehydes containing α-hydrogens,

(I) CH_3CH_2CHO
(II) $H_2C{=}CH{—}CHO$

The correct statement(s) is/are :

(a) both undergo aldol condensation ☐
(b) both do not undergo aldol condensation ☐
(c) only aldehyde (I) undergoes aldol condensation ☐
(d) only aldehyde (II) undergoes aldol condensation ☐

34. An organic compound (A) of molecular formula $C_5H_{10}O$ forms a phenyl hydrazone and gives negative Tollens' and iodoform test. Compound (A) on reduction gives n-pentane. Compound (A) is :

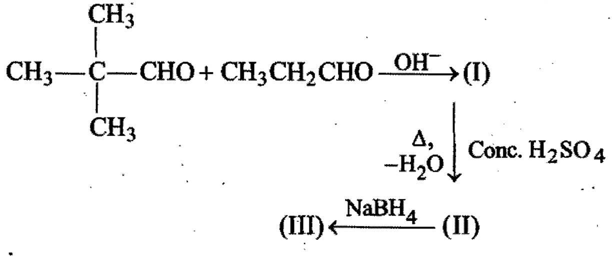
(a) pentanal ☐ (b) 2-methoxy hexanone ☐
(c) pentan-3-one ☐ (d) amyl alcohol ☐

35. The final product 'B' in the following sequence of chemical reaction is :

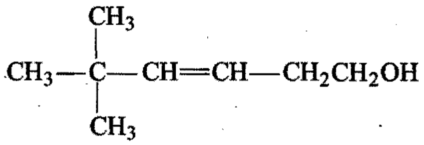
$$\text{CH}_3\text{OH} \xrightarrow[300°\text{C}]{\text{Cu}} A \xrightarrow{\text{NaOH}} B + \text{CH}_3\text{OH}$$

(a) an alkene ☐
(b) a carboxylic acid ☐
(c) an aldehyde ☐
(d) sodium salt of carboxylic acid ☐

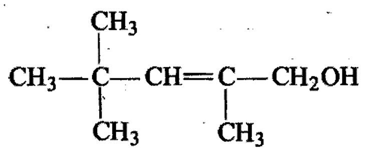
36. The final product (III) obtained in the reaction,

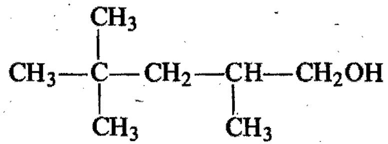


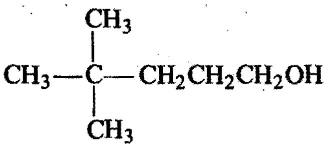
is :

(a)  ☐

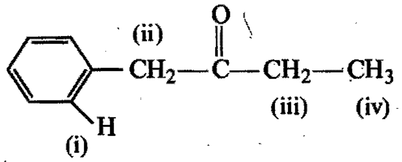
$$\text{CH}_3\text{—}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{—CH=CH—CH}_2\text{CH}_2\text{OH}$$

(b) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=\underset{\underset{CH_3}{|}}{C}-CH_2OH$ ☐

(c) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$ ☐

(d) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_2CH_2OH$ ☐

37. Which of the following four hydrogens is most acidic ?



(a) (i) ☐ (b) (ii) ☐
(c) (iii) ☐ (d) (iv) ☐

[**Hint :** Hydrogen (ii) will be most acidic because it is attached to two electron withdrawing groups, *i.e.*, phenyl group and carbonyl group.]

38. Match the List I with List II and select the correct answer from the codes given below the lists:

List I (Reaction)

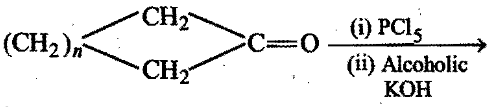
A. $CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCOOH$
B. $CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCH_2OH$
C. $R{-}COOH \longrightarrow R{-}CH_2OH$
D. $CH_3CH_2COCl \longrightarrow CH_3CH_2CHO$

List II (Reagent)

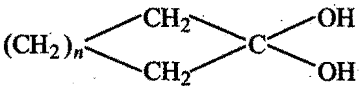
1. $LiAlH_4$
2. $NaBH_4, LiAlH_4$
3. Ammoniacal $AgNO_3$
4. H_2; $Pd/BaSO_4$

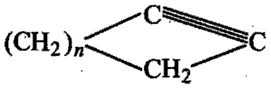
Codes :	A	B	C	D	
(a)	4	3	2	1	☐
(b)	1	2	3	4	☐
(c)	3	1	2	4	☐
(d)	2	3	1	4	☐

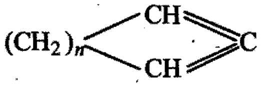
39. The final product of the following reaction,



is :

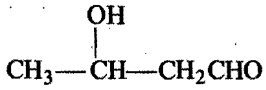
(a)  ☐

(b)  ☐

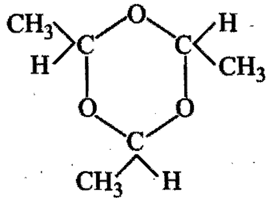
(c)  ☐

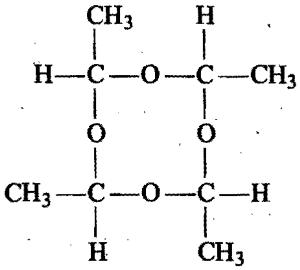
(d) all of the above ☐

40. In acidic medium, in presence of conc. H_2SO_4, acetaldehyde will give :

(a) 
$CH_3-\overset{\overset{OH}{|}}{CH}-CH_2CHO$ ☐

(b) $CH_3-CH{=}CH-CHO$ ☐

(c)  ☐

(d)  ☐

ANSWERS : BRAIN STORMING PROBLEMS

11. (c)	12. (b)	13. (d)	14. (a)	15. (b)	16. (b)	17. (a)	18. (a,b)	19. (b)	20. (c)
21. (a)	22. (d)	23. (d)	24. (a)	25. (b)	26. (d)	27. (a)	28. (d)	29. (d)	30. (c)
31. (b)	32. (b)	33. (c)	34. (c)	35. (d)	36. (b)	37. (b)	38. (c)	39. (b,c)	40. (c,d)

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

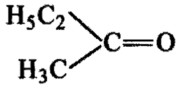
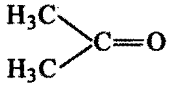
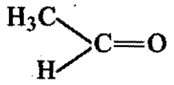
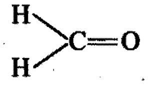
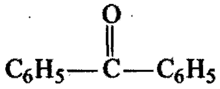
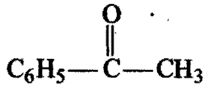
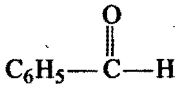
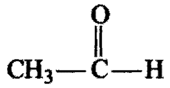
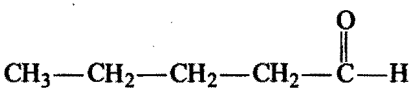
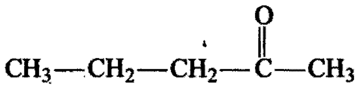
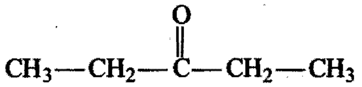
Aldehydes and ketones are specially susceptible to nucleophilic addition because carbonyl group $>C=O$ is polar (due to electronegativity difference between carbon and oxygen).

$$>\overset{\delta+}{C}=\overset{\delta-}{O}$$

Positive charge on carbon makes it reactive towards the nucleophile. This addition is catalysed by acid.

Reactivity of carbonyl compound towards nucleophilic addition increases with increase in the electron deficiency at carbonyl carbon. Thus, (–I.E.) groups increase while (+I.E.) groups decrease the reactivity of carbonyl compound.

Answer the following questions:

1. Which among the following is most reactive to give nucleophilic addition?
   (a) FCH_2CHO (b) $ClCH_2CHO$
   (c) $BrCH_2CHO$ (d) ICH_2CHO
2. Carbonyl compounds show nucleophilic addition with:
   (a) HCN (b) $NaHSO_3$
   (c) $(CH_3OH + HCl)$ (d) all of these
3. Which among the following carbonyl compounds is most polar?
   (a) 
   (b) 
   (c) 
   (d) 
4. Select the least reactive carbonyl compound for nucleophilic addition:
   (a)  $C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$
   (b)  $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$
   (c)  $C_6H_5-\overset{O}{\overset{\|}{C}}-H$
   (d)  $CH_3-\overset{O}{\overset{\|}{C}}-H$
5. Which among the following isomeric compounds is most reactive?
   (a)  $CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$
   (b)  $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$
   (c)  $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$
   (d) All are equally reactive

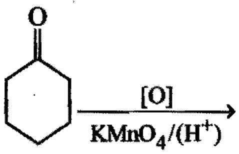
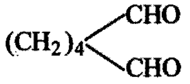
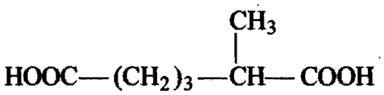
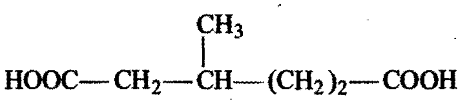
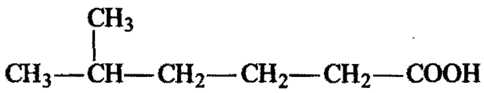
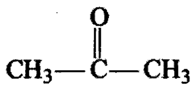
Passage 2

Carbonyl compounds give different oxidation products with different reagents. Several oxidising agents can be used to oxidise carbonyl compounds. Ammoniacal silver nitrate (Tollens' reagent) oxidises aliphatic as well as aromatic aldehydes.

$$R-CHO \xrightarrow{\text{Tollens' reagent}} R-COOH + Ag \text{ (Silver mirror)}$$

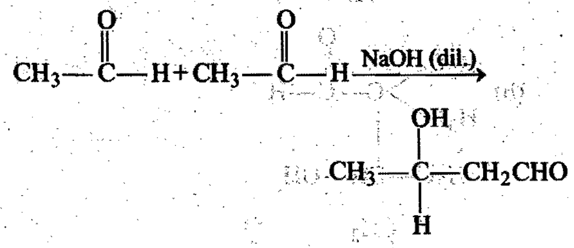
Strong oxidising agents like $KMnO_4/H^+$, HNO_3, $K_2Cr_2O_7/H^+$ oxidise aldehydes as well as ketones. Open chain ketones on oxidation give mixture of two carboxylic acids. Oxidation of unsymmetrical ketones takes place according to Popoff 's rule. According to this rule, α-carbon whose bond breaks in oxidation always belongs to the alkyl group which has more number of carbons.

Answer the following questions:

1. Tollens' reagent gives positive test with:
   (a) $RCHO$ (b) $R-C\equiv CH$
   (c) HCOOH (d) all of these
2. The reagent which oxidise only aliphatic ketone is:
   (a) Tollens' reagent (b) Fehling's solution
   (c) Baeyer reagent (d) $K_2Cr_2O_7/H^+$
3. The product of given reaction  ? is:
   (a) $HOOC-(CH_2)_4-COOH$
   (b) $CH_3-(CH_2)_4-COOH$
   (c) 
   (d) 
4. 2-Methyl cyclohexanone on oxidation will give :
   (a) $HOOC-(CH_2)_5-COOH$
   (b)  $HOOC-(CH_2)_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-COOH$
   (c)  $HOOC-CH_2-\overset{CH_3}{\overset{|}{CH}}-(CH_2)_2-COOH$
   (d)  $CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_2-COOH$
5. Which of the following is most reactive towards oxidation ?
   (a) HCHO (b) CH_3CHO
   (c)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (d) CH_3-CH_2-CHO

Passage 3

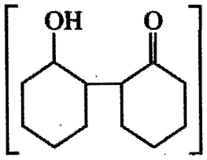
Aldehydes with atleast one α-hydrogen undergo aldol condensation. Two molecules of same or different aldehydes take part in such condensation. One of the two aldehyde molecules must have an α-hydrogen. Ketones under similar condition give ketol condensation. These reactions take place in presence of NaOH, KOH, $Ba(OH)_2$. The ketol condensation is best done with $Ba(OH)_2$. Intramolecular aldol condensation is given by dialdehydes, diketones or keto aldehydes. The diketones should be 2,5; 2,6; 2,7 and 2,8-diketones. Intramolecular aldol condensation is the best method for preparation of five and six membered ring. For example:



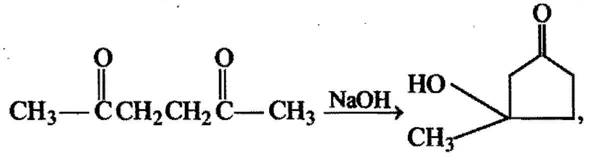
$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaOH\,(dil.)} CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2CHO$$

Predict whether the following statements are true or false.

1. CCl_3-CHO gives aldol condensation.
   (a) True (b) False
2. Cyclohexanone when treated with $Ba(OH)_2$ gives,



as a result of aldol condensation.
   (a) True (b) False
3. When mixture of ethanal and propanal is treated with aqueous NaOH, the product contains 4 aldols.
   (a) True (b) False
4. In the reaction,



the product formed is due to intramolecular ketol condensation.
   (a) True (b) False
5. Mixture of HCHO and CH_3CHO will not give aldol condensation.
   (a) True (b) False

Passage 4

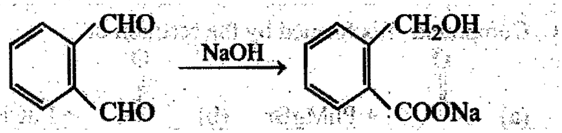
Aldehydes undergo disproportionation reaction in presence of aqueous NaOH. Simultaneous oxidation and reduction of a compound is scientifically called as disproportionation.

Aldehydes having no α-hydrogen show this reaction called Cannizzaro's reaction. Few exceptions are also there to this generalisation.

The reaction may be represented as:

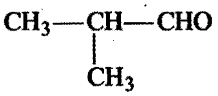
$$C_6H_5CHO + C_6H_5CHO \xrightarrow[\Delta]{NaOH} C_6H_5COONa + C_6H_5CH_2OH$$

Intramolecular Cannizzaro's reaction is also possible.



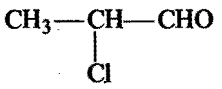
Answer the following questions:

1. The aldehyde which shows Cannizzaro's reaction is:
   (a) HCHO (b) C_6H_5CHO
   (c) CCl_3-CHO (d) all of these
2. The aldehyde having α-hydrogen which gives Cannizzaro's reaction is:
   (a) CH_3-CH_2-CHO (b)



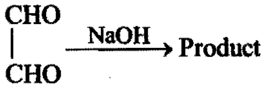
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CHO$$

   (c)



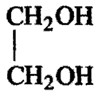
$$CH_3-\underset{Cl}{\underset{|}{CH}}-CHO$$

   (d) $C_2H_5-CH_2-CHO$
3. The product formed in the following reaction will be:



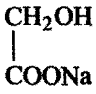
$$\begin{array}{c}CHO\\|\\CHO\end{array} \xrightarrow{NaOH} \text{Product}$$

   (a)



$$\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}$$

   (b)



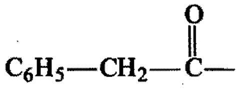
$$\begin{array}{c}CH_2OH\\|\\COONa\end{array}$$

   (c)

$$\begin{array}{c}COONa\\|\\COONa\end{array}$$

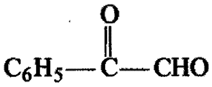
   (d) all of these
4. Mixture of C_6H_5CHO and HCHO is treated with NaOH then Cannizzaro's reaction involves:
   (a) oxidation of HCHO
   (b) reduction of HCHO
   (c) oxidation of C_6H_5CHO
   (d) reduction of C_6H_5CHO
5. Which of the following compounds gives internal crossed Cannizzaro's reaction?

   (a)



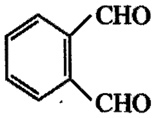
$$C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-H$$

   (b)

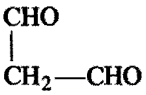


$$C_6H_5-\overset{O}{\overset{\|}{C}}-CHO$$

   (c)



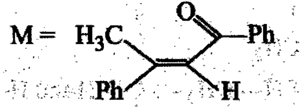
   (d)



$$\begin{array}{l}CHO\\|\\CH_2-CHO\end{array}$$

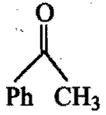
Passage 5

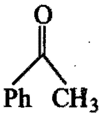
A tertiary alcohol *H* on acid catalysed dehydration gives a product *I*. Ozonolysis of *I* leads to compounds *J* and *K*. Compound *J* upon reaction with KOH gives benzyl alcohol and a compound *L*, whereas *K* on reaction with KOH gives only *M*.

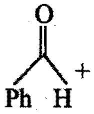


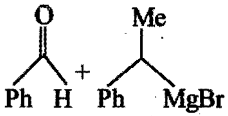
Answer the following questions:

1. Compound *H* is formed by the reaction of:

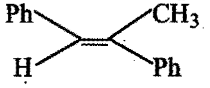
(a)  + PhMgBr

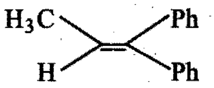
(b)  + $PhCH_2MgBr$

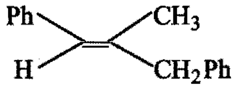
(c)  + $PhCH_2MgBr$

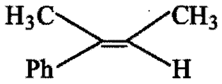
(d) 

2. The structure of compound *I* is:

(a) 

(b) 

(c) 

(d) 

3. The structures of compounds *J*, *K* and *L*, respectively, are:

(a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2CO\bar{O}K^+$

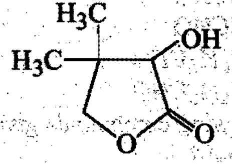
(b) PhCHO, $PhCH_2CHO$ and $PhCO\bar{O}K^+$

(c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3CO\bar{O}K^+$

(d) PhCHO, $PhCOCH_3$ and $PhCO\bar{O}K^+$

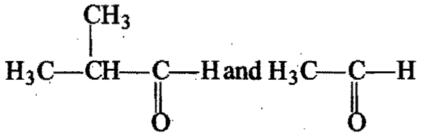
Passage 6

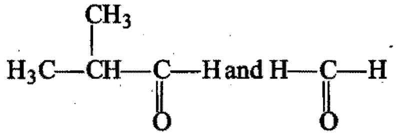
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating S gives the product shown below :

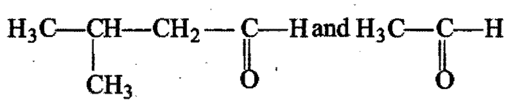


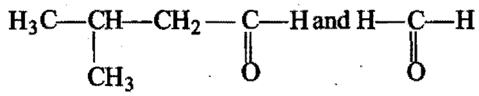
Answer the following questions: **[IIT 2010]**

1. The comopund P and Q respectively are :

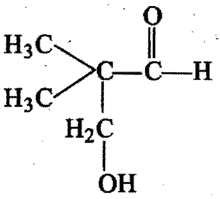
(a) 
$H_3C-\overset{CH_3}{\overset{|}{C}H}-\underset{O}{\underset{\|}{C}}-H$ and $H_3C-\underset{O}{\underset{\|}{C}}-H$

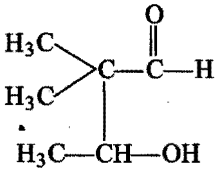
(b) 
$H_3C-\overset{CH_3}{\overset{|}{C}H}-\underset{O}{\underset{\|}{C}}-H$ and $H-\underset{O}{\underset{\|}{C}}-H$

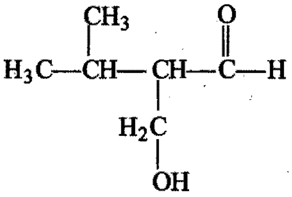
(c) 
$H_3C-\underset{CH_3}{\underset{|}{C}H}-CH_2-\underset{O}{\underset{\|}{C}}-H$ and $H_3C-\underset{O}{\underset{\|}{C}}-H$

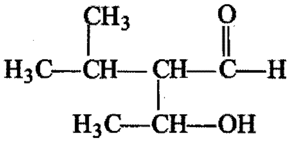
(d) 
$H_3C-\underset{CH_3}{\underset{|}{C}H}-CH_2-\underset{O}{\underset{\|}{C}}-H$ and $H-\underset{O}{\underset{\|}{C}}-H$

2. The compound R is :

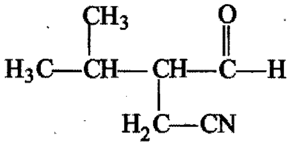
(a) 

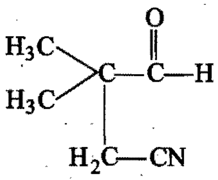
(b) 

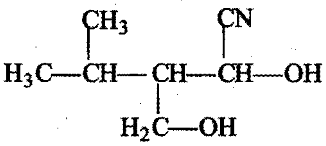
(c) 
$H_3C-\overset{CH_3}{\overset{|}{C}H}-\underset{\underset{OH}{|}}{\underset{H_2C}{\underset{|}{C}H}}-\overset{O}{\overset{\|}{C}}-H$

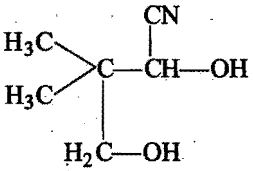
(d) 
$H_3C-\overset{CH_3}{\overset{|}{C}H}-\underset{H_3C-CH-OH}{\underset{|}{C}H}-\overset{O}{\overset{\|}{C}}-H$

3. The compound S is :

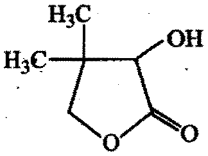
(a) 
$H_3C-\overset{CH_3}{\overset{|}{C}H}-\underset{H_2C-CN}{\underset{|}{C}H}-\overset{O}{\overset{\|}{C}}-H$

(b) 

(c) 
$H_3C-\overset{CH_3}{\overset{|}{C}H}-\underset{H_2C-OH}{\underset{|}{C}H}-\overset{CN}{\overset{|}{C}H}-OH$

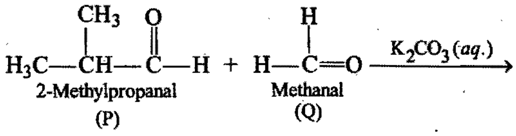
(d) 

[Hint : $P+Q \xrightarrow{K_2CO_3(aq.)} R \xrightarrow{HCN} S \xrightarrow{H^+,\,\Delta}$



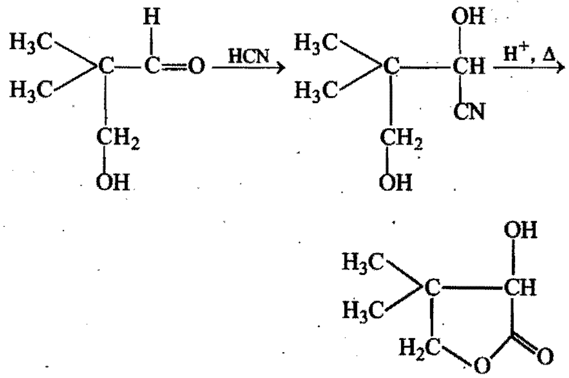
R reacts with HCN so, it must contain $>C=O$ group.

Since the compound S gives the given product formed on treatment with H^+ followed by heating thus S must have a —COOH group with one carbon more than that in R. Therefore, P and Q are $(CH_3)_2CHCHO$ and HCHO respectively.



$$H_3C-\overset{CH_3}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}-H + H-\overset{H}{\overset{|}{C}}=O \xrightarrow{K_2CO_3(aq.)}$$

2-Methylpropanal (P) Methanal (Q)



ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

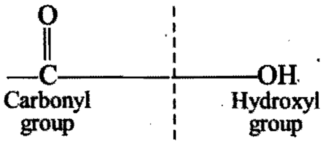
Passage 1	**1.** (a)	**2.** (d)	**3.** (d)	**4.** (a)	**5.** (a)
Passage 2	**1.** (d)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (a)
Passage 3	**1.** (b)	**2.** (a)	**3.** (a)	**4.** (a)	**5.** (b)
Passage 4	**1.** (d)	**2.** (b)	**3.** (b)	**4.** (a,d)	**5.** (b)
Passage 5	**1.** (b)	**2.** (a)	**3.** (d)		
Passage 6	**1.** (b)	**2.** (a)	**3.** (d)		

12

CARBOXYLIC ACIDS

12.1 INTRODUCTION

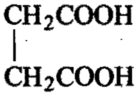
Organic compounds containing carboxylic group ($-\overset{\overset{\displaystyle O}{\|}}{C}-OH$) or groups are called carboxylic acids. The name carboxyl is derived from carbonyl ($>C=O$) and hydroxyl ($-OH$) because in this group both carbonyl and hydroxyl groups are directly linked to each other.



However, the properties of the carboxylic group are not simply the combined properties of these groups but it has its own distinctive properties. The acidic character in carboxylic acids is due to the presence of a replaceable hydrogen atom in the carboxylic group.

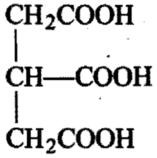
Carboxylic acids are further classified as monocarboxylic acids, dicarboxylic acids, tricarboxylic acids, etc., depending on the number of —COOH groups present in the molecule. Since, —COOH group has one replaceable hydrogen atom, its basicity is one and the acid having one carboxylic group is, thus, a monobasic acid. Similarly acids containing two or three carboxylic groups in their molecules are designated as dibasic, tribasic acids, respectively.

CH_3COOH ;
Monocarboxylic acid
(Monobasic)



$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

Dicarboxylic acid
(Dibasic)



$$\begin{array}{l} CH_2COOH \\ | \\ CH—COOH \\ | \\ CH_2COOH \end{array}$$

Tricarboxylic acid
(Tribasic)

Monocarboxylic acids of aliphatic series are commonly called as *fatty acids* as many of them, particularly higher members (C_{12}—C_{18}), such as palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$) are constituents of oils and fats. Monocarboxylic acids may be saturated or unsaturated depending on the nature of the carbon chain attached to the carboxylic group.

$$\underset{\text{Saturated acid}}{CH_3CH_2COOH} \qquad \underset{\text{Unsaturated acid}}{H_2C=CHCOOH}$$

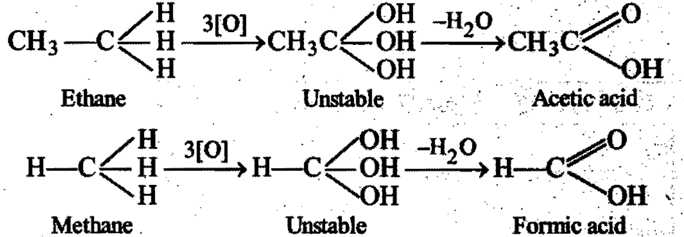
Saturated monocarboxylic acids form a homologous series which has a general formula, $C_nH_{2n+1}COOH$ or $C_nH_{2n}O_2$. Formic acid (HCOOH) is the first member of the series. Saturated monocarboxylic acids may be considered as derived from paraffins by the replacement of one hydrogen atom with one carboxylic group.

$$\underset{\text{Methane}}{CH_4} \xrightarrow[+COOH]{-H} \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\underset{\text{Ethane}}{C_2H_6} \xrightarrow[+COOH]{-H} \underset{\text{Propionic acid}}{C_2H_5COOH}$$

$$\underset{\text{Propane}}{C_3H_8} \xrightarrow[+COOH]{-H} \underset{\text{Butyric acid}}{C_3H_7COOH}$$

Thus, first member of the series, formic acid (HCOOH) has no corresponding paraffin. To consider formic acid also as the derivative of paraffins, monocarboxylic acids may be alternatively considered as obtained by the oxidation of —CH_3 group, *i.e.*, the third oxidation product of paraffins.

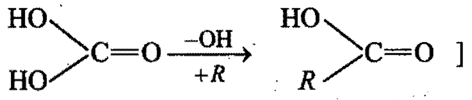


or $\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow{[O]} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$

$$\underset{\text{Methane}}{H—CH_3} \xrightarrow{[O]} \underset{\text{Methyl alcohol}}{HCH_2OH} \xrightarrow{[O]} \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{[O]} \underset{\text{Formic acid}}{HCOOH}$$

So, saturated monocarboxylic acids are the first oxidation products of aldehydes or second oxidation products of primary alcohols.

[Monocarboxylic acids may also be regarded as the derivatives of carbonic acid in which one —OH group has been replaced by an alkyl group.



Carbonic acid Monocarboxylic acid

Monocarboxylic acids are represented by the general formula, *R*COOH, where *R* may be either a hydrogen atom or an alkyl group. *R*COOH are also called **monoprotic acids** because they give one proton in the solution.

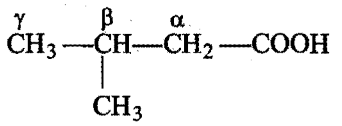
12.2 NOMENCLATURE

The monocarboxylic acids are named according to the following systems:

1. Common or trivial names : The names of lower members are derived from the Latin or Greek words that indicate the source of the particular acid. The common names have ending –ic acid.

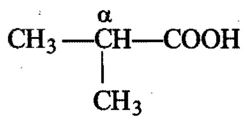
Formula	Source	Common name
HCOOH	Red ant (Latin; Ant = Formica)	Formic acid
CH_3COOH	Vinegar (Latin; Vinegar = Acetum)	Acetic acid
C_2H_5COOH	Proton-pion (Greek; Proton = First, Pion = Fat)	Propionic acid
C_3H_7COOH	Butter (Latin; Butter = Butyrum)	Butyric acid
C_4H_9COOH	Root of Valerian plant	Valeric acid

The higher members are named on the basis of number of carbon atoms. In case of substituted acids, the position of the substituent is indicated by Greek letters α, β, γ, δ, etc.



$$\overset{\gamma}{CH_3}—\overset{\beta}{\underset{|\atop CH_3}{CH}}—\overset{\alpha}{CH_2}—COOH$$

β-Methyl butyric acid
(Isovaleric acid)

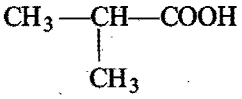


$$CH_3—\overset{\alpha}{\underset{|\atop CH_3}{CH}}—COOH$$

α-Methyl propionic acid
(Isobutyric acid)

2. Derived system : Monocarboxylic acids may be named as alkyl derivatives of acetic acid.

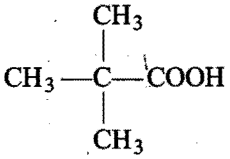
CH_3CH_2COOH
Methyl acetic acid



$$CH_3—\underset{|\atop CH_3}{CH}—COOH$$

Dimethyl acetic acid

$(CH_3)_2CHCH_2COOH$
Isopropyl acetic acid



$$CH_3—\underset{|\atop CH_3}{\overset{CH_3\atop |}{C}}—COOH$$

Trimethyl acetic acid

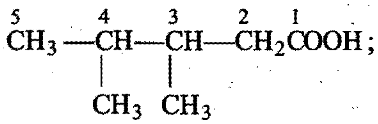
3. IUPAC system : Acids are named as alkanoic acids (Alkane – e + oic acid). The name is derived by replacing 'e' of the corresponding alkane by –oic acid.

HCOOH	Methanoic acid (Methane – e + oic acid)
CH_3COOH	Ethanoic acid (Ethane – e + oic acid)
C_2H_5COOH	Propanoic acid (Propane – e + oic acid)

In case of substituted acids, the longest chain including the carboxyl group is selected and numbering is done from the side of carboxyl group, *i.e.*, carbon atom of the carboxyl group is numbered as 1.

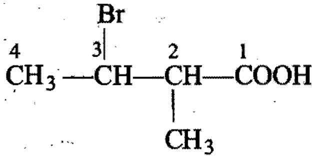
$$\overset{5}{C}—\overset{4}{C}—\overset{3}{C}—\overset{2}{C}—\overset{1}{COOH}$$

For example,



$$\overset{5}{CH_3}—\overset{4}{\underset{|\atop CH_3}{CH}}—\overset{3}{\underset{|\atop CH_3}{CH}}—\overset{2}{CH_2}\overset{1}{COOH}$$

3,4-Dimethyl pentanoic acid



$$\overset{4}{CH_3}—\overset{3}{\overset{Br\atop |}{CH}}—\overset{2}{\underset{|\atop CH_3}{CH}}—\overset{1}{COOH}$$

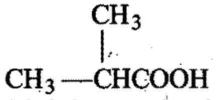
3-Bromo-2-methyl butanoic acid

12.3 ISOMERISM

Monocarboxylic acids show chain and functional isomerism.

1. Chain isomerism : This is due to the difference in the structure of carbon chain.

$CH_3CH_2CH_2COOH$;
Butanoic acid

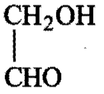


$$CH_3—\overset{CH_3\atop |}{CH}COOH$$

2-Methyl propanoic acid

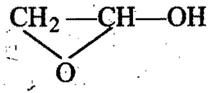
2. Functional isomerism : Monocarboxylic acids show functional isomerism with the esters of the acids, hydroxy carbonyl compounds and hydroxy oxiranes.

$(C_2H_4O_2)$: CH_3COOH; Acetic acid $HCOOCH_3$; Methyl formate



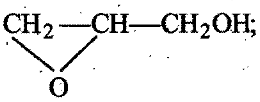
$$\underset{CHO}{\overset{CH_2OH}{|}}$$

Glycolaldehyde



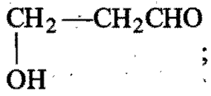
Hydroxy ethylene oxide

$(C_3H_6O_2)$: CH_3CH_2COOH; Propionic acid



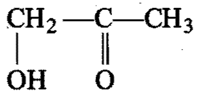
2,3-Epoxypropan-1-ol

$HCOOC_2H_5$; Ethyl formate CH_3COOCH_3; Methyl acetate



$$\underset{|\atop OH}{CH_2}—CH_2CHO$$

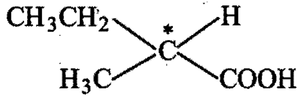
3-Hydroxy propanal



$$\underset{|\atop OH}{CH_2}—\underset{\|\atop O}{C}—CH_3$$

1-Hydroxy propan-2-one

3. Optical isomerism : Monocarboxylic acids having atleast one chiral atom exhibit optical isomerism.



2 - Methyl butanoic acid
(Active valeric acid)

12.4 GENERAL METHODS OF PREPARATION

1. Oxidation of alcohols, aldehydes and ketones : Primary alcohols and aldehydes on oxidation form monocarboxylic acids with the same number of carbon atoms. The primary alcohol is first oxidised to an aldehyde and then to an acid. The oxidation is best done with a mixture of potassium dichromate and dilute sulphuric acid, alkaline or acidified potassium permanganate etc. The oxidation with CrO_3—H_2SO_4 (Jone's reagent) or air in presence of catalyst can also be used.

$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow{[O]} \underset{\text{Aldehyde}}{RCHO} \xrightarrow{[O]} \underset{\text{Acid}}{RCOOH}$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[H_2SO_4\text{(dil.)}]{K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{(ii) }H^+]{\text{(i) }KMnO_4,\, OH^-,\, \Delta} \underset{\text{Acetic acid}}{CH_3COOH}$$

The oxidation with $K_2Cr_2O_7$ or CrO_3 in acidic media often gives small amount of esters. Therefore, oxidation with $KMnO_4$ in neutral or alkaline medium is preferred.

$$\underset{1^\circ\text{ Alcohol}}{RCH_2OH} \xrightarrow[\Delta]{KMnO_4/KOH} \underset{\text{Pot. carboxylate}}{RCO\bar{O}K^+} \xrightarrow{H_3O^+} \underset{\text{Carboxylic acid}}{RCOOH}$$

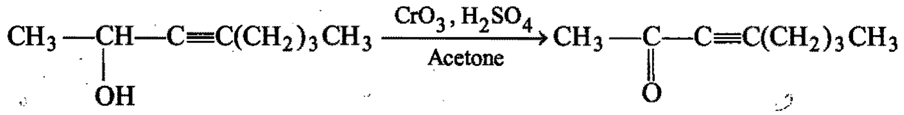
$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{(ii) Dil. }H_2SO_4]{\text{(i) }KMnO_4/KOH,\, \Delta} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

[Aldehydes can be oxidised to corresponding carboxylic acids even with mild oxidising agents such as ammoniacal silver nitrate solution, Ag_2O {or $Ag(NH_3)_2^+OH^-$}].

Unsaturated alcohols (containing C═C or C≡C) can be oxidised to corresponding acids (without affecting the unsaturation) by using oxidising agents such as CrO_3, H_2SO_4 in acetone solution.

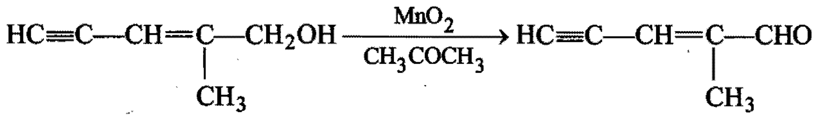
$$HC{\equiv}C{-}CH{=}CH{-}CH_2OH \xrightarrow[\text{Acetone}]{CrO_3,\, H_2SO_4} HC{\equiv}C{-}CH{=}CH{-}COOH$$

On the other hand, secondary alcohols are selectively oxidised to ketone.



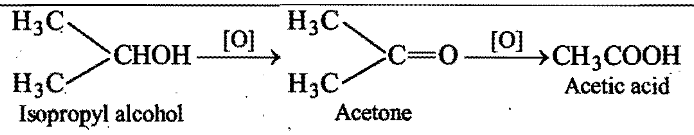
$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}C{\equiv}C(CH_2)_3CH_3 \xrightarrow[\text{Acetone}]{CrO_3,\, H_2SO_4} CH_3{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}C{\equiv}C(CH_2)_3CH_3$$

Primary alcohols are selectively oxidised to aldehydes with MnO_2 in acetone.



$$HC{\equiv}C{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2OH \xrightarrow[CH_3COCH_3]{MnO_2} HC{\equiv}C{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CHO$$

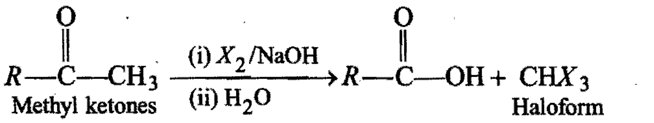
Note : Ketones and secondary alcohols can also form acids with fewer carbon atoms. Oxidation of ketone occurs with difficulty by using strong oxidising agent like $Cr_2O_7^{2-}$.



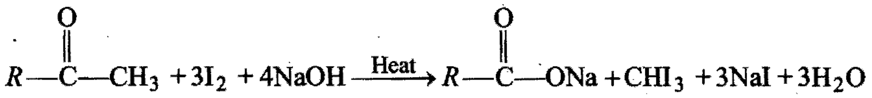
$$\underset{\text{Ethyl methyl ketone}}{CH_3COCH_2CH_3} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{2CH_3COOH}$$

$$\underset{\text{Pentan-2-one}}{CH_3COCH_2CH_2CH_3} \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

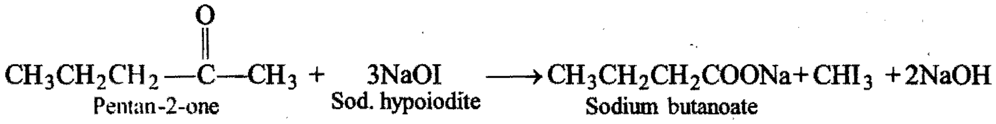
Methyl ketones can also be converted to carboxylic acids through the **haloform reaction.**



$$\underset{\text{Methyl ketones}}{R-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{NaOH}} R-\overset{\overset{O}{\|}}{C}-OH + \underset{\text{Haloform}}{CHX_3}$$



$$R-\overset{\overset{O}{\|}}{C}-CH_3 + 3I_2 + 4NaOH \xrightarrow{\text{Heat}} R-\overset{\overset{O}{\|}}{C}-\bar{O}Na + CHI_3 + 3NaI + 3H_2O$$

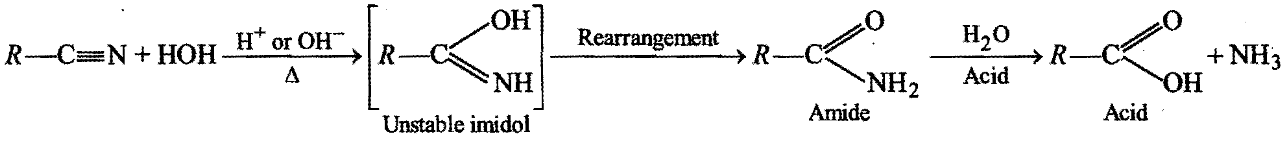


$$\underset{\text{Pentan-2-one}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{\text{Sod. hypoiodite}}{3NaOI} \longrightarrow \underset{\text{Sodium butanoate}}{CH_3CH_2CH_2COONa} + CHI_3 + 2NaOH$$

The sodium salts of carboxylic acids (containing one carbon atom less) on acidification give the corresponding acids.

$$CH_3CH_2CH_2CO\bar{O}Na^+ + HCl \xrightarrow{\text{Hydrolysis}} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH} + NaCl$$

2. Hydrolysis of alkyl cyanides or nitriles : When an alkyl cyanide or nitrile is hydrolysed with hydrochloric acid or sulphuric acid mixed with an equal volume of water, the —CN group is hydrolysed to a carboxyl group. This is a very useful method for the synthesis of acids.



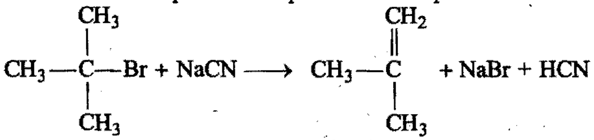
$$\underset{\substack{\text{Ethane nitrile}\\ \text{(Methyl cyanide)}}}{CH_3C\equiv N} + 2H_2O \xrightarrow[\Delta]{\text{HCl (dil.)}} \underset{\substack{\text{Ethanoic acid}\\ \text{(Acetic acid)}}}{CH_3COOH} + NH_4Cl$$

So, in acidic medium, the products are RCOOH and NH_4^+ ($NH_3 + H^+ \longrightarrow \overset{+}{N}H_4$) and in alkaline medium, $RCOO^-$ ($RCOONa \longrightarrow RCOO^- + Na^+$) and NH_3 are the products.

Note : (i) Hydrolysis can be done with an alkali also, $\underset{\text{Methyl cyanide}}{CH_3C\equiv N} + NaOH + H_2O \xrightarrow{\Delta} \underset{\text{Sodium acetate}}{CH_3COONa} + NH_3$

(ii) Alkyl halides are actually used, $\underset{\text{Methyl bromide}}{CH_3Br} \xrightarrow[\text{or KCN}]{\text{NaCN}} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[H^+,\ \Delta]{H_2O} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$

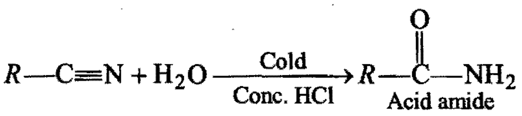
The acid formed by this method contains one carbon atom more than the original alkyl halide. With 2° alkyl halide the yield of nitrile is very poor, however, in case of 3° alkyl halide, elimination takes place at the place of nucleophilic substitution.



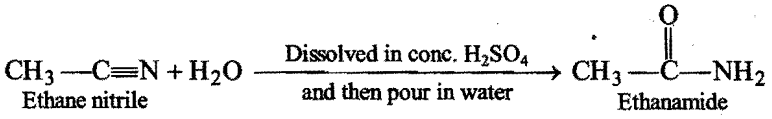
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + NaCN \longrightarrow \underset{\text{2-Methyl propene}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{\|}}{C}}} + NaBr + HCN$$

(iii) HCN on hydrolysis forms formic acid, $HCN + 2H_2O + HCl \longrightarrow HCOOH + NH_4Cl$

Mild conditions are used to stop the reaction at the amide stage.

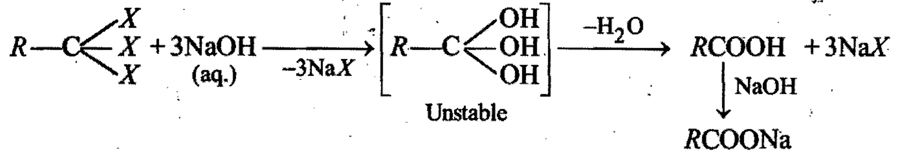


$$R-C\equiv N + H_2O \xrightarrow[\text{Conc. HCl}]{\text{Cold}} \underset{\text{Acid amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2}$$



$$\underset{\text{Ethane nitrile}}{CH_3-C\equiv N} + H_2O \xrightarrow[\text{and then pour in water}]{\text{Dissolved in conc. } H_2SO_4} \underset{\text{Ethanamide}}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2}$$

3. Hydrolysis of terminal trihalogen derivatives of alkanes : Trihalogen derivatives of alkanes in which all the three halogen atoms are attached to the terminal carbon atom, on hydrolysis with aqueous alkali solution, form monocarboxylic acids.



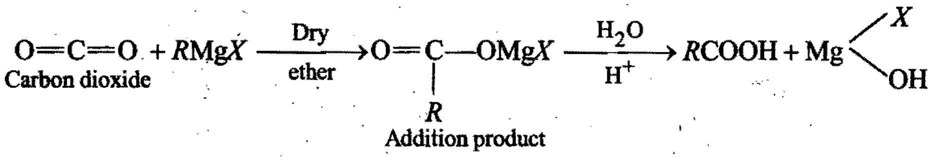
$$R{-}CX_3 + \underset{(aq.)}{3NaOH} \xrightarrow[-3NaX]{} \underset{\text{Unstable}}{[R{-}C(OH)_3]} \xrightarrow{-H_2O} RCOOH + 3NaX \xrightarrow{NaOH} RCOONa$$

$$\underset{\text{Chloroform}}{CHCl_3} + \underset{(aq.)}{3NaOH} \longrightarrow \underset{\text{Formic acid}}{HCOOH} + 3NaCl$$

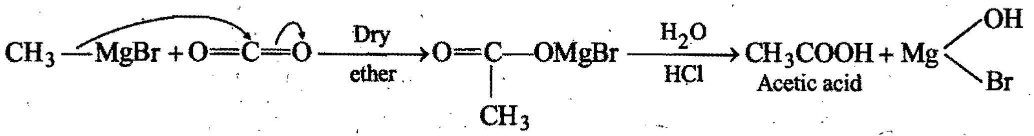
$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{NaOH} \underset{\text{Sodium formate}}{HCOONa}$$

$$\underset{\text{1,1,1-Trichloroethane}}{CH_3CCl_3} + 3KOH(aq.) \xrightarrow[-3KCl]{} \underset{\text{Unstable}}{CH_3C(OH)_3} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

4. From Grignard reagents and carbon dioxide (carbonation of Grignard reagents) : When carbon dioxide is passed through an ethereal solution of Grignard reagents, an addition product is formed which on hydrolysis with a mineral acid yields a fatty acid.



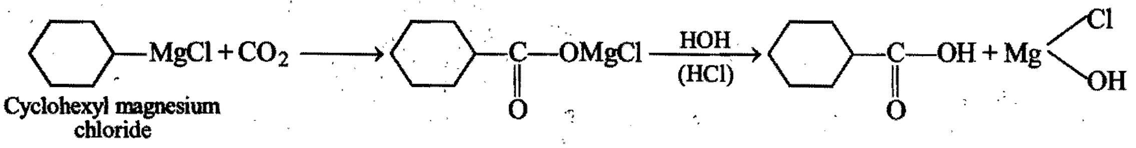
$$\underset{\text{Carbon dioxide}}{O{=}C{=}O} + RMgX \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Addition product}}{O{=}C(R){-}OMgX} \xrightarrow[H^+]{H_2O} RCOOH + Mg(X)(OH)$$



$$CH_3{-}MgBr + O{=}C{=}O \xrightarrow[\text{ether}]{\text{Dry}} O{=}C(CH_3){-}OMgBr \xrightarrow[HCl]{H_2O} \underset{\text{Acetic acid}}{CH_3COOH} + Mg(OH)(Br)$$

This synthesis of carboxylic acids is applicable to primary, secondary and tertiary (allyl, benzyl and aryl) halides, provided they have no groups inconsistent with a Grignard reaction.

$$\underset{\text{Tert. butyl chloride}}{(CH_3)_3C{-}Cl} \xrightarrow[\text{(Ether)}]{Mg} (CH_3)_3CMgCl \xrightarrow[\text{(ii) HOH}]{\text{(i) } CO_2} \underset{\text{2,2-Dimethyl propionic acid}}{(CH_3)_3C{-}COOH}$$



$$R{-}CH_2{-}X \xrightarrow[\text{(Diethyl ether)}]{Mg} RCH_2MgX \xrightarrow[\text{(ii) HOH}]{\text{(i) } CO_2} \underset{\text{Higher acid}}{RCH_2COOH}$$

Note : The acid formed has one carbon atom more than the alkyl group present in the Grignard reagents.

5. Hydrolysis of esters : Esters on hydrolysis with mineral acids or alkali form fatty acids. So, esters not only undergo acid hydrolysis, but they also undergo a base-promoted hydrolysis.

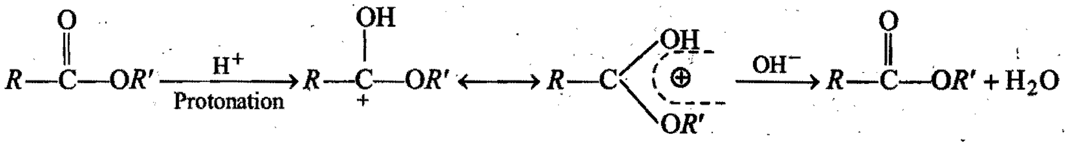
$$RCOOR' + H_2O \xrightarrow[\Delta]{HCl} RCOOH + R'OH$$

$$\underset{\text{Ester}}{RCOOR'} + NaOH \xrightarrow[\Delta]{} \underset{\text{Sodium carboxylate}}{RCOONa} + R'OH$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow[\Delta]{H^+ \text{ or } OH^-} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

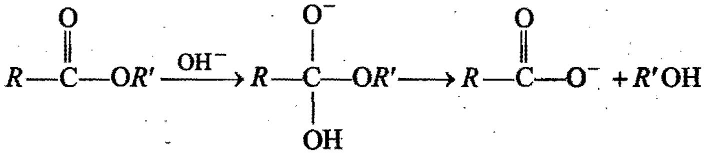
Hydrolysis in acidic medium is reversible but in basic medium it is irreversible. **Mechanism** of ester hydrolysis in basic and acidic medium may be given as,

(Acidic medium)



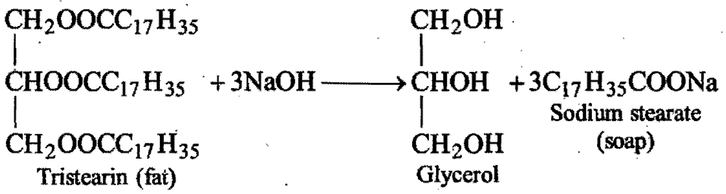
$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[\text{Protonation}]{H^+} R-\overset{OH}{\overset{|}{\underset{+}{C}}}-OR' \longleftrightarrow R-C\begin{smallmatrix}OH\\ \oplus\\ OR'\end{smallmatrix} \xrightarrow{OH^-} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

(Basic medium)



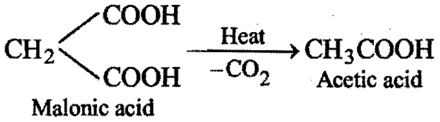
$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow{OH^-} R-\overset{O^-}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-OR' \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^- + R'OH$$

This method is particularly useful for the preparation of higher fatty acids from oils and fats which are triesters of glycerol. When oils and fats are heated with an alkali, they are hydrolysed forming salt (soap) and glycerol. The process is known as **saponification.**

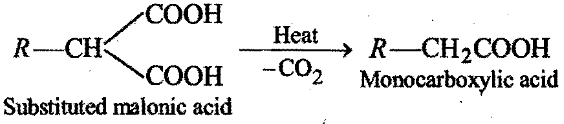


$$\begin{matrix}CH_2OOCC_{17}H_{35}\\ |\\ CHOOCC_{17}H_{35}\\ |\\ CH_2OOCC_{17}H_{35}\\ \text{Tristearin (fat)}\end{matrix} + 3NaOH \longrightarrow \begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{Glycerol}\end{matrix} + \underset{\text{Sodium stearate (soap)}}{3C_{17}H_{35}COONa}$$

6. Action of heat on gem dicarboxylic acids : The dicarboxylic acids of malonic acid series, in which two carboxylic groups are linked with the same carbon atom, on heating eliminate a molecule of carbon dioxide giving fatty acids.

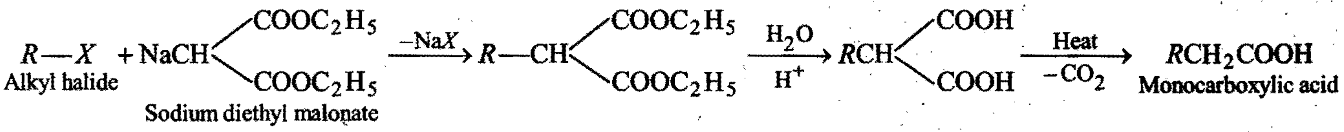


$$\underset{\text{Malonic acid}}{CH_2\begin{matrix}COOH\\ COOH\end{matrix}} \xrightarrow[-CO_2]{\text{Heat}} \underset{\text{Acetic acid}}{CH_3COOH}$$



$$\underset{\text{Substituted malonic acid}}{R-CH\begin{matrix}COOH\\ COOH\end{matrix}} \xrightarrow[-CO_2]{\text{Heat}} \underset{\text{Monocarboxylic acid}}{R-CH_2COOH}$$

The reaction is actually carried out between an alkyl halide and the sodium derivative of diethyl malonate. The substituted malonic ester formed is hydrolysed and then heated to get the monocarboxylic acid.

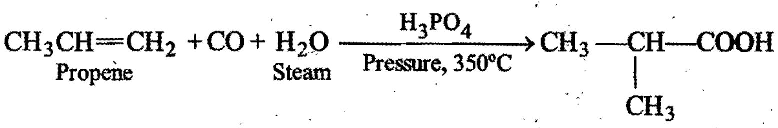


$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Sodium diethyl malonate}}{NaCH\begin{matrix}COOC_2H_5\\ COOC_2H_5\end{matrix}} \xrightarrow{-NaX} R-CH\begin{matrix}COOC_2H_5\\ COOC_2H_5\end{matrix} \xrightarrow[H^+]{H_2O} RCH\begin{matrix}COOH\\ COOH\end{matrix} \xrightarrow[-CO_2]{\text{Heat}} \underset{\text{Monocarboxylic acid}}{RCH_2COOH}$$

The acid obtained contains two more carbon atoms than the starting alkyl halide.

7. Carbonylation of alkenes (Koch reaction) : When a mixture of an alkene, carbon monoxide and steam is heated under pressure at 350°C in presence of phosphoric acid (H_3PO_4), monocarboxylic acid is formed.

$$\underset{\text{Ethene}}{H_2C=CH_2} + CO + \underset{\text{Steam}}{H_2O} \xrightarrow[\text{Pressure, 350°C}]{H_3PO_4} \underset{\text{Propionic acid}}{CH_3-CH_2COOH}$$



$$\underset{\text{Propene}}{CH_3CH=CH_2} + CO + \underset{\text{Steam}}{H_2O} \xrightarrow[\text{Pressure, 350°C}]{H_3PO_4} CH_3-\underset{CH_3}{\underset{|}{CH}}-COOH$$

2-Methyl propanoic acid

This is a recent method of making carboxylic acids and this acid-catalysed hydrocarboxylation of alkenes is called **Koch reaction.**

8. Heating sodium alkoxide with carbon monoxide : By the action of carbon monoxide on heating with sodium alkoxide under pressure, a sodium salt of the carboxylic acid is obtained which on treatment with an acid yields carboxylic acid.

$$\underset{\text{Sod. alkoxide}}{RONa} + CO \xrightarrow[\text{Under pressure}]{\text{Heat, 160°C}} \underset{\text{Sod. salt}}{RCOONa} \xrightarrow{HCl} \underset{\text{Acid}}{RCOOH}$$

$$\underset{\text{Sod. methoxide}}{CH_3ONa} + CO \longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa} \xrightarrow{HCl} \underset{\text{Acetic acid}}{CH_3COOH}$$

9. From acid amides, acid halides and anhydrides : Acid amides when boiled with mineral acids or alkalies are hydrolysed into corresponding fatty acids and ammonia. They also react with nitrous acid ($NaNO_2$ + HCl) to form fatty acids.

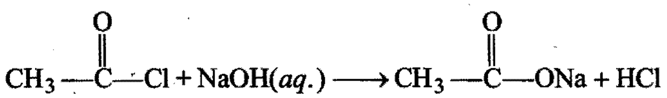
$$\underset{\text{Amide}}{RCONH_2} + H_2O \xrightarrow[\Delta]{H^+ \text{ or } OH^-} \underset{\text{Acid}}{RCOOH} + NH_3$$

$$\underset{\text{Amide}}{RCONH_2} + \underset{\text{Nitrous acid}}{HNO_2} \longrightarrow RCOOH + N_2 + H_2O$$

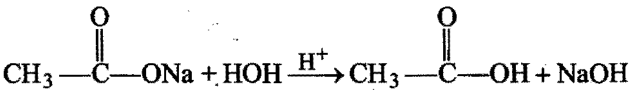
$$\underset{\text{Acetamide}}{CH_3CONH_2} + HNO_2 \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + N_2 + H_2O$$

Acyl chlorides and anhydrides are easily hydrolysed with water or alkalies.

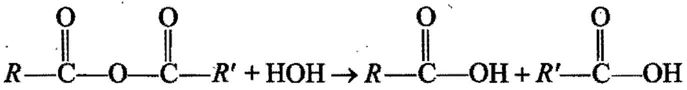
$$\underset{\text{Acid chloride}}{RCOCl} + HOH \longrightarrow \underset{\text{Carboxylic acid}}{RCOOH} + HCl$$



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + NaOH(aq.) \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONa + HCl$$



$$CH_3-\overset{O}{\overset{\|}{C}}-ONa + HOH \xrightarrow{H^+} CH_3-\overset{O}{\overset{\|}{C}}-OH + NaOH$$



$$\underset{\text{Anhydride}}{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R'} + HOH \rightarrow \underset{\text{Carboxylic acids}}{R-\overset{O}{\overset{\|}{C}}-OH + R'-\overset{O}{\overset{\|}{C}}-OH}$$

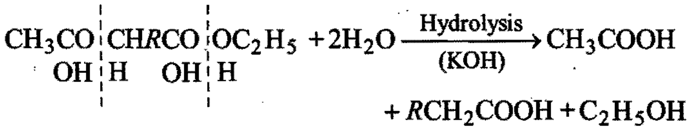
10. Oxidation of long chain hydrocarbons : Long chain hydrocarbons are oxidised by air at 120°C in presence of a catalyst manganese acetate or manganous stearate. It is a recent method of preparing higher fatty acids.

$$\underset{\text{Higher alkane}}{2RCH_3} + 3O_2 \longrightarrow \underset{\text{Fatty acid}}{2RCOOH} + 2H_2O$$

$$\underset{\text{Long chain alkane}}{2CH_3(CH_2)_nCH_3} + 3O_2 \xrightarrow[100\text{–}160^\circ C]{\text{Manganous stearate}} \underset{\text{Mono carboxylic acid}}{2CH_3(CH_2)_nCOOH} + 2H_2O$$

$$\underset{\text{Neo pentane}}{(CH_3)_3C-CH_3} + 4O_2 \xrightarrow{\text{Conc. } HNO_3} 2CH_3COOH + CO_2 + H_2O$$

11. From malonic or acetoacetic esters : Many fatty acids are synthesised from malonic and acetoacetic esters. Alkyl substituted acetoacetic ester on hydrolysis with conc. ethanolic KOH yields corresponding alkyl acetic acid.



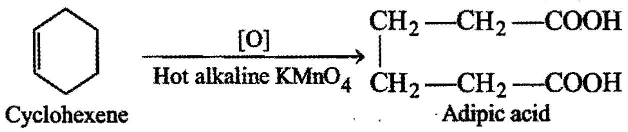
$$\underset{OH}{CH_3CO}\,\vdots\,\underset{H\quad\ \ OH}{CHRCO}\,\vdots\,\underset{H}{OC_2H_5} + 2H_2O \xrightarrow[\text{(KOH)}]{\text{Hydrolysis}} CH_3COOH + RCH_2COOH + C_2H_5OH$$

12. Oxidation of alkenes and alkynes : Alkenes can be oxidised to carboxylic acids with acidified or hot alkaline $KMnO_4$ or $K_2Cr_2O_7$.

$$\underset{\text{Alkene}}{RCH{=}CHR'} + 4[O] \xrightarrow[\Delta]{K_2Cr_2O_7/H_2SO_4} RCOOH + R'COOH$$

$$\underset{\text{But-2-ene}}{CH_3CH{=}CHCH_3} \xrightarrow[\text{(ii) Dil. } H_2SO_4]{\text{(i) } KMnO_4/OH^-, \Delta} \underset{\text{Acetic acid}}{2CH_3COOH}$$

Cyclic alkenes can also be oxidised to dicarboxylic acid.



Alternatively, ozonides can be subjected to oxidation with H_2O_2 to give carboxylic acids. Alkynes on ozonolysis also give carboxylic acids.

$$\underset{\text{Alkyne}}{R-C{\equiv}C-R'} + 3[O] + H_2O \xrightarrow{KMnO_4/H^+} RCOOH + R'COOH$$

$$\underset{\text{Alkyne}}{R-C{\equiv}C-R'} \xrightarrow[\text{(ii) } H_2O_2]{\text{(i) } O_3} R-COOH + R'COOH$$

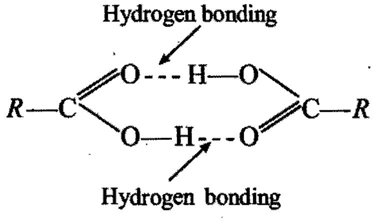
12.5 GENERAL PHYSICAL PROPERTIES

(i) The lower fatty acids upto C_{10} are colourless liquids. The higher ones are colourless waxy solids.

(ii) The first three members have a sharp pungent odour. The middle ones, C_4 to C_9, have an odour of rancid butter. The higher members do not possess any smell.

(iii) The lower members are highly soluble in water but the solubility decreases with the rise of molecular mass. The acids from C_{10} onwards are insoluble in water. Carboxylic acids are polar and readily soluble in alcohol and ether, as they have the tendency to undergo hydrogen bonding with each other and with other kinds of molecule.

(iv) Boiling points of carboxylic acids increase regularly with increase of molecular mass. Boiling points of carboxylic acids are higher than those of alcohols of same molecular mass. This is due to the intermolecular hydrogen bonding between two acid molecules.



The lower members exist as dimers in vapour phase and in aqueous solution, but in liquid phase they exist as polymers.

Ether, alcohol and acid having same molecular mass have boiling points in following sequence:

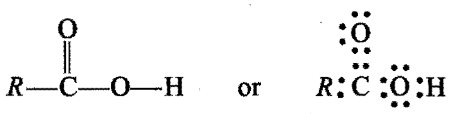
$$\underset{\text{Methoxy ethane}}{CH_3CH_2-O-CH_3} < \underset{\text{Propanol}}{CH_3CH_2CH_2OH} < \underset{\text{Ethanoic acid}}{CH_3COOH}$$

$$\xrightarrow{\hspace{12em}}$$

Increasing hydrogen bond strength and boiling point.

Electronic Structure of the Carboxylic Group

The electronic structure of a carboxylic acid is:

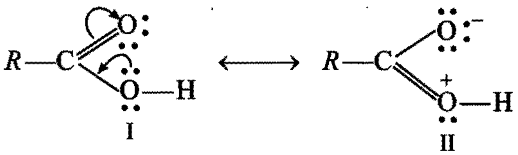


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H \quad \text{or} \quad R:\overset{:\ddot{O}}{\ddot{C}}:\ddot{O}:H$$

(where, *R* is H or any alkyl group)

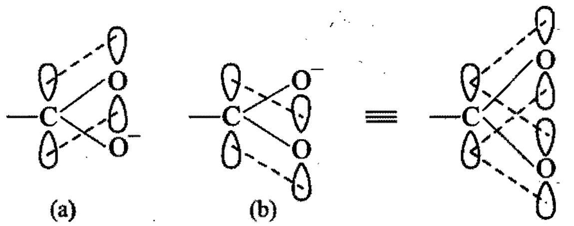
In carboxylic group, the carbon atom and the two oxygen atoms are sp^2-hybridized. The two sp^2-hybridized orbitals of the carboxylic carbon atom overlap with one sp^2-hybridized orbital of each oxygen atom while the third sp^2-hybridized orbital of carbon atom overlaps with a sp^3-hybridized orbital of carbon atom of the alkyl group to form three σ-bonds. One unhybridized *p*-orbital is perpendicular to the σ-bonding skeleton.

All the bonds to the carboxylic carbon atom lie on one plane and are separated by about 120° from each other. The molecule of carboxylic acid can be represented as a resonance hybrid of the following structures:



From these structures, it is clear that the carbonyl part of the carboxylic group is electrically neutral (compare it with aldehydes and ketones in which only one structure is electrically neutral) and does not have a double bond character but a reduced double bond character. Thus, carboxylic acid does not give the reactions of the carbonyl group.

The stability of carboxylate ion can also be explained in terms of **delocalization** of π-electron density. As the carbonyl carbon involves sp^2-hybridization leaving one unhybridized π-orbital, therefore, this π-orbital can overlap sidewise with either of the π-orbitals of oxygen atom forming π-bond[as shown below in the figures (a) and (b)]. The resulting π-orbital cloud is spread over both oxygen atoms and carbon atom.

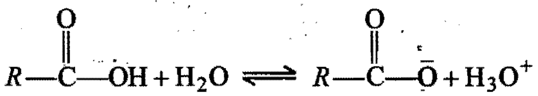


(Delocalized π-closed in carboxylate ion)

This delocalization gives stability to the carboxylate ion.

12.6 ACIDITY OF CARBOXYLIC ACIDS

The strength of an acid depends on the ability of the acid to lose a proton when dissolved in water. It is expressed in terms of dissociation constant (K_a).



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H_2O \rightleftharpoons R-\overset{\overset{\displaystyle O}{\|}}{C}-\bar{O} + H_3O^+$$

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

The dissociation constant is generally called **acidity constant** because it measures the relative strength of an acid. The stronger the acid, the larger will be its K_a value.

The acidic nature decreases with increase in molecular mass as K_a value decreases. Thus, formic acid is the strongest of all fatty acids.

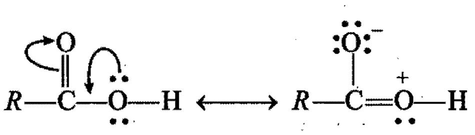
	$HCOOH$ >	CH_3COOH >	C_2H_5COOH
K_a value at 25°C	17.7×10^{-5}	1.75×10^{-5}	1.4×10^{-5}

The carboxylic acids have K_a values in the range of 10^{-4}—10^{-5} ($pK_a = 4$—5). The pK_a of water is about 16 and the apparent pK_a of H_2CO_3 is about 7. These relative acidities mean that the carboxylic acids react readily with aqueous solutions of NaOH and $NaHCO_3$ to form soluble sodium salts.

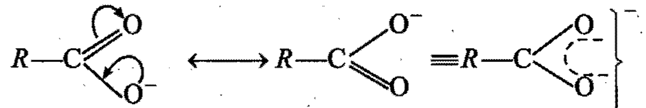
Table—Ionisation constant of some Carboxylic acids

Name of Acid	Molecular Formula	Ionisation Constant K_a
Trichloroacetic acid	CCl_3COOH	23200×10^{-5}
Dichloroacetic acid	$Cl_2CHCOOH$	5530×10^{-5}
Oxalic acid	$\begin{matrix}COOH\\ \vert\\ COOH\end{matrix}$	$5400 \times 10^{-5} (K_{a_1})$ for first ionisation
Fluoroacetic acid	FCH_2COOH	260×10^{-5}
Malonic acid	$CH_2(COOH)_2$	$140 \times 10^{-5} (K_{a_1})$ for first ionisation
2-Chlorobutanoic acid	$CH_3CH_2\underset{\underset{\displaystyle Cl}{\vert}}{C}HCOOH$	139×10^{-5}
Chloroacetic acid	$ClCH_2COOH$	136×10^{-5}
Bromoacetic acid	$BrCH_2COOH$	125×10^{-5}
Iodoacetic acid	ICH_2COOH	67×10^{-5}
Formic acid	$HCOOH$	17.9×10^{-5}
Acetic acid	CH_3COOH	1.75×10^{-5}
Propanoic acid	CH_3CH_2COOH	1.40×10^{-5}
n-Butyric acid	$CH_3CH_2CH_2COOH$	1.32×10^{-5}

Cause of acidic nature : The molecule of the carboxylic acid can be represented as a resonance hybrid of the following forms:

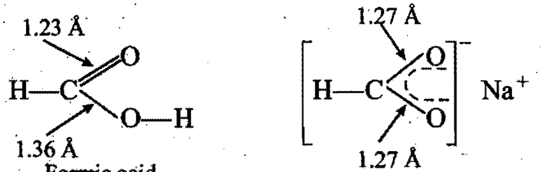

I II

Due to electron deficiency on oxygen atom of the hydroxyl group (structure II), there is displacement of electron pair of the O—H bond towards the oxygen atom. This helps in release of hydrogen as proton. The resulting carboxylate ion is also stabilised by resonance as resonance energy of the carboxylate ion is much higher than that of undissociated acid.


Resonance forms of carboxylate ion Resonance hybrid

Thus, the acidity of the carboxylic acid is due to powerful resonance stabilization of the anion.

[Resonance is confirmed by measuring bond length in formic acid and sodium formate]



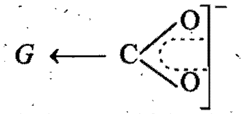
Formic acid Sodium formate

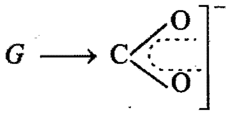
Alkoxide anion from alcohol does not show resonance and is not stabilized since, the alkyl group has electron repelling inductive effect. This lack of stabilization is responsible for a very weak acidity of alcohols.

$$\underset{\text{Alcohol}}{R—O—H} \rightleftharpoons \underset{\text{No resonance hybrid}}{R—O^-} + H^+$$

Effect of substituents on acidity : Any factor that stabilizes the anion more than it stabilizes the acid should increase the acidity and any factor that makes the anion less stable should decrease the acidity of the carboxylic acid.

An electron withdrawing group, **EWG** (having $-I$ effect) stabilises the anion by dispersing the negative charge and therefore, increases the acidity. On the other hand, electron-donating group, **EDG** ($+I$ effect) intensify the negative charge on the anion resulting in the decrease of stability and thus decreases the acidity of the acid.


G-electron withdrawing group, acidity increases

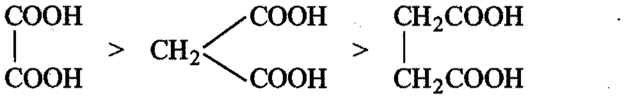

G-electron releasing group, acidity decreases

Hence, the following sequences are observed.

$HCOOH > C_6H_5COOH > CH_3COOH > C_2H_5COOH$

pK_a 3.77 4.17 4.71 4.88

or K_a (17.7×10^{-5}) (6.3×10^{-5}) (1.75×10^{-5}) (1.30×10^{-5})



[Alkyl group is **electron releasing group** and decreases acidity as size increases.]

$CH_3— < CH_3CH_2— < (CH_3)_2CH— < (CH_3)_3C—$.

[Chlorine is **electron withdrawing group.** The acidity of the acid increases as the number of chlorine atoms increases in the α-position.]

$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$

pK_a 0.64 1.48 2.85 4.71

[Electron withdrawing nature of halogens decreases from fluorine to iodine, *i.e.*, $F > Cl > Br > I$]

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

[Inductive effect is stronger at α-position than β-position. Similarly, at β-position it is more stronger than at γ-position.]

$\overset{\gamma}{CH_3}\overset{\beta}{CH_2}\overset{\alpha}{CH}ClCOOH > \overset{\gamma}{CH_3}\overset{\beta}{CH}Cl\overset{\alpha}{CH_2}COOH >$

pK_a 2.86 4.05

$\overset{\gamma}{CH_2}Cl\overset{\beta}{CH_2}\overset{\alpha}{CH_2}COOH$

4.52

Relative acid-strength:

(a) $RH < NH_3 < HC{\equiv}CR < R—OH < H—OH < Ar—OH < R—COOH$

(b) $CH_3CH_2COOH < HCH_2COOH < C_6H_5CH_2COOH <$

pK_a 4.87 4.76 4.31

$HOCH_2COOH < ClCH_2COOH$

pK_a 3.87 2.87

Relative basic-strength (of conjugate bases):

$RCOO^- < HO^- < RO^- < HC{\equiv}C^- < NH_2^- < R^-$

12.7 GENERAL CHEMICAL CHARACTERISTICS OF FATTY ACIDS

A molecule of a monocarboxylic acid is composed of (i) carboxylic group; the functional group and (ii) an alkyl group. Hence, the chemical properties of monocarboxylic acids are due to these groups. The chemical reactions, in general, may be discussed under following heads:

1. Due to carboxyl group ($—\overset{\overset{\displaystyle O}{\|}}{C}—OH$)
   (i) Reactions involving proton (removal of hydrogen of the —OH group).
   (ii) Reactions involving hydroxyl group (—OH).
   (iii) Reactions involving carbonyl group ($>C{=}O$).
   (iv) Reactions involving carboxyl group as a whole.
2. Reactions due to alkyl group.

1. Reactions due to Carboxyl Group

(i) Reactions Involving Proton:

(a) Reaction with strongly electropositive metals : Monocarboxylic acids react with strongly electropositive metals (such as Na, K, Ca, Zn, etc.) evolving hydrogen and forming corresponding salts **(acidic character).**

$$R\text{—COOH} \rightleftharpoons R\text{COO}^- + \text{H}^+$$

$$R\text{—COOH} + \text{H}_2\text{O} \rightleftharpoons R\text{COO}^- + \text{H}_3\overset{+}{\text{O}}$$

They exhibit acidic character due to their ability to ionise to give proton (H^+).

$$\underset{\text{Formic acid}}{2\text{HCOOH}} + 2\text{Na} \longrightarrow \underset{\text{Sodium formate}}{2\text{HCOONa}} + \text{H}_2$$

$$\underset{\text{Acetic acid}}{2\text{CH}_3\text{COOH}} + 2\text{K} \longrightarrow \underset{\text{Potassium acetate}}{2\text{CH}_3\text{COOK}} + \text{H}_2$$

$$\underset{\text{Acetic acid}}{2\text{CH}_3\text{COOH}} + \text{Zn} \longrightarrow \underset{\text{Zinc acetate}}{(\text{CH}_3\text{COO})_2\text{Zn}} + \text{H}_2$$

(b) Reaction with alkalies : Monocarboxylic acids neutralise hydroxides to form corresponding salts and water.

$$\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$$

$$\underset{\text{Acetic acid}}{\text{CH}_3\text{COOH}} + \text{NH}_4\text{OH} \longrightarrow \underset{\text{Ammonium acetate}}{\text{CH}_3\text{COONH}_4} + \text{H}_2\text{O}$$

Carboxylic acids can be regenerated by treating these salts with dilute mineral acids.

$$\underset{\text{Sodium acetate}}{\text{CH}_3\text{COONa}} + \text{HCl} \longrightarrow \underset{\text{Acetic acid}}{\text{CH}_3\text{COOH}} + \text{NaCl}$$

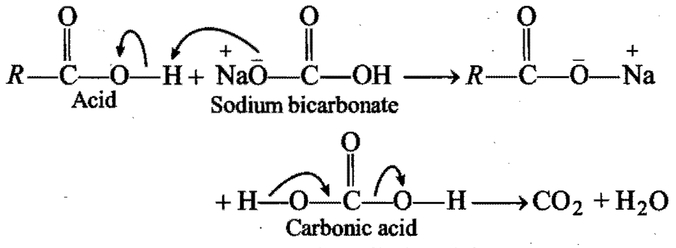
(c) Reaction with carbonates and bicarbonates : Monocarboxylic acids react with weaker bases such as carbonates and bicarbonates forming corresponding salts with evolution of carbon dioxide (effervescences). It is a **laboratory test of —COOH group.**

$$\text{CH}_3\text{COOH} + \text{NaHCO}_3 \longrightarrow \text{CH}_3\text{COONa} + \text{CO}_2 + \text{H}_2\text{O}$$

$$2\text{CH}_3\text{COOH} + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{CH}_3\text{COONa} + \text{CO}_2 + \text{H}_2\text{O}$$

$$2\text{CH}_3\text{COOH} + \text{CaCO}_3 \longrightarrow \underset{\text{Calcium acetate}}{(\text{CH}_3\text{COO})_2\text{Ca}} + \text{CO}_2 + \text{H}_2\text{O}$$

During the reaction of carboxylic acids with NaHCO_3 or Na_2CO_3, the CO_2 evolved comes from NaHCO_3 or Na_2CO_3 and not from the carboxylic group as shown below:



$$\underset{\text{Acid}}{R\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—O—H}} + \underset{\text{Sodium bicarbonate}}{\text{Na}\overset{+}{\text{O}}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—OH}} \longrightarrow R\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\overset{-}{\text{O}}\text{—}\overset{+}{\text{Na}}$$

$$+ \underset{\text{Carbonic acid}}{\text{H—O—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—O—H}} \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$$

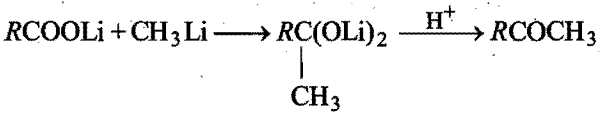
This reaction can be used to distinguish carboxylic acids from phenols (because phenols do not give effervescence with aqueous solution of NaHCO_3).

(d) Reaction with organo-metallic reagents : Carboxylic acids react with Grignard reagents extremely rapidly to give hydrocarbons and the magnesium salts of the acids. As most of these salts are insoluble and precipitate in the reaction mixture, no reaction occurs with additional quantities of Grignard reagents.

$$R'\text{CH}_2\text{MgBr} + R\text{COOH} \xrightarrow{\text{Ether}} R'\text{CH}_3 + R\text{COOMgBr}$$

However, lithium alkyls react to give lithium salts which are often soluble and further react to form a dilithium salt which gives a ketone with acid.

$$R\text{COOH} + \text{CH}_3\text{Li} \longrightarrow \text{CH}_4 + R\text{COOLi}$$



$$R\text{COOLi} + \text{CH}_3\text{Li} \longrightarrow \underset{\underset{\text{CH}_3}{|}}{R\text{C}}(\text{OLi})_2 \xrightarrow{\text{H}^+} R\text{COCH}_3$$

(ii) Reactions Involving Hydroxyl Group:

(a) Formation of esters (Reaction with alcohols) : When carboxylic acids are heated with alcohols in presence of dehydrating agents like conc. H_2SO_4 or dry HCl gas, esters are formed.

$$R\text{—COOH} + \text{HO}R' \xrightleftharpoons{\text{Conc. H}_2\text{SO}_4} \underset{\text{Ester}}{R\text{COO}R'} + \text{H}_2\text{O}$$

$$\underset{\text{Acetic acid}}{\text{CH}_3\text{COOH}} + \underset{\text{Ethyl alcohol}}{\text{HOC}_2\text{H}_5} \xrightleftharpoons{\text{Conc. H}_2\text{SO}_4} \underset{\text{Ethyl acetate}}{\text{CH}_3\text{COOC}_2\text{H}_5} + \text{H}_2\text{O}$$

This reaction is termed **esterification.** It is a reversible and slow reaction, but is speeded up by the presence of small amount of inorganic acids as catalyst, *e.g.*,

$$R\text{—COOH} + \text{HO}R' \xrightarrow{\text{Conc. H}_2\text{SO}_4} R\text{—COO}R' + \text{H}_2\text{O}$$

Since, esterification is an equilibrium reaction, therefore, to shift the equilibrium in the forward direction, water is removed as soon as it is formed and either carboxylic acid or the alcohol is used in excess. The rate at which a carboxylic acid is esterified depends primarily upon the stearic hindrance in the alcohol and the carboxylic acid.

The reactivity of alcohols towards esterification increases as:

$$\text{Tertiary } (R_3\text{C—OH}) < \text{Secondary } (R_2\text{CH—OH}) < \text{Primary } (R\text{—CH}_2\text{OH}) < \text{CH}_3\text{OH}$$

Similarly, reactivity of carboxylic acids increases as:

$$R_3\text{C—COOH} < R_2\text{CH—COOH} < R\text{CH}_2\text{COOH} < \text{CH}_3\text{COOH} < \text{HCOOH}$$

(Mechanism of esterification of carboxylic acids See Problem 8 on **page** 675-676.)

(b) Formation of acid chlorides (Reaction with phosphorus halides or thionyl chlorides) : Acid chlorides are formed when monocarboxylic acids are heated with phosphorus chlorides or thionyl chlorides in pyridine. Similar reactions are observed with phosphorus bromides.

$$\underset{\text{Acetic acid}}{\text{CH}_3\text{COOH}} + \text{PCl}_5 \xrightarrow[\Delta]{\text{Pyridine}} \underset{\text{Acetyl chloride}}{\text{CH}_3\text{COCl}} + \text{POCl}_3 + \text{HCl}$$

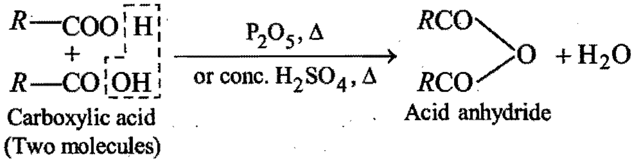
$$3\text{CH}_3\text{COOH} + \text{PCl}_3 \xrightarrow{\Delta} 3\text{CH}_3\text{COCl} + \text{H}_3\text{PO}_3$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Ethanoyl chloride}}{CH_3COCl} + SO_2 + HCl$$

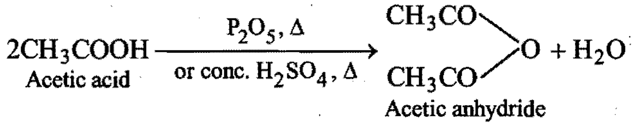
In, laboratory, acetyl chloride is prepared by this method.

Thionyl chloride is preferred because the other two products (SO_2 and HCl) are gases and easily escapes.

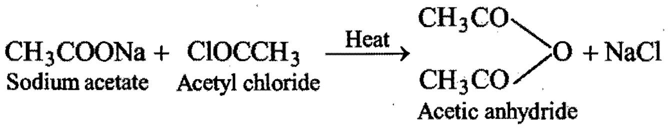
(c) Formation of acid anhydrides (Dehydration) : Monocarboxylic acids, when heated with a dehydrating agent, such as conc. H_2SO_4 or (phosphorus pentoxide) or when their sodium salt is heated with acid chloride, form acid anhydride.



$$\underset{\substack{\text{Carboxylic acid}\\\text{(Two molecules)}}}{R—COOH + R—COOH} \xrightarrow[\text{or conc. } H_2SO_4,\, \Delta]{P_2O_5,\, \Delta} \underset{\text{Acid anhydride}}{(RCO)_2O} + H_2O$$



$$\underset{\text{Acetic acid}}{2CH_3COOH} \xrightarrow[\text{or conc. } H_2SO_4,\, \Delta]{P_2O_5,\, \Delta} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + H_2O$$



$$\underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Acetyl chloride}}{ClOCCH_3} \xrightarrow{\text{Heat}} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NaCl$$

Note : Formic acid does not form an anhydride.

(d) Formation of amides and nitriles : Monocarboxylic acids when treated with ammonia form ammonium salts. Ammonium salts on heating lose a water molecule and are converted into corresponding acid amides.

$$\underset{\text{Acid}}{RCOOH} + NH_3 \longrightarrow \underset{\text{Ammonium salt}}{RCOONH_4} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Amide}}{RCONH_2}$$

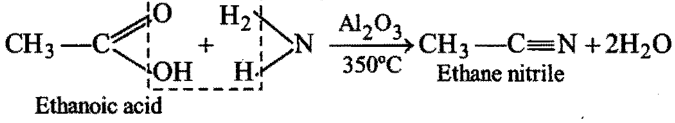
$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow \underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2}$$

The amide on heating with phosphorus pentoxide loses one more water molecule forming a cyanide (nitrile).

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Alkyl nitrile}}{RCN} + H_2O$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\substack{\text{Methyl cyanide}\\\text{(Ethane nitrile)}}}{CH_3CN} + H_2O$$

A mixture of carboxylic acid and ammonia vapours on passing over heated alumina gives alkane nitrile.



$$\underset{\text{Ethanoic acid}}{CH_3—C(=O)OH} + H_2NH \xrightarrow[350°C]{Al_2O_3} \underset{\text{Ethane nitrile}}{CH_3—C{\equiv}N} + 2H_2O$$

(iii) Reactions Involving Carbonyl Group ($\rangle C{=}O$):

The carbonyl group of $\overset{\overset{O}{\|}}{—C—}OH$ does not give the usual reactions of $\rangle C{=}O$ group, mainly due to reduced double bond character of the carbon-oxygen bond (because of resonance).

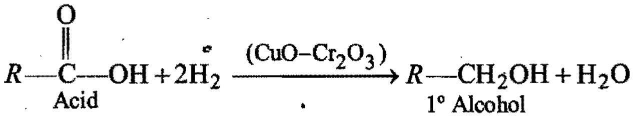
Reduction to alcohols : It depends on the nature of reducing agent. With $LiAlH_4$ (lithium aluminium hydride) in ether solution or with hydrogen in presence of copper chromite ($CuCr_2O_4$) catalyst or BH_3/THF (or diborane, B_2H_6) or H_2/Ru, etc., reduce monocarboxylic acids easily into primary alcohols.

$$\underset{\text{Acid}}{RCOOH} + 2H_2 \xrightarrow[\text{or } B_2H_6/\text{ether, } H^+]{LiAlH_4/\text{ether}} \underset{\text{Alcohol}}{RCH_2OH} + H_2O$$

$$4RCOOH + 3LiAlH_4 \longrightarrow 4H_2 + 2LiAlO_2 + (RCH_2O)_4LiAl$$

$$(RCH_2O)_4LiAl + 4H_2O \longrightarrow \underset{1°\text{Alcohol}}{4RCH_2OH} + LiOH + Al(OH)_3$$

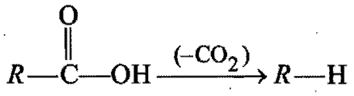
$$\underset{\text{Acetic acid}}{CH_3COOH} + 2H_2 \xrightarrow[\text{or } B_2H_6/\text{ether, } H^+]{LiAlH_4/\text{ether}} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + H_2O$$



$$\underset{\text{Acid}}{R—\overset{\overset{O}{\|}}{C}—OH} + 2H_2 \xrightarrow{(CuO{-}Cr_2O_3)} \underset{1°\text{ Alcohol}}{R—CH_2OH} + H_2O$$

(iv) Reactions Involving Carboxyl Group as a Whole:

(a) Decarboxylation : The reaction whereby a carboxylic acid loses CO_2 is called decarboxylation.



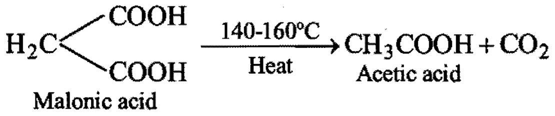
$$R—\overset{\overset{O}{\|}}{C}—OH \xrightarrow{(-CO_2)} R—H$$

Although, the unusual stability of carbon dioxide means that decarboxylation of most acids is exothermic, but in practice the reaction is not always easy to carry out because the reaction is very slow. When anhydrous alkali salt of a carboxylic acid is heated with sodalime (NaOH/CaO in the ratio 3 : 1), an alkane is formed.

$$\underset{\text{Sodium salt}}{RCOONa} + NaOH \xrightarrow[\text{Heat}]{CaO} \underset{\text{Alkane}}{R—H} + Na_2CO_3$$

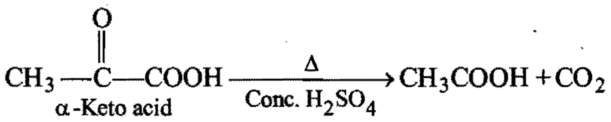
$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \xrightarrow[\text{Heat}]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

When two carboxylic groups are attached to the same carbon atom (gem. dicarboxylic acids), decarboxylation takes place simply on heating.



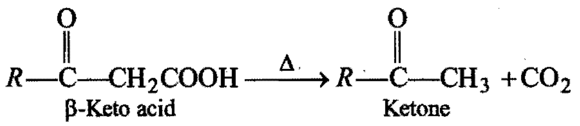
$$\underset{\text{Malonic acid}}{H_2C(COOH)_2} \xrightarrow[\text{Heat}]{140\text{-}160°C} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

α-Keto acids on heating with conc. H_2SO_4 undergo decarboxylation to give monocarboxylic acid.



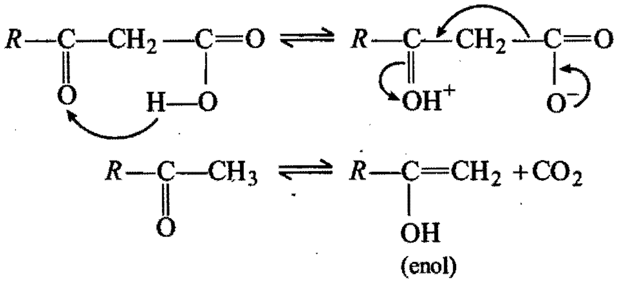
$$\underset{\alpha\text{-Keto acid}}{CH_3—\overset{\overset{O}{\|}}{C}—COOH} \xrightarrow[\text{Conc. } H_2SO_4]{\Delta} CH_3COOH + CO_2$$

In case of some β-keto acids, the decarboxylation takes place simply by heating.



$$\underset{\text{β-Keto acid}}{R-\overset{O}{\overset{\|}{C}}-CH_2COOH} \xrightarrow{\Delta} \underset{\text{Ketone}}{R-\overset{O}{\overset{\|}{C}}-CH_3} + CO_2$$

β-Keto acids are unstable acids. These readily undergo decarboxylation through a cyclic transition state.



Similarly, if unsaturation is present at β and γ-positions then again decarboxylation takes place simply on heating.

$$H_2\overset{\gamma}{C}=\overset{\beta}{C}H-\overset{\alpha}{C}H_2-COOH \xrightarrow{\text{Heat}} H_2C=CH-CH_3+CO_2\uparrow$$

(b) Dry distillation of calcium salts of carboxylic acids : When calcium salts of fatty acids other than calcium formate are heated, ketones are formed.

$$\underset{\text{Calcium salt}}{(RCOO)_2Ca} \xrightarrow[\text{distil.}]{\text{Dry}} \underset{\text{Ketone}}{RCOR} + CaCO_3$$

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow[\text{distil.}]{\text{Dry}} \underset{\text{Acetone}}{CH_3COCH_3} + CaCO_3$$

When calcium formate is heated, formaldehyde is evolved.

$$(HCOO)_2Ca \xrightarrow{\text{Heat}} \underset{\text{Formaldehyde}}{HCHO} + CaCO_3$$

However, when a mixture of calcium salt of a fatty acid (other than formic acid) and calcium formate is heated, an aldehyde is formed.

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium formate}}{(HCOO)_2Ca} \xrightarrow{\text{Heat}} \underset{\text{Acetaldehyde}}{2CH_3CHO} + CaCO_3$$

Note : Instead of calcium salts, vapours of fatty acids can be passed over manganous oxide at 300°C or Al_2O_3 at 400°C when similar aldehydes and ketones are obtained.

(c) Electrolysis of sodium or potassium salts of carboxylic acids (Kolbe's synthesis) : Electrolysis of sodium or potassium salts (concentrated aqueous solution) of fatty acids yields alkanes.

$$RCOONa \rightleftharpoons RCOO^- + Na^+$$

At anode $2RCOO^- \longrightarrow R-R + 2CO_2 + 2e^-$

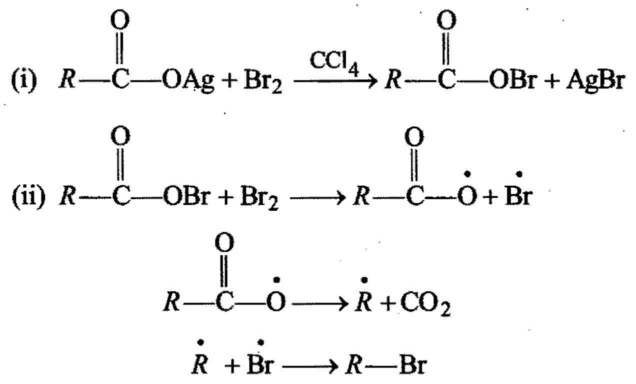
At cathode $2Na^+ + 2e^- \longrightarrow 2Na \xrightarrow{2H_2O} 2NaOH + H_2$

$$\underset{\text{Potassium acetate}}{2CH_3COOK} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ethane}}{CH_3-CH_3} + 2CO_2 + 2KOH + H_2$$

(d) Formation of alkyl halides (Hunsdiecker's reaction) : An alkyl halide is formed when the silver salt of monocarboxylic acid is heated with halogen.

$$\underset{\text{Silver acetate}}{CH_3COOAg} + Br_2 \xrightarrow[\text{Heat}]{CCl_4} \underset{\text{Methyl bromide}}{CH_3Br} + AgBr + CO_2\uparrow$$

A carboxyl radical is produced in a two-steps process as follows:



$$\text{(i)}\quad R-\overset{O}{\overset{\|}{C}}-OAg + Br_2 \xrightarrow{CCl_4} R-\overset{O}{\overset{\|}{C}}-OBr + AgBr$$

$$\text{(ii)}\quad R-\overset{O}{\overset{\|}{C}}-OBr + Br_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-\dot{O} + \dot{B}r$$

$$R-\overset{O}{\overset{\|}{C}}-\dot{O} \longrightarrow \dot{R} + CO_2$$

$$\dot{R} + \dot{B}r \longrightarrow R-Br$$

(e) Formation of amines (Action of N_3H) : Primary amines containing one carbon atom less than the parent acid are formed when monocarboxylic acids react with hydrazoic acid (N_3H) in presence of concentrated sulphuric acid.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Hydrazoic acid}}{N_3H} \xrightarrow{H_2SO_4\text{(conc.)}} \underset{\text{Primary amine}}{RNH_2} + CO_2 + N_2$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + N_3H \xrightarrow{H_2SO_4\text{(conc.)}} \underset{\text{Methylamine}}{CH_3NH_2} + CO_2 + N_2$$

This reaction is called **Schmidt reaction.**

(f) Reaction with CH_2N_2 : Diazomethane undergoes condensation with carboxylic acid to give an ester.

$$R-COOH + CH_2N_2 \xrightarrow{\Delta} R-COOCH_3 + N_2\uparrow$$

(g) Reaction with ketene : Forms acid anhydride.

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ketene}}{CH_2CO} \longrightarrow \underset{\text{Acetic anhydride}}{CH_3CO\cdot O\cdot COCH_3}$$

(h) Reduction to alkanes : On heating with conc. HI and red P at 200°C or by catalytic reduction, the —COOH converts into $-CH_3$ to form an alkane.

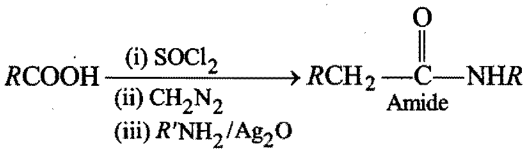
$$RCH_2COOH + 6HI \xrightarrow[200°C]{\text{Red P}} \underset{\text{Alkane}}{RCH_2CH_3} + 2H_2O + 3I_2$$

$$RCOOH + 3H_2 \xrightarrow[\Delta]{Ni} RCH_3 + 2H_2O$$

(i) Arndt-Eistert reaction : This reaction is a method for converting an acid $RCOOH$ to a homologous series, $R—CH_2COOH$, in which Wolff rearrangement is the key step. In this reaction, $R—COCl$ from $R—COOH$ is converted to $R—CH_2COOH$ by diazomethane via formation of α-diazoketone.

$$R—COOH \xrightarrow[\text{or } SOCl_2]{PCl_5} R—COCl \xrightarrow{CH_2N_2} \underset{\text{Diazo ketone}}{RCOCHN_2} \xrightarrow{HOH} \underset{\text{Higher acid}}{RCH_2COOH}$$

$$RCOOH \xrightarrow[\substack{\text{(ii) } CH_2N_2 \\ \text{(iii) } R'OH/Ag_2O}]{\text{(i) } SOCl_2} \underset{\text{Ester}}{RCH_2COOR'}$$



$$RCOOH \xrightarrow[\substack{\text{(ii) } CH_2N_2 \\ \text{(iii) } R'NH_2/Ag_2O}]{\text{(i) } SOCl_2} \underset{\text{Amide}}{RCH_2—\overset{\overset{\displaystyle O}{\|}}{C}—NHR}$$

2. Reactions due to Alkyl Group

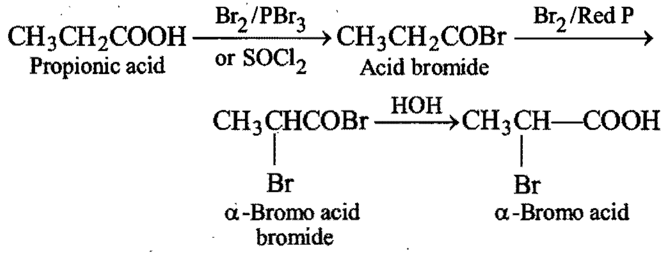
(i) Halogenation : The α-H atoms are highly reactive due to the presence of electronegative —COOH group.

$$CH_3COOH + Cl_2 \xrightarrow[\Delta]{\text{Red P}} \underset{\text{Chloroacetic acid}}{CH_2ClCOOH} \xrightarrow{Cl_2}$$

$$\underset{\text{Dichloroacetic acid}}{CHCl_2COOH} \xrightarrow{Cl_2} \underset{\text{Trichloroacetic acid}}{CCl_3COOH}$$

When a carboxylic acid that contains α-hydrogen atoms is treated with Cl_2 or Br_2 in presence of a catalyst (P, I, Fe, etc.), the α-hydrogen atoms are replaced by chlorine or bromine atoms. The reaction occurs in presence of sunlight or on boiling. This reaction is known as **Hell-Volhard-Zelinsky (HVZ) reaction.**

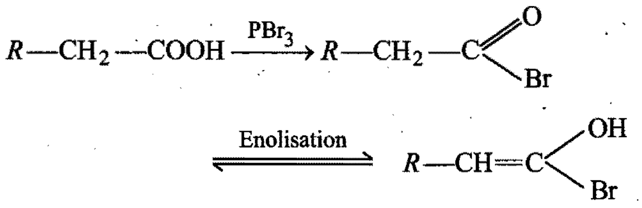
$$\underset{\text{Carboxylic acid}}{R\overset{\alpha}{C}H_2COOH} + Cl_2 \xrightarrow[-HCl]{\text{Red P}} \underset{\alpha\text{-Chlorinated acid}}{RCHClCOOH} \xrightarrow[-HCl]{\text{Red P}/Cl_2} \underset{\alpha,\alpha'\text{-Dichloro acid}}{RCCl_2COOH}$$



$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow[\text{or } SOCl_2]{Br_2/PBr_3} \underset{\text{Acid bromide}}{CH_3CH_2COBr} \xrightarrow{Br_2/\text{Red P}} \underset{\alpha\text{-Bromo acid bromide}}{CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCOBr} \xrightarrow{HOH} \underset{\alpha\text{-Bromo acid}}{CH_3\underset{\displaystyle Br}{\underset{|}{C}H}—COOH}$$

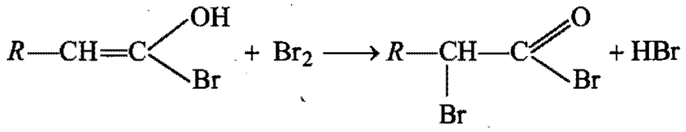
Mechanism of HVZ reaction : Red P reacts with Br_2 to form a little of PBr_3 which converts carboxylic acid into carboxylic acid bromide. The acid bromide thus formed undergoes enolisation.

$$2P + 3Br_2 \longrightarrow 2PBr_3$$



$$R—CH_2—COOH \xrightarrow{PBr_3} R—CH_2—C(=O)Br \xrightleftharpoons{\text{Enolisation}} R—CH=C(OH)Br$$

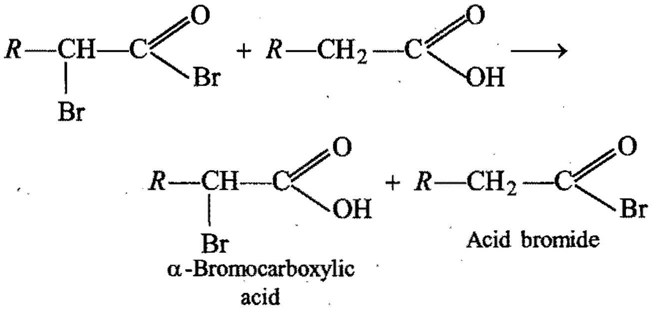
Enol thus formed undergoes further bromination.



$$R—CH=C(OH)Br + Br_2 \longrightarrow R—CH(Br)—C(=O)Br + HBr$$

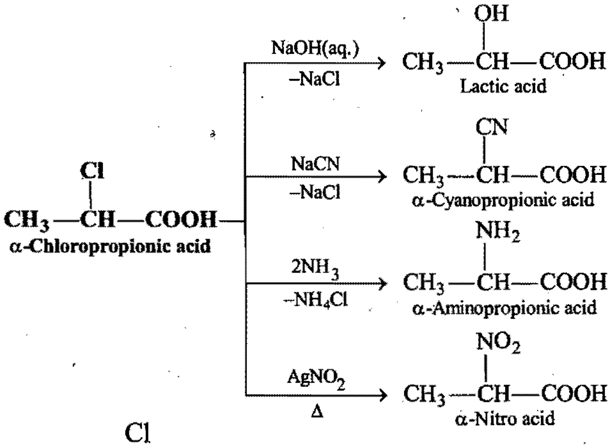
(A)

Intermediate (A) reacts with another molecule of carboxylic acid by interchange of —Br and —OH to form a halogenated acid.



$$R—CH(Br)—C(=O)Br + R—CH_2—C(=O)OH \longrightarrow \underset{\alpha\text{-Bromocarboxylic acid}}{R—CH(Br)—C(=O)OH} + \underset{\text{Acid bromide}}{R—CH_2—C(=O)Br}$$

α-Halogenated acids act as starting materials for preparing other substituted acids.

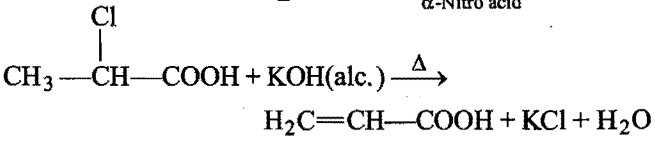


$$\underset{\alpha\text{-Chloropropionic acid}}{CH_3—CH(Cl)—COOH} \xrightarrow[-NaCl]{NaOH(aq.)} \underset{\text{Lactic acid}}{CH_3—CH(OH)—COOH}$$

$$\xrightarrow[-NaCl]{NaCN} \underset{\alpha\text{-Cyanopropionic acid}}{CH_3—CH(CN)—COOH}$$

$$\xrightarrow[-NH_4Cl]{2NH_3} \underset{\alpha\text{-Aminopropionic acid}}{CH_3—CH(NH_2)—COOH}$$

$$\xrightarrow[\Delta]{AgNO_2} \underset{\alpha\text{-Nitro acid}}{CH_3—CH(NO_2)—COOH}$$



$$CH_3—\overset{\overset{\displaystyle Cl}{|}}{C}H—COOH + KOH(alc.) \xrightarrow{\Delta} \underset{\text{Prop-2-en-1-oic acid}}{H_2C=CH—COOH} + KCl + H_2O$$

Note : Formic acid does not show this reaction.

(ii) Oxidation : Monocarboxylic acids except formic acid are extremely resistant to oxidation. Formic acid on oxidation gives carbon dioxide and water.

$$HCOOH + \tfrac{1}{2}O_2 \longrightarrow CO_2 + H_2O$$

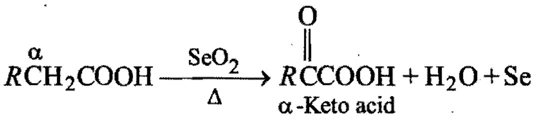
However, prolonged heating with powerful oxidising agents oxidises acids into carbon dioxide and water.

With 3% H_2O_2, they are oxidised to β-hydroxy acids.

$$\overset{\gamma}{C}H_3\overset{\beta}{C}H_2\overset{\alpha}{C}H_2COOH \xrightarrow[H_2O_2]{[O]} CH_3CHOHCH_2COOH$$

Butyric acid β-Hydroxy butyric acid

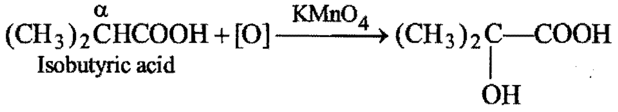
Oxidation of α-methylene group takes place by SeO_2 to give α-keto acid.



$$R\overset{\alpha}{C}H_2COOH \xrightarrow[\Delta]{SeO_2} R\overset{\overset{O}{\|}}{C}COOH + H_2O + Se$$

α-Keto acid

When oxidised with $KMnO_4$, the α-H atom is oxidised to —OH group.



$$(CH_3)_2\overset{\alpha}{C}HCOOH + [O] \xrightarrow{KMnO_4} (CH_3)_2\underset{\underset{OH}{|}}{C}—COOH$$

Isobutyric acid

12.8 GENERAL TESTS FOR CARBOXYLIC GROUP

(i) The aqueous solution of the acid turns blue litmus into red.

(ii) The aqueous solution of the acid gives effervescence of carbon dioxide with sodium bicarbonate and sodium carbonate.

(iii) On heating with alcohol and concentrated sulphuric acid, a fruity smell of ester is formed.

12.9 FORMIC ACID OR METHANOIC ACID (HCOOH)

Formic acid is the first member of monocarboxylic acids series. It occurs in the sting of bees, wasps, red ants, stinging nettles and fruits. In traces, it is present in perspiration, urine, blood and in caterpillars. It was first prepared by the distillation of red ants (Latin : *ant* = formica) and hence the name was given formic acid.

Methods of preparation : The following general methods can be used for its preparation:

(i) Oxidation of methyl alcohol or formaldehyde passed over platinum black.

The oxidation is also done with acidified dichromate (potassium or sodium) or alkaline potassium permanganate.

$$CH_3OH \xrightarrow{[O]} HCHO \xrightarrow{[O]} HCOOH$$

(ii) Hydrolysis of hydrocyanic acid.

(iii) Hydrolysis of chloroform or iodoform.

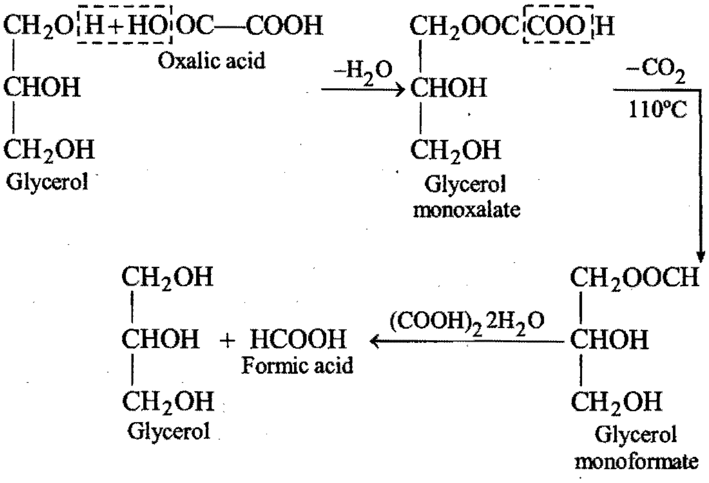
(iv) Hydrolysis of methyl formate.

(v) Hydrolysis of ethyl isocyanide in acidic medium.

$$C_2H_5NC + 2H_2O \xrightarrow{H^+} C_2H_5NH_2 + HCOOH$$

Ethyl isocyanide Ethylamine Formic acid

Laboratory preparation : Formic acid is conveniently prepared in the laboratory by heating glycerol with oxalic acid at 100–120°C.



The following procedure is applied for obtaining anhydrous formic acid.

$$2HCOOH + PbCO_3 \longrightarrow (HCOO)_2Pb + CO_2 + H_2O$$

Lead formate

$$(HCOO)_2Pb + H_2S \longrightarrow PbS + 2HCOOH$$

ppt. Formic acid

Industrial preparation : Formic acid is prepared on industrial scale by heating sodium hydroxide with carbon monoxide at 210°C under a pressure of about 10 atmospheres.

$$CO + NaOH \longrightarrow HCOONa$$

Sodium formate

Sodium formate thus formed is distilled with sodium hydrogen sulphate, when anhydrous formic acid distils over.

$$HCOONa + NaHSO_4 \longrightarrow HCOOH + Na_2SO_4$$

Physical properties : (i) It is a colourless pungent smelling liquid.

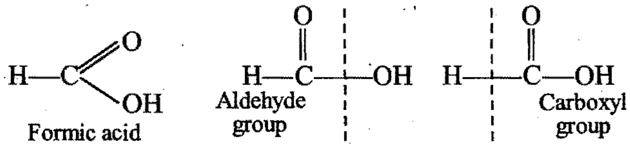
(ii) It melts at 8.4°C and boils at 100.5°C.

(iii) It is miscible with water, alcohol and ether. It forms azeotropic mixture with water (b.pt. 107.1°C).

(iv) It is strongly corrosive and causes blisters on skin.

(v) It exists in aqueous solution as a **dimer** involving hydrogen bonding.

Chemical properties : Formic acid is the strongest acid among all the members of the homologous series. It exhibits some characteristics which are not shown by other members. This unique nature is due to the fact that it contains both aldehyde and carboxyl groups.



(i) Acidic properties : It is a monobasic acid. Its dissociation constant value is 18×10^{-5} at 25°C. Its acidic properties are due to its ionisation in an aqueous solution.

$$HCOOH \rightleftharpoons HCOO^- + H^+$$

Formic acid Formate ion

(ii) Action of heat : When heated above 160°C, it decomposes to give carbon dioxide and hydrogen.

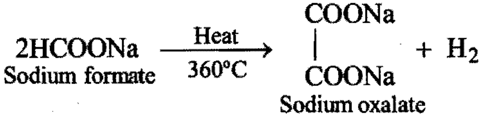
$$HCOOH \longrightarrow CO_2 + H_2$$

(iii) Dehydration : When formic acid is warmed with conc. H_2SO_4 it decomposes to give carbon monoxide and water.

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

Note : 1. Formic acid does not form an anhydride.
2. The above reaction is used for the preparation of CO in the laboratory.

(iv) Action of heat on formates : (a) When sodium formate is heated to 360°C, it decomposes to form sodium oxalate and hydrogen.



$$\underset{\text{Sodium formate}}{2HCOONa} \xrightarrow[360°C]{\text{Heat}} \underset{\text{Sodium oxalate}}{\begin{matrix}COONa\\ |\\ COONa\end{matrix}} + H_2$$

(b) It does not form a hydrocarbon when sodium formate is heated with soda lime or its aqueous solution is electrolysed but hydrogen is evolved.

$$HCOONa + NaOH \xrightarrow[\Delta]{CaO} Na_2CO_3 + H_2$$

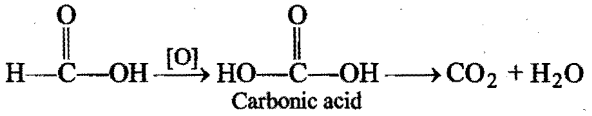
(c) Formaldehyde is formed when dry calcium formate is heated.

$$\underset{\text{Dry calcium formate}}{(HCOO)_2Ca} \longrightarrow \underset{\text{Formaldehyde}}{HCHO} + CaCO_3$$

(d) Formamide is formed when ammonium formate is heated.

$$\underset{\text{Amm. formate}}{HCOONH_4} \longrightarrow \underset{\text{Formamide}}{HCONH_2} + H_2O$$

(v) Reducing properties : Like aldehydes, formic acid behaves as a reducing agent. It is oxidised to an unstable acid, carbonic acid, which decomposes into CO_2 and H_2O.



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{[O]} \underset{\text{Carbonic acid}}{HO-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \longrightarrow CO_2 + H_2O$$

(a) It decolourises acidified potassium permanganate solution and turns $K_2Cr_2O_7$ solution green.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$[HCOOH + O \longrightarrow CO_2 + H_2O] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5HCOOH \longrightarrow K_2SO_4 + 2MnSO_4 + 5CO_2 + 8H_2O$$

(b) It reduces mercuric chloride to mercurous chloride which change to mercury black.

$$HCOOH + \underset{\text{Mercuric chloride}}{2HgCl_2} \longrightarrow \underset{\text{(White ppt.)}}{Hg_2Cl_2} + CO_2 + 2HCl$$

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Mercurous chloride}}{Hg_2Cl_2} \longrightarrow CO_2 + 2HCl + \underset{\substack{\text{Mercury}\\ \text{(black)}}}{2Hg}$$

(c) It reduces ammoniacal silver nitrate (Tollens' reagent).

$$HCOOH + Ag_2O \xrightarrow{\text{Heat}} \underset{\text{Silver mirror}}{2Ag} + CO_2 + H_2O$$

(d) It reduces Fehling's solution, *i.e.*, gives red precipitate of cuprous oxide.

$$HCOOH + 2CuO \longrightarrow \underset{\text{Red ppt.}}{Cu_2O} + CO_2 + H_2O$$

Uses : Formic acid is used,

(i) in the laboratory for preparation of carbon monoxide.
(ii) in the preservation of fruits.
(iii) in textile dyeing and finishing.
(iv) in leather tanning.
(v) as a coagulating agent for rubber latex.
(vi) as an antiseptic and in the treatment of gout.
(vii) in the manufacture of plastics and water proofing compounds.
(viii) in electroplating to give proper deposits of metals.
(ix) in the preparation of nickel formate which is used as a catalyst in the hydrogenation of oils.
(x) as a reducing agent.
(xi) in the manufacture of oxalic acid.
(xii) as a strong irritant.

Tests of Formic Acid

(i) It turns blue litmus red.

(ii) Its aqueous solution gives effervescences with sodium bicarbonate.

(iii) Its neutral solution gives red precipitate with Fehling's solution.

(iv) Its neutral solution with Tollens' reagent gives silver mirror or a black precipitate.

(v) It gives white precipitate with mercuric chloride which changes to grey.

$$HgCl_2 \longrightarrow \underset{\text{White ppt.}}{Hg_2Cl_2} \longrightarrow \underset{\text{Grey}}{Hg}$$

(vi) When heated with conc. sulphuric acid, it evolves CO which burns with blue flame on the mouth of the test tube.

(vii) Its neutral solution gives greenish-blue colour when treated with sodium bisulphite and sodium nitroprusside solution.

(viii) On adding a freshly prepared ferric chloride solution to a neutral solution of the acid, a red colour is produced which changes to a brown precipitate on heating.

12.10 ACETIC ACID, ETHANOIC ACID, CH_3COOH

Acetic acid is the oldest known fatty acid. It is the chief constituent of vinegar and hence its name (Latin; *acetum* = vinegar). In free state, it occurs in a number of fruit juices, which have undergone fermentation and have turned sour. In the combined state, it is present in biological fluids and plant extracts. Acetic acid was the first organic compound, synthesised in the laboratory from its elements by Kolbe in 1844.

Preparation : It can be prepared by any of the general methods described in **section 12.4.**

Manufacture of Acetic acid

(i) **From pyroligneous acid** (An old method)

(ii) **From ethyl alcohol** (Quick Vinegar process)

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + O_2 \xrightarrow[\text{Bacteria}]{\textit{Mycoderma aceti}} \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

It is a slow process and takes about 8 to 10 days for completion.

(iii) Modern Methods:

(a) From acetylene : Acetylene is first converted into acetaldehyde by passing through 40% sulphuric acid at 60°C in presence of 1% $HgSO_4$ (catalyst).

$$\underset{\text{Acetylene}}{HC{\equiv}CH} + H_2O \xrightarrow[HgSO_4]{H_2SO_4\,(\text{dil.})} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

The acetaldehyde is oxidised to acetic acid by passing a mixture of acetaldehyde vapour and air over manganous acetate at 70°C.

$$2CH_3CHO + O_2 \xrightarrow[70^\circ C]{\text{Manganous acetate}} 2CH_3COOH$$

In the laboratory, it can be prepared by:

$$CH_3CHO \xrightarrow[{[O]}]{Na_2Cr_2O_7/H_2SO_4} CH_3COOH$$

$$2CH_3CHO + O_2 \xrightarrow[\text{or cobalt acetate at } 80^\circ C]{\text{Pt. black}} 2CH_3COOH$$

Note : Acetylene required for this purpose is obtained by action of water on calcium carbide.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

The yield is very good and the strength of acid prepared is 97%. The method is also quite cheap.

(b) By air oxidation of *n*-butane : The oxidation of butane is done by air at 200°C in presence of catalyst cobalt acetate, $(CH_3COO)_2Co$. The butane required for this purpose is obtained from petroleum.

$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} + O_2 \xrightarrow[200^\circ C]{(CH_3COO)_2Co} \underset{\text{Acetic acid}}{CH_3COOH}$$

Besides acetic acid, formic acid, propionic acid and acetone are also formed.

(c) By the action of CO on methyl alcohol : Methyl alcohol and carbon monoxide react together under a pressure of 30 atmospheres and 200°C in presence of a catalyst cobalt octacarbonyl, $Co_2(CO)_8$ to form acetic acid.

$$\underset{\text{Methyl alcohol}}{CH_3OH} + CO \xrightarrow[30\text{ atm. }200^\circ C]{Co_2(CO)_8} \underset{\text{Acetic acid}}{CH_3COOH}$$

Physical properties : (i) At ordinary temperature, acetic acid is a colourless, corrosive liquid with a sharp pungent odour of vinegar. It has a sour taste.

(ii) Below 16.5°C, it solidifies as an icy mass, hence it is named glacial acetic acid.

(iii) It boils at 118°C and is miscible with water, alcohol and ether in all proportions.

(iv) It is a good solvent for phosphorus, sulphur, iodine and many organic compounds.

Chemical properties : Acetic acid is a typical member of fatty acids. It shows all the general characteristics of monocarboxylic acids (see **Section 12.6**).

Uses : Acetic acid is used:

(i) as a solvent and a laboratory reagent.

(ii) as vinegar for table purpose and for manufacturing pickles.

(iii) in coagulation of rubber latex.

(iv) for making various organic compounds such as acetone, acetic anhydride, acetyl chloride, acetamide and esters.

(v) for making various useful metallic acetates, such as:

(a) basic copper acetate which is used for making green paints.

(b) Al, Fe and Cr acetates which are used as mordants in dyeing.

(c) lead tetra-acetate which is a good oxidising agent.

(d) basic lead acetate which is used in the manufacture of white lead.

(e) aluminium acetate which is used in the manufacture of water-proof fabrics.

(f) alkali acetates which are used as diuretics.

(vi) for making cellulose acetate which is required for the manufacture of artificial silk and celluloid.

(vii) for making various dyestuffs, perfumes and medicines.

Tests : (i) Its aqueous solution turns blue litmus red.

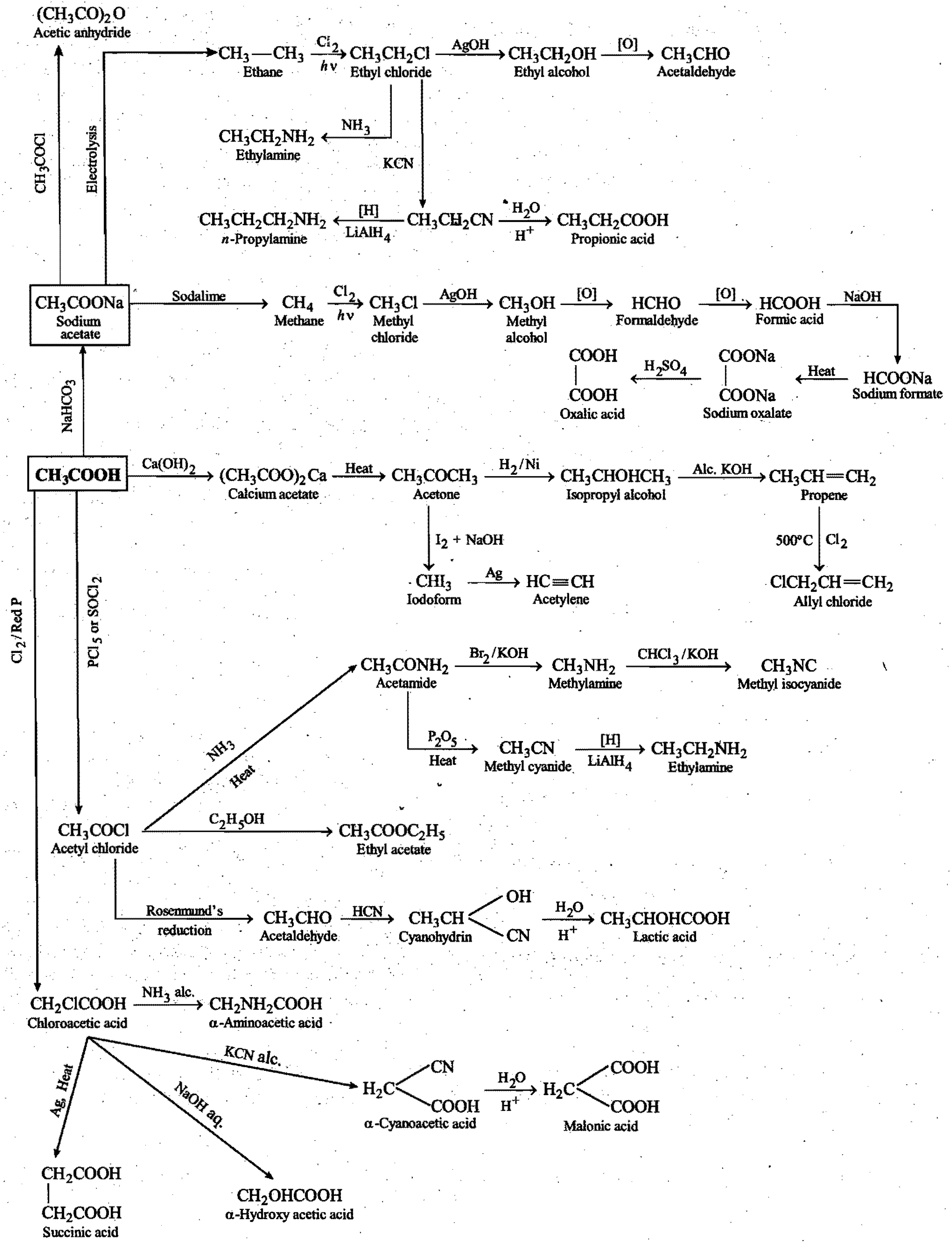
(ii) Its aqueous solution gives effervescences with sodium bicarbonate.

(iii) The neutral solution of the acetic acid gives a wine red colour with neutral ferric chloride solution.

(iv) When heated with ethyl alcohol in presence of a small amount of concentrated sulphuric acid, it forms ethyl acetate which has a fruity smell.

(v) Acetic acid does not show reducing properties like formic acid, *i.e.*, it does not reduce Tollens' reagent, Fehling's solution and mercuric chloride.

Conversion of Acetic acid into other Organic Compounds



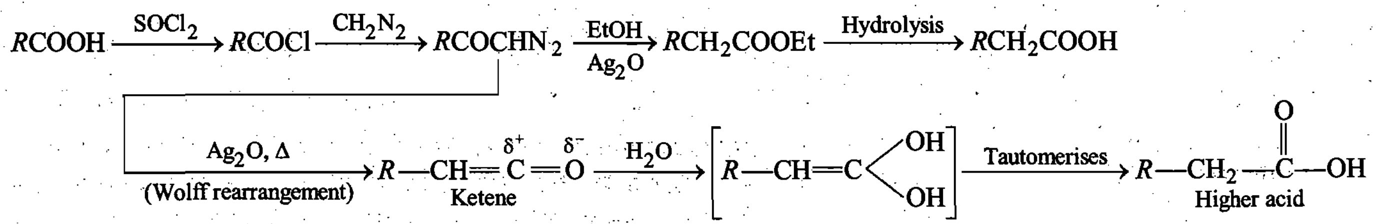
12.11 INTERCONVERSIONS

1. Ascent of series : Conversion of formic acid into acetic acid.

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium formate}}{(HCOO)_2Ca} \xrightarrow{\text{Heat}} \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{CH_3MgBr} \underset{\text{Addition product}}{CH_3CH_2OMgBr} \xrightarrow[H^+]{H_2O} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{H_2/Ni} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{HI} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{KCN(Alc.)} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[H^+]{H_2O} \underset{\text{Acetic acid}}{CH_3COOH}$$

Arndt-Eistert homologation : This is a convenient method of converting an acid, *R*COOH into its next higher homologue, *R*CH$_2$COOH.



$$RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{CH_2N_2} RCOCHN_2 \xrightarrow[Ag_2O]{EtOH} RCH_2COOEt \xrightarrow{\text{Hydrolysis}} RCH_2COOH$$

$$RCOCHN_2 \xrightarrow[\text{(Wolff rearrangement)}]{Ag_2O,\ \Delta} \underset{\text{Ketene}}{R—CH{=}\overset{\delta^+}{C}{=}\overset{\delta^-}{O}} \xrightarrow{H_2O} \left[R—CH{=}C(OH)_2\right] \xrightarrow{\text{Tautomerises}} \underset{\text{Higher acid}}{R—CH_2—\overset{\overset{O}{\|}}{C}—OH}$$

2. Descent of series : Conversion of acetic acid into formic acid.

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[H_2SO_4]{N_3H} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{NaNO_2/HCl} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{[O]} \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{[O]} \underset{\text{Formic acid}}{HCOOH}$$

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Methylamine}}{CH_3NH_2}$$

$$CH_3COOH \xrightarrow{NaOH} \underset{\text{Sodium acetate}}{CH_3COONa} \xrightarrow[\text{Heat}]{\text{Soda lime}} \underset{\text{Methane}}{CH_4} \xrightarrow[h\nu]{Cl_2} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow{AgOH} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow[Na_2Cr_2O_7\,+\,H_2SO_4]{[O]} \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{[O]} \underset{\text{Formic acid}}{HCOOH}$$

SOME SOLVED PROBLEMS

Problem 1. *Convert acetic acid to propionic acid.*

Solution :

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} \underset{\text{Sodium acetate}}{CH_3COONa} \xrightarrow{\text{Electrolysis}} \underset{\text{Ethane}}{C_2H_6} \xrightarrow[h\nu]{Cl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl}$$

$$\underset{\text{Ethyl chloride}}{C_2H_5Cl} \xrightarrow{KCN(alc.)} \underset{\text{Ethyl cyanide}}{C_2H_5CN} \xrightarrow[H^+]{H_2O} \underset{\text{Propionic acid}}{C_2H_5COOH}$$

Problem 2. *Convert propionic acid to acetic acid.*

Solution :

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow{NaOH} \underset{\text{Sodium propionate}}{CH_3CH_2COONa} \xrightarrow[\text{Heat}]{\text{Soda lime}} \underset{\text{Ethane}}{CH_3CH_3}$$

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[h\nu]{Cl_2} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow{AgOH} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

or

$$CH_3CH_2COOH \xrightarrow[H_2SO_4]{N_3H} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[HCl]{NaNO_2} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

Problem 3. *Account for the following:*

(*a*) *Boiling points of carboxylic acids are higher than those of corresponding alcohols.*

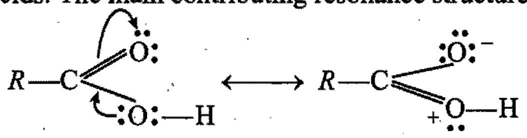
(*b*) *The* C—O *bond in* RCOOH *is shorter than in R*—OH.

(*c*) *Acetic acid in the vapour state has a molecular mass of* 120.

Solution : (a) The intermolecular hydrogen bonding and dipole-dipole attraction are greater in carboxylic acids and exists as a dimer than in alcohols.

These forces are responsible for higher boiling points of carboxylic acids.

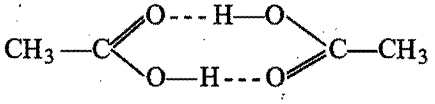
(b) Resonance exists in carboxylic acids. The main contributing resonance structures are:



(I) (II)

(II) Resonance structure suggests that there is some double bond character in C—O bond of the acid. This is responsible for the shorter bond length of C—O bond in *R*COOH.

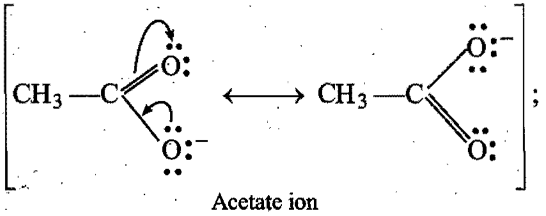
(c) Acetic acid undergoes intermolecular hydrogen bonding and exists as a dimer.



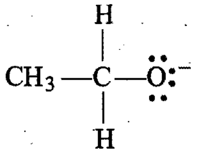
Thus, the molecular mass of acetic acid is 120 in vapour state.

Problem 4. *Explain : (a) Acetic acid is a stronger acid than ethyl alcohol. (b) Trichloro acetic acid is a stronger acid than acetic acid.*

Solution : (a) Acetic acid is a stronger acid than ethyl alcohol because the acetate ion formed by ionisation is stabilized by resonance while the ethoxide ion has no resonance. The negative charge in acetate ion is delocalized over two oxygen atoms while the negative charge in ethoxide ion is localized on the single oxygen atom.



Acetate ion
(Resonance structure)



Ethoxide ion
(No resonance is present)

Hence, CH_3COO^- ion is more stable and a weaker base than $CH_3CH_2O^-$ ion. As a weaker base has a stronger conjugate acid, CH_3COOH is a stronger acid than CH_3CH_2OH.

(b) Electron withdrawing substituents decrease the negative charge on the carboxylate ion and stabilise it, *i.e.*, loss of proton becomes relatively easy. Three chlorine atoms are electron withdrawing substituents in trichloro acetic acid and thus, it is a stronger acid than acetic acid.

Problem 5. *How will you obtain?*

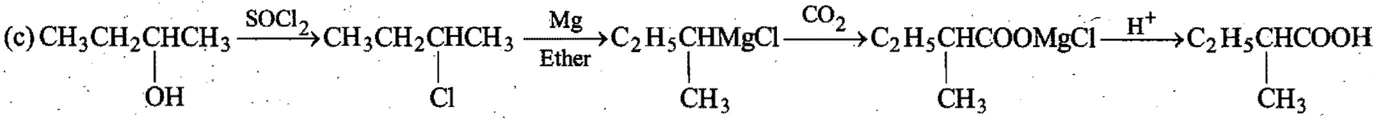
(*a*) *Butanoic acid from* 1-*bromopropane,* (*b*) *Propanoic acid from ethyne,*

(*c*) 2-*Methyl butanoic acid from butan*-2-*ol,* (*d*) *Butanoic acid from ethyl bromide.*

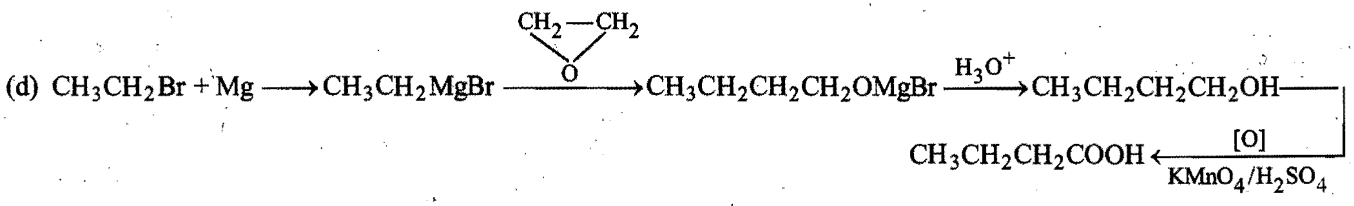
Solution : (a) $CH_3CH_2CH_2Br \xrightarrow{KCN} CH_3CH_2CH_2CN \xrightarrow{H_3O^+} CH_3CH_2CH_2COOH$

or $CH_3CH_2CH_2Br \xrightarrow[\text{Ether}]{Mg} CH_3CH_2CH_2MgBr \xrightarrow{CO_2} CH_3CH_2CH_2COOMgBr \xrightarrow{H^+} CH_3CH_2CH_2COOH$

(b) $HC{\equiv}CH \xrightarrow[Hg^{2+}]{HCl} H_2C{=}CHCl \xrightarrow[\text{Ether}]{Mg} H_2C{=}CHMgCl \xrightarrow{CO_2} H_2C{=}CHCOOMgCl \xrightarrow{H^+} H_2C{=}CHCOOH \xrightarrow{H_2/Pd} CH_3CH_2COOH$



(c) $\underset{\displaystyle OH}{CH_3CH_2\overset{}{C}HCH_3} \xrightarrow{SOCl_2} \underset{\displaystyle Cl}{CH_3CH_2CHCH_3} \xrightarrow[\text{Ether}]{Mg} \underset{\displaystyle CH_3}{C_2H_5CHMgCl} \xrightarrow{CO_2} \underset{\displaystyle CH_3}{C_2H_5CHCOOMgCl} \xrightarrow{H^+} \underset{\displaystyle CH_3}{C_2H_5CHCOOH}$



(d) $CH_3CH_2Br + Mg \longrightarrow CH_3CH_2MgBr \xrightarrow{\overset{CH_2—CH_2}{O}} CH_3CH_2CH_2CH_2OMgBr \xrightarrow{H_3O^+} CH_3CH_2CH_2CH_2OH \xrightarrow[KMnO_4/H_2SO_4]{[O]} CH_3CH_2CH_2COOH$

Problem 6. (*a*) *Write a note on Hell-Volhard-Zelinsky (HVZ) reaction.*

(*b*) *Write a short note on Koch reaction.*

Solution : (a) When a carboxylic acid that contains α-hydrogen atoms is treated with chlorine or bromine in presence of phosphorus, the α-hydrogen atoms are replaced by halogen atoms. This reaction is called Hell-Volhard-Zelinsky (HVZ) reaction. This reaction is used for the synthesis of α-substituted carboxylic acids.

$$CH_3COOH \xrightarrow[(P)]{Cl_2} ClCH_2COOH + HCl$$

$$R\overset{\alpha}{C}H_2COOH + Cl_2 \xrightarrow[(P)]{h\nu} RCH(Cl)COOH \rightarrow RC(Cl_2)COOH$$

(b) This reaction is used for the conversion of alkenes into monocarboxylic acids. When a mixture of alkene, carbon monoxide and steam is heated under pressure at 350°C in presence of *ortho* phosphoric acid (H_3PO_4), monocarboxylic acid is formed.

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + CO + H_2O \xrightarrow[\text{Pressure, 350°C}]{H_3PO_4} \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

Problem 7. *Arrange the following in order of increasing acidity:*

(*i*) HCOOH, $ClCH_2COOH$, CH_3COOH

(*ii*) CH_3COOH, $(CH_3)_2CHCOOH$, $(CH_3)_3CCOOH$

(*iii*) $ClCH_2COOH$, $Cl_2CHCOOH$, Cl_3CCOOH

(*iv*) $ClCH_2COOH$, CH_3CH_2COOH, $ClCH_2CH_2COOH$, $(CH_3)_2CHCOOH$, CH_3COOH

(*v*) CH_3COOH, $Cl_2CHCOOH$, CH_3CH_2COOH, Cl_3CCOOH, $ClCH_2COOH$

(*vi*) $HClO$, $HClO_2$, $HClO_3$, $HClO_4$. **[IIT 2001]**

Solution : (i) $CH_3COOH < HCOOH < ClCH_2COOH$

(ii) $(CH_3)_3CCOOH < (CH_3)_2CHCOOH < CH_3COOH$

(iii) $ClCH_2COOH < Cl_2CHCOOH < Cl_3CCOOH$

(iv) $(CH_3)_2CHCOOH < CH_3CH_2COOH < CH_3COOH < ClCH_2CH_2COOH < ClCH_2COOH$

(v) $CH_3CH_2COOH < CH_3COOH < ClCH_2COOH < Cl_2CHCOOH < Cl_3CCOOH$

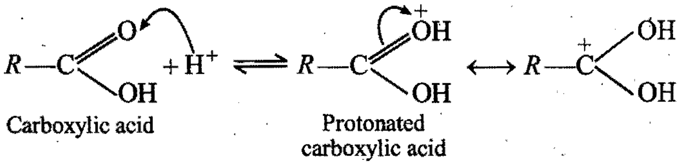
(vi) $HClO < HClO_2 < HClO_3 < HClO_4$.

Problem 8. *Explain the mechanism of esterification of carboxylic acids.*

Solution : Mechanism of esterification of carboxylic acids : It is a kind of nucleophilic acyl substitution. The mechanism of esterification involves the following steps:

Step I. *Protonation of the carbonyl group.*

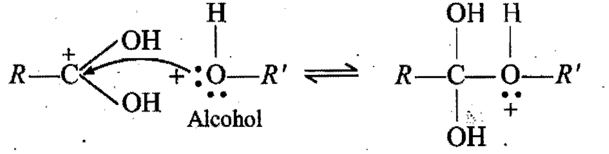
In presence of mineral acids (conc. H_2SO_4 or HCl gas), the carbonyl oxygen of carboxylic acid accepts a proton to form protonated carboxylic acid (I).



(I)

Step II. *Nucleophilic attack by the alcohol molecule.*

The electron rich oxygen atom of alcohol molecule attaches itself at positively charged carbon atom to form tetrahedral intermediate (II).

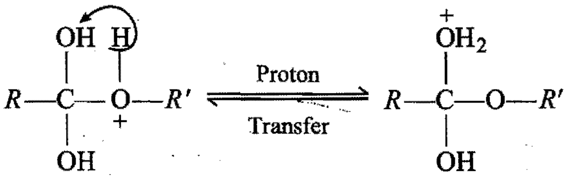


Tetrahedral intermediate

(II)

Step III. *Transfer of proton.*

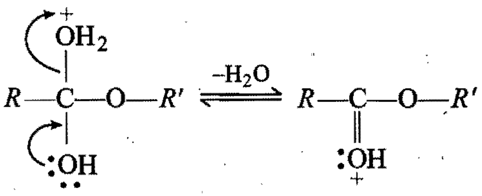
From the resulting intermediate, a proton shifts to —OH and forms another tetrahedral intermediate (III).



(III)

Step IV. *Loss of water molecule.*

The intermediate (III) loses a molecule of water to afford protonated ester (IV).



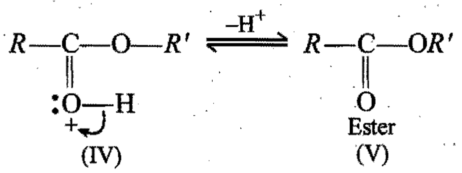
(III)

Protonated ester

(IV)

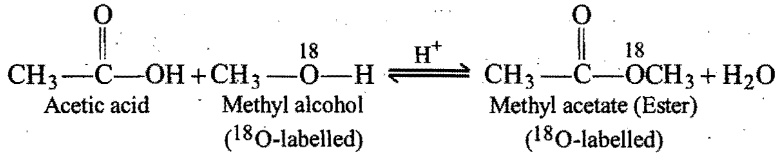
Step V. *Loss of proton.*

The protonated ester finally loses a proton to form an ester (V).

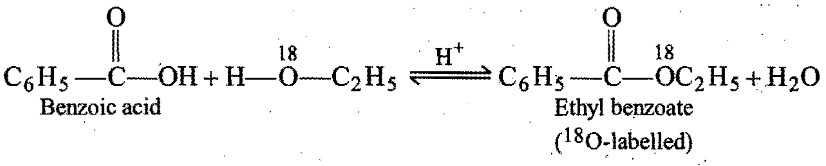


$$\underset{\text{(IV)}}{R{-}\overset{\overset{+}{:O}{-}H}{C}{-}O{-}R'} \xrightleftharpoons{-H^+} \underset{\text{Ester (V)}}{R{-}\underset{\underset{O}{\|}}{C}{-}OR'}$$

The mechanism is supported by the isotropic tracer studies that esterification involves the cleavage of H of O—H bond of alcohols and —OH of —CO—OH bond of carboxylic acids as suggested by the above mechanism. For example, when acetic acid is esterified with isotopically labelled methanol ($CH_3{}^{18}OH$), the ester (*i.e.*, methyl acetate) thus formed was found to contain ^{18}O while water formed did not have any isotopic oxygen.



$$\underset{\text{Acetic acid}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH} + \underset{\substack{\text{Methyl alcohol}\\(^{18}\text{O-labelled})}}{CH_3{-}\overset{18}{O}{-}H} \xrightleftharpoons{H^+} \underset{\substack{\text{Methyl acetate (Ester)}\\(^{18}\text{O-labelled})}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}\overset{18}{O}CH_3} + H_2O$$

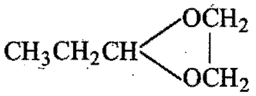


$$\underset{\text{Benzoic acid}}{C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}OH} + H{-}\overset{18}{O}{-}C_2H_5 \xrightleftharpoons{H^+} \underset{\substack{\text{Ethyl benzoate}\\(^{18}\text{O-labelled})}}{C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}\overset{18}{O}C_2H_5} + H_2O$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. What is obtained when acetic acid is heated with chlorine in presence of red phosphorus? **[BVP (Med.) 2004]**
(a) Acetyl chloride (b) α-Chloroacetic acid
(c) Trichloroacetic acid (d) Chloral
[**Ans.** (b)]
[**Hint:** HVZ reaction]

2. $CH_3CH_2COOH \xrightarrow{SOCl_2} (A) \xrightarrow[\text{(Tert. but. oxide)}]{LiAlH_4} (B) \xrightarrow{HOCH_2{-}CH_2OH} (C)$ **[PMT (Raj.) 2004]**
What is *C* ?
(a)



$CH_3CH_2CH\langle{}^{OCH_2}_{OCH_2}$ (b) CH_3CH_2COCl
(c) $CH_3CH_2CH_2NH_2$ (d) None of these
[**Ans.** (a)]

3. Which of the following acids cannot be prepared from Grignard reagents?
(a) Acetic acid (b) Propionic acid
(c) Formic acid (d) Isobutyric acid
[**Ans.** (c)]

4. Carboxylic acid undergoes ionization due to:
(a) hydrogen bonding
(b) absence of α-hydrogen
(c) high reactivity of α-hydrogen
(d) resonance stabilization of carboxylate ion
[**Ans.** (d)]
[**Hint:** Resonance energy of carboxylate ion is much higher than that of undissociated acid.]

5. What will be the final product (*B*) in the given reaction ?
$$HC{\equiv}CH \xrightarrow{HgSO_4/H_2SO_4} (A) \xrightarrow{[O]} (B)$$
(a) CH_3COOH (b) $HCOOH$
(c) CH_3CH_2OH (d) CH_4
[**Ans.** (a)]

6. Which of the following compounds is the strongest acid? **[AMU (Engg.) 2004]**
(a) $HCOOH$ (b) CH_3COOH
(c) $Cl_2CHCOOH$ (d) C_6H_5COOH
[**Ans.** (c)]

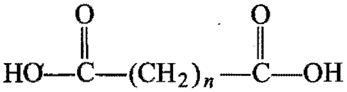
7. Aqueous 10% $NaHCO_3$ solution is used as a reagent for identifying *X*. Which one of the following compounds yields *X* on hydrolysis? **[EAMCET (Med.) 2004]**
(a) $CH_3CO_2C_2H_5$ (b) $C_2H_5{-}O{-}C_2H_5$
(c) CH_3CHO (d) CH_3CH_2OH
[**Ans.** (a)]
[**Hint:** Acetic acid liberates CO_2 gas on reaction with 10% $NaHCO_3$ solution. Ethyl acetate hydrolyses to give acetic acid.]

8. The compounds formed at anode in the electrolysis of an aqueous solution of potassium acetate are: **[EAMCET (Med.) 2005]**
(a) C_2H_6 and CO_2 (b) C_2H_4 and CO_2
(c) CH_4 and H_2 (d) CH_4 and CO_2
[**Ans.** (a)]

9. Which of the following is an unsaturated fatty acid?
   (a) Lauric acid (b) Linolic acid
   (c) Stearic acid (d) Palmitic acid
   [Ans. (b)]

12.12 DICARBOXYLIC ACIDS

The acids containing two carboxylic groups are called dicarboxylic acids. Both the carboxylic groups are present at the end carbon atoms of the carbon chain. The **saturated** dicarboxylic acids are represented by the general formula $C_nH_{2n}(COOH)_2$ where $n = 0, 1, 2, 3$, etc.



$$\mathrm{HO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_n{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH} \quad \text{or} \quad \mathrm{HOOC(CH_2)_nCOOH}$$

The dicarboxylic acids are generally called by their common names. The common names are usually based on their source from which they are obtained, *e.g.*, oxalic acid as it is found in plants of oxalis group.

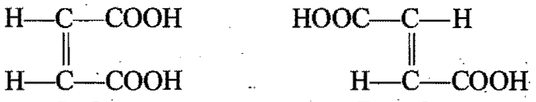
According to IUPAC system, the suffix-dioic acid is added to the name of the parent alkane, *i.e.*, **Alkanedioic acids.** The formulae and names of some lower members are given below:

Formula	**Common name**	**IUPAC name**
HOOC—COOH	Oxalic acid	Ethane-1,2-dioic acid
$HOOCCH_2COOH$	Malonic acid	Propane-1,3-dioic acid
$HOOCCH_2CH_2COOH$	Succinic acid	Butane-1,4-dioic acid
$HOOC(CH_2)_3COOH$	Glutaric acid	Pentane-1,5-dioic acid
$HOOC(CH_2)_4COOH$	Adipic acid	Hexane-1,6-dioic acid

10. Which type of organic compound is most resistant to oxidation by acidified potassium dichromate?
    (a) Alkene (b) Alcohol
    (c) Aldehyde (d) Acid
    [Ans. (d)]

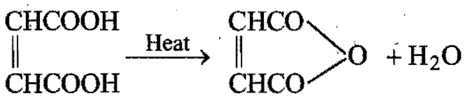
Unsaturated Dicarboxylic Acids

The molecular formula of the simplest unsaturated dicarboxylic acid is HOOC—CH═CH—COOH. This formula, however, represents two chemical compounds, maleic acid and fumaric acid, which are geometrical isomers.



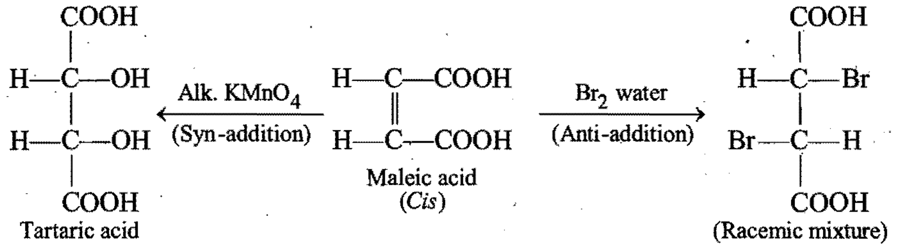
Cis-form (Maleic acid) *Trans*-form (Fumaric acid)

Chemically, both the acids give the reactions of alkenes and dibasic acids except that the maleic acid on heating forms an anhydride while fumaric acid does not give anhydride.

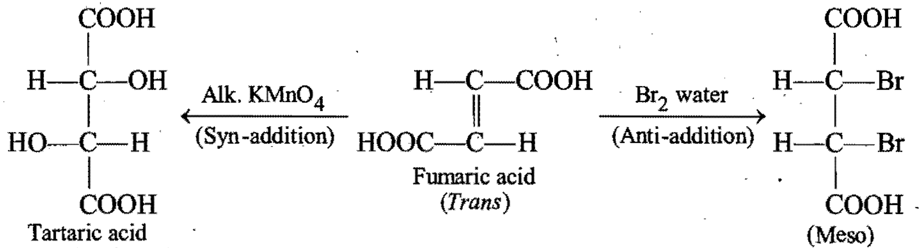


Maleic acid Maleic anhydride

Both form succinic acid on reduction with sodium amalgam. They undergo addition reactions with bromine, hydrobromic acid, water, etc., and form salts, esters and acid chlorides as usual. With alkaline $KMnO_4$ solution, they get oxidised to tartaric acid.



Tartaric acid (Meso) Maleic acid (*Cis*) (Racemic mixture)



Tartaric acid (Racemic mixture) Fumaric acid (*Trans*) (Meso)

12.13 HIGHER FATTY ACIDS

Palmitic, stearic and **oleic acids** are found in natural fats and oils as glyceryl esters. They have derived their names from the natural source from which they are prepared by hydrolysis with alkali.

Palmitic acid takes its name from **Palm oil,** stearic acid from **Stear** (meaning tallow) and oleic acid from **Olive oil.** The molecular formulae of these acids are:

Palmitic acid	$CH_3(CH_2)_{14}COOH$	Saturated acid
Stearic acid	$CH_3(CH_2)_{16}COOH$	Saturated acid
Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Unsaturated acid

Palmitic and stearic acids are waxy colourless solids with melting points 64°C and 72°C, respectively. They are insoluble in water but soluble in ethanol and ether. They find use in the manufacture of soaps and candles. Soaps contain sodium or potassium salts of these higher fatty acids.

Oleic acid has low melting point, *i.e.*, 16°C. It is insoluble in water but soluble in alcohol and ether. Besides the reactions of acids, it also gives reactions of alkenes. Two aldehydes are formed on ozonolysis.

$$\underset{\text{Oleic acid}}{CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH} \xrightarrow[\text{(ii) Zn + H}_2\text{O}]{\text{(i) O}_3} CH_3(CH_2)_7CHO + HOOC(CH_2)_7CHO$$

It is used for making soaps, lubricants and detergents.

SOME SOLVED PROBLEMS

Problem 9. *How will you distinguish between:*

(*a*) *Formic acid and acetic acid?*

(*b*) *Oxalic acid and acetic acid?*

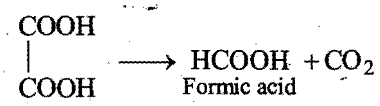
(*c*) *Succinic acid and oxalic acid?*

Solution : (a) (i) Formic acid produces silver mirror with ammoniacal silver nitrate solution. Acetic acid does not give this test.

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Tollens' reagent}}{2Ag(NH_3)_2NO_3} \longrightarrow \underset{\text{Silver mirror}}{2Ag} + CO_2 + 2NH_4NO_3 + 2NH_3$$

(ii) Formic acid forms a white precipitate with $HgCl_2$ solution. Acetic acid does not respond to this test.

(b) (i) Oxalic acid when heated decomposes and evolves CO_2. The gas when passed through lime water forms a white precipitate.



$$\begin{matrix}COOH\\ |\\ COOH\end{matrix} \longrightarrow \underset{\text{Formic acid}}{HCOOH} + CO_2$$

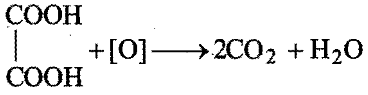
Oxalic acid

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

Acetic acid does not give this test.

(ii) Oxalic acid acts as a reducing agent. The decolourisation of acidified $KMnO_4$ solution occurs when oxalic acid is added to it and the solution is warmed. This test is also not given by acetic acid.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$



$$\begin{matrix}COOH\\ |\\ COOH\end{matrix} + [O] \longrightarrow 2CO_2 + H_2O$$

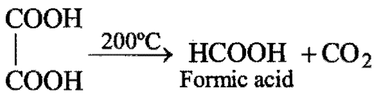
iii) Oxalic acid is a solid while acetic acid is a liquid with characteristic odour.

(c) Both the chemical tests used in part (b) of this question can also be employed to make distinction between oxalic acid and succinic acid.

Problem 10. *Compare the products formed on heating the following dicarboxylic acids:*

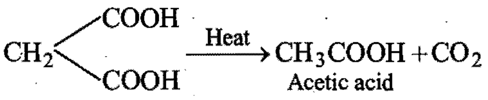
(*a*) *Oxalic acid*, (*b*) *Malonic acid*, (*c*) *Succinic acid*, (*d*) *Adipic acid.*

Solution : (a) Oxalic acid on heating loses a molecule of CO_2 and is converted into formic acid.



$$\begin{matrix}COOH\\ |\\ COOH\end{matrix} \xrightarrow{200°C} \underset{\text{Formic acid}}{HCOOH} + CO_2$$

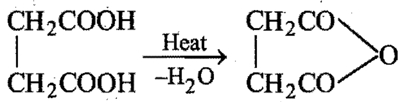
(b) Malonic acid, on heating undergoes decarboxylation.



$$CH_2(COOH)_2 \xrightarrow{\text{Heat}} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

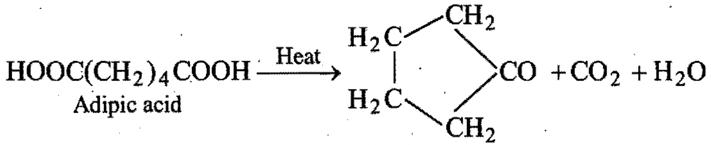
Malonic acid

(c) Succinic acid forms anhydride by eliminating a water molecule.



Succinic acid Succinic anhydride

(d) Adipic acid on heating at 300°C is converted into a cyclic compound, *i.e.*, cyclopentanone.

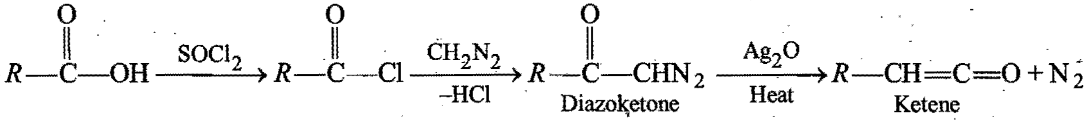


Adipic acid

Cyclopentanone

Problem 11. *Using diazomethane (CH_2N_2) and any other appropriate reagents how can RCOOH be converted into:*
(*a*) $R-CH_2COOH$ (*b*) $R-COCH_2Cl$ (*c*) $R-COCH_2NH_2$ (*d*) $R-CH_2COOC_2H_5$ (*e*) $R-COCH_2OH$

Solution : Diazomethane is used in the **Arndt-Eistert synthesis.** This is a method of converting an acid (aliphatic, aromatic, alicyclic or heterocyclic) into the next higher homologue.



$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SOCl_2} R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[-HCl]{CH_2N_2} \underset{\text{Diazoketone}}{R-\overset{O}{\overset{\|}{C}}-CHN_2} \xrightarrow[\text{Heat}]{Ag_2O} \underset{\text{Ketene}}{R-CH=C=O} + N_2$$

This rearrangement of diazoketone is called **Wolff rearrangement.**

(a) When the rearrangement of diazoketone is carried out in the presence of water, a carboxylic acid is formed.

$$\underset{\text{Ketene}}{R-CH=C=O} + H_2O \xrightarrow{\text{Heat}} R-CH_2COOH$$

(b)
$$\underset{\text{Diazoketone}}{RCOCHN_2} + HCl \longrightarrow \underset{\text{Chloromethyl ketone}}{RCOCH_2Cl} + N_2$$

(c)
$$RCOCHN_2 + NH_3 \xrightarrow[\text{Catalyst}]{Ag_2O} \underset{\text{Amide}}{RCH_2CONH_2} + N_2$$

(d)
$$RCOCHN_2 + C_2H_5OH \xrightarrow{Ag_2O} \underset{\text{Ester}}{RCH_2COOC_2H_5} + N_2$$

(e)
$$RCOCHN_2 + H_2O \xrightarrow[\text{Heat}]{HCOOH} \underset{\text{Hydroxy methyl ketone}}{RCOCH_2OH} + N_2$$

Problem 12. *Write down structure of that dicarboxylic acid which on reaction with alk. $KMnO_4$ gives meso tartaric acid.*

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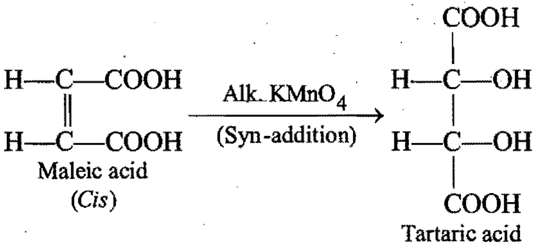
Solution :



Maleic acid (*Cis*)

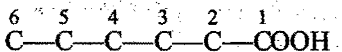
Tartaric acid (meso)

12.14 SUBSTITUTED CARBOXYLIC ACIDS

The compounds formed by the replacement of one or more hydrogen atoms of the hydrocarbon chain part of the carboxylic acids by atoms or groups such as *X* (halogen), OH or NH_2, are referred to as substituted acids.

For example,	$CH_2ClCOOH$	$CH_2OHCOOH$	CH_2NH_2COOH
	Chloroacetic acid	Hydroxy acetic acid	Amino acetic acid

The position of the substituents on the carbon chain are indicated by Greek letters or numbers.



$$\underset{\varepsilon}{\overset{6}{C}}—\underset{\delta}{\overset{5}{C}}—\underset{\gamma}{\overset{4}{C}}—\underset{\beta}{\overset{3}{C}}—\underset{\alpha}{\overset{2}{C}}—\overset{1}{COOH}$$

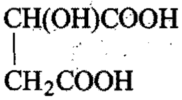
For example, $CH_3\overset{\alpha}{C}HOHCOOH$; $CH_3\overset{\beta}{C}HOHCH_2COOH$

α-Hydroxy propionic acid, 2-Hydroxy propanoic acid ; β-Hydroxy butyric acid, 3-Hydroxy butanoic acid

The following are important hydroxy acids.

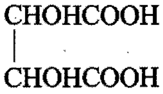
$CH_2OHCOOH$; Glycollic acid

$CH_3CHOHCOOH$; Lactic acid



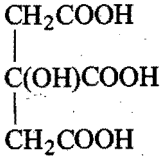
$CH(OH)COOH—CH_2COOH$;

Malic acid



$CHOHCOOH—CHOHCOOH$;

Tartaric acid

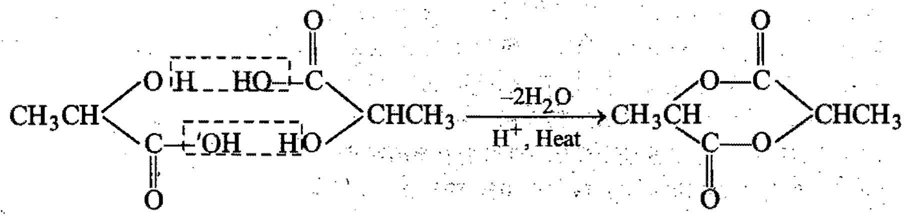


$CH_2COOH—C(OH)COOH—CH_2COOH$

Citric acid

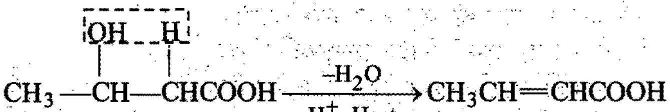
Hydroxy acids when heated in presence of a little mineral acid (HCl or H_2SO_4) yield a number of products depending on the distance between OH and COOH groups.

Alpha hydroxy acids form an intermolecular cyclic diester called a **lactide.**



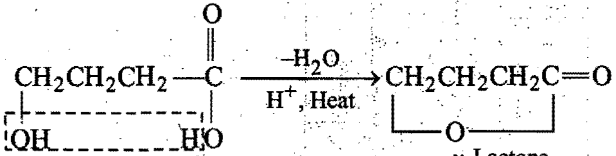
Lactic acid Lactide

Beta hydroxy acids form **unsaturated acids.**



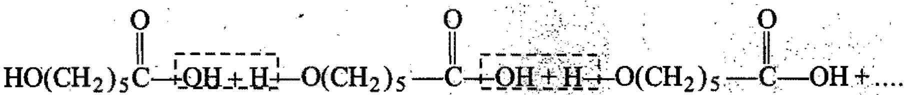
β-Hydroxy butyric acid Crotonic acid

Gamma and delta hydroxy acids form internal esters known as **lactones.**



γ-Hydroxy butyric acid γ-Lactone

Epsilon and longer hydroxy acids form linear polymers.



Polymer

IMPORTANT POINTS TO REMEMBER (SUMMARY)

☐ Organic compounds containing carboxylic $\left(-\overset{\overset{\displaystyle O}{\|}}{C}-OH\right)$ functional group are called **carboxylic acids.** The —COOH group has its own distinctive properties and has no relation with $>C=O$ and —OH compounds.

☐ Carboxylic acids are further classified as mono, di and tri carboxylic acids depending on the number of —COOH groups present in the molecule.

☐ Monocarboxylic acids of aliphatic series are commonly called as **fatty acids** because the higher members of homologues series (palmitic acid, stearic acid, oleic acid) are obtained from fats.

☐ The saturated monocarboxylic acids are the first oxidation products of aldehydes or second oxidation products of *p*-(1°) alcohols or third oxidation products of alkanes.

☐ *R*COOH are also called **monoprotic acids** because they give one proton in solution or due to one ionisable H-atom, they are also called as **monobasic acids.**

☐ **Isomerism :** Monocarboxylic acids show **chain isomerism** (due to the difference in the structure of C-chain) and **functional isomerism** (with esters of the acids, hydroxy carbonyl compounds and hydroxy oxiranes).

General methods of preparation

☐ **By Oxidation of alcohols, aldehydes and ketones :** Using oxidising agents $K_2Cr_2O_7/H_2SO_4$(dil.) or alkaline $KMnO_4$ or air in presence of catalyst. Aldehydes can be oxidised to corresponding carboxylic acid even with mild oxidising agents such as ammoniacal $AgNO_3$ (Tollens' reagent).

☐ Ketones and 2° alcohols can also form acids with less number of C-atoms. Oxidation of ketone occurs with difficulty using strong oxidising agents like acidified $K_2Cr_2O_7$. CrO_3, H_2SO_4 in acetone solution selectively oxidise 1° alcohols to —COOH and 2° alcoholic group to ketone respectively without affecting $-C\equiv C-$ and $>C=C<$.

☐ MnO_2 in acetone selectively oxidises 1° alcohols to aldehydes.

☐ **By hydrolysis of alkane nitriles :** Compounds containing a—CN group can be hydrolysed to —COOH group in presence of H^+ (HCl or H_2SO_4) or with alkali.

☐ **By hydrolysis of terminal trihaloalkanes :** With an aqueous alkali solution.

☐ **By hydrolysis of esters :** With a mineral acid or alkali.

☐ **By hydrolysis of amides, anhydrides and acid halides :** With a boiling dil. acid or alkali.

☐ **By carbonation of Grignard reagents :** When CO_2 (solid ice) is passed through an etheral solution of $R-MgX$, an addition product is formed which on hydrolysis with a mineral acid yields a carboxylic acid.

☐ **By gem-dicarboxylic acids :** On heating eliminates a molecule of CO_2 to give monocarboxylic acid.

☐ **From alkenes (By carbonylation) :** A mixture of an alkene, CO and steam is heated under pressure at 350°C in presence of catalyst H_3PO_4, monocarboxylic acid is formed. This reaction is called **Koch reaction.**

☐ **By heating sodium alkoxide with CO :** Sodium salt of the fatty acid is obtained which on treatment with an acid yields a fatty acid.

☐ **By oxidation of higher alkanes :** Long chain hydrocarbons on oxidation with manganous stearate at 100–160°C give long chain fatty acids. Neo-alkanes can be oxidised by conc. HNO_3.

☐ **By oxidation of alkenes and alkynes :** Using oxidising agents such as acidified or hot alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$. Oxidative cleavage takes place to form monocarboxylic acids.

☐ **By oxidation of methyl ketones :** With X_2/NaOH followed by hydrolysis, methyl ketones can be converted into carboxylic acids through the haloform reaction.

☐ **From malonic ester or acetoacetic ester :** On hydrolysis with conc. alcoholic KOH yields fatty acids.

Physical properties

☐ First three members (C_1–C_3) have a sharp pungent odour. The middle ones (C_4–C_9) have an odour of rancid butter. The lower members are highly soluble in water but the solubility decreases with increase in molecular mass. The solubility in water is due to the formation of H-bonds with water.

☐ Boiling points of carboxylic acids are higher than those of alcohols of same molecular mass. This is due to intermolecular H-bonding between two acid molecules (Dimers). The lower members exist as dimers in vapour phase and in aqueous solution, but in the liquid phase they exist as polymers.

Acidity of carboxylic acids

☐ The acidic character decreases with the rise of molecular weight. HCOOH is the strongest acid of all fatty acids. Thus, the acidity of carboxylic acid is due to powerful resonance stabilization of the anion.

☐ Electron attracting group (**–*I* effect**) stabilises the anion and therefore increases ionization of the acid. The greater is the –*I* effect, greater will be the acidic strength, *i.e.*,
$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$
and

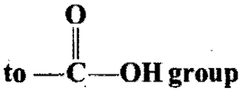
$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$ (because F > Cl > Br > I).

☐ Inductive effect is stronger at α-position than β-position and than γ-position.

☐ Electron releasing group (**+*I* effect**) destabilises the anion and so decreases the acidity, *i.e.*,

$$HCOOH > CH_3COOH > CH_3CH_2COOH > (CH_3)_2CH—COOH > (CH_3)_3C—COOH$$

Chemical properties



(1) Reactions due to $—\overset{O}{\overset{\|}{C}}—OH$ group

(a) Reactions involving proton (removal of H-atom of —OH group) :

☐ **Salt formation :** Monocarboxylic acids react with Na, K, NaOH, $NaHCO_3$ or Na_2CO_3, etc., with the evolution of hydrogen and form corresponding salt.

☐ **Reaction with organometallic reagents :** *R*COOH reacts with *R*′Mg*X* (GR) rapidly to give an alkane (*R*′H) corresponding to the alkyl group of Grignard reagent.

(b) Reactions involving —OH group:

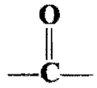
☐ **Ester formation :** *R*COOH reacts with *R*OH in presence of dehydrating agents like conc. H_2SO_4 or dry HCl gas, to form esters.

☐ **Formation of acid chlorides :** By the action of PCl_5, PCl_3, $SOCl_2$/pyridine or Cl_2/Br_2 in presence of red P on carboxylic acids, acid halides are formed.

☐ **Formation of acid anhydrides :** Dehydration of monocarboxylic acids on heating with P_2O_5 gives acid anhydride or when sodium salt of acid is heated with acid chloride, acid anhydrides are formed.

☐ **Formation of amides and nitriles :** Monocarboxylic acids on treatment with NH_3 form ammonium salts which on heating lose a molecule of water to form corresponding amides.

☐ The acid amide ($RCONH_2$) on heating with P_2O_5 loses one more water molecule forming a cyanide (*R*CN) or nitrile.



(c) Reactions involving $—\overset{O}{\overset{\|}{C}}—$ (carbonyl) group:

☐ **Reduction to alcohols :** Reduction products depend on the nature of reducing agent. By using $LiAlH_4$(LAH) in ether solution or ruthenium (Ru) and carbon as catalyst, the —COOH group is reduced to $—CH_2OH$ (1° alcohol). BH_3/THF or H_2 in presence of copper chromite ($CuO + Cr_2O_3$) also reduces —COOH into $—CH_2OH$.

(d) Reactions involving —COOH group as a whole:

☐ **Decarboxylation :** On heating anhydrous salt of acid with sodalime, forms an alkane with the elimination of CO_2. When sodium formate is heated with sodalime, hydrogen is evolved.

☐ **By dry distillation of calcium salts of monocarboxylic acids :** Calcium acetate gives acetone and calcium formate gives formaldehyde. However, when a mixture of calcium acetate and calcium formate is heated, acetaldehyde is formed.

☐ By passing the vapours of fatty acids over MnO at 300°C or Al_2O_3 at 400°C similar aldehydes and ketones are obtained.

☐ **By Kolbe's electrolytic reaction :** Electrolysis of Na or K salts (concentrated aqueous solution) of fatty acids yields alkanes.

☐ **By Borodine Hunsdiecker reaction :** An alkyl halide is formed when the silver salt of monocarboxylic acid is heated with halogens.

☐ **By Schmidt reaction :** Monocarboxylic acids react with hydrazoic acid (N_3H) in presence of conc. H_2SO_4 to give a primary amine containing one C-atom less than the parent acid.

☐ **Reaction with diazomethane (CH_2N_2) :** Diazomethane undergoes condensation with fatty acids to give methyl ester with the evolution of N_2.

☐ **Reaction with ketene ($CH_2C{=}O$) :** Forms acid anhydride.

☐ **Reduction to alkanes :** On heating with conc. HI and red P at 200°C or catalytic reduction, the —COOH converts into $—CH_3$ to form an alkane.

☐ **Arndt-Eistert reaction :** This reaction is a method for converting an acid *R*COOH to a homologous series, RCH_2COOH and its derivatives such as esters and amides. In this reaction, *R*—COCl from *R*—COOH is converted to RCH_2COOH (by hydrolysis), RCH_2COOR' (by reacting with $R'OH/Ag_2O$) and RCH_2CONHR (by reacting with $R'NH_2/Ag_2O$).

(2) Reactions due to *R* (alkyl) group

☐ **Halogenation :** The α-hydrogen atoms are highly reactive due to the presence of electronegative —COOH group. On halogenation (Cl_2 or Br_2) in presence of a catalyst (red P or Fe, etc.,), the α-H atoms are replaced by chlorine or bromine atoms. The reaction occurs in presence of sunlight or on boiling. This reaction is known as **Hell-Volhard-Zelinsky (HVZ) reaction.**

☐ Direct iodination can be done in presence of an oxidising agent like HIO_3 or HgO.

☐ **Oxidation :** Carboxylic acids having at least one β-hydrogen convert into β-hydroxy carboxylic acids on oxidation with H_2O_2. Oxidation of α-**methylene** group takes place by SeO_2 to give α-keto acid.

QUESTIONS

❖ Very Short Answer Type

1. Fill in the blanks:
   - (a) Formic acid when heated with conc. H_2SO_4 produces ....
   - (b) Formic acid is .... acid than acetic acid.
   - (c) Formic acid .... Tollens' reagent.
   - (d) K_a value of chloroacetic acid is .... than the K_a value of acetic acid.
   - (e) Oxalic acid when heated with glycerol at 110°C forms ....
   - (f) Oxalic acid is a .... carboxylic acid.
   - (g) .... acetic acid is called glacial acetic acid.
   - (h) .... is formed when acetic acid is heated with phosphorus pentoxide.
   - (i) Sucrose on heating with concentrated nitric acid forms ....
   - (j) When carbon monoxide is passed on NaOH under pressure, the compound formed is ....
   - (k) Sodium formate when heated, forms ....
   - (l) Neutral solution of acetic acid gives .... colour with neutral ferric chloride.
   - (m) $LiAlH_4$ reduces acetic acid to ....
   - (n) Electrolysis of an aqueous solution of sodium propionate will form ....
   - (o) Ethanoic acid when reacted with sodium carbonate liberates ....
   - (p) Propionic acid and ethyl formate are .... isomers.
   - (q) Acid hydrolysis of alkyl nitriles gives ....
   - (r) The reaction in which an alkene is converted to monocarboxylic acid with CO and steam in presence of H_3PO_4 is called ....
   - (s) Substitution of chlorine in the alkyl group of a carboxylic acid ....the strength of the acid.
   - (t) Monocarboxylic acids have higher boiling points than the corresponding alcohols due to ....
   - (u) Carboxylic acids can be obtained from the reaction of carbon dioxide and ....
   - (v) Malonic acid on heating yields ....
   - (w) The formula of the main product obtained when PCl_5 reacts with acetic acid is ....
   - (x) Kolbe's electrolysis of ....produces *n*-hexane on anode.
   - (y) In Hell-Volhard-Zelinsky reaction the carboxylic acids are halogenated at the ....position by using .... and ....
   - (z) Ammonium salts of carboxylic acids on heating form ....
2. State whether the following statements are **True** or **False:**
   - (a) Monocarboxylic acids are called fatty acids.
   - (b) The IUPAC name of acetic acid is methanoic acid.
   - (c) Formic acid is not the typical acid of the monocarboxylic acids series.
   - (d) Acetic acid like formic acid shows reducing properties.
   - (e) Oxalic acid is non-poisonous in nature.
   - (f) Calcium oxalate is soluble in acetic acid.
   - (g) Hydrolysis of an ester in presence of a dilute acid is known as saponification.
   - (h) When some insect like honey-bee bites, irritation is felt due to formic acid.
   - (i) Formic acid undergoes halogenation.
   - (j) Methyl formate is the isomer of acetic acid.
   - (k) Oxalic acid is used for the removal of ink and rust stains.
   - (l) Hell-Volhard-Zelinsky reaction is given by those acids which have α-hydrogen atoms.
   - (m) The boiling point of propionic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular mass.
   - (n) Acetyl chloride on heating with anhydrous sodium acetate forms acetic anhydride.
   - (o) A carboxylic acid shows the reactions of carbonyl group also.
   - (p) Acetic acid exists as a dimer in vapour state.
   - (q) 2-Chloropropanoic acid is weaker than 3-chloropropanoic acid.
   - (r) Formic acid is decomposed into carbon monoxide and H_2O when treated with conc. H_2SO_4.
   - (s) Formic acid when heated with P_2O_5 forms an anhydride.
   - (t) Formic acid is the only acid which gives reactions of a carboxylic acid as well as an aldehyde.
   - (u) Acetate ion is a stronger base than methoxide ion.
   - (v) All the C—O bond lengths in carboxylate ions are identical.
   - (w) Formic acid acts as a reducing agent while acetic acid does not show this property.
   - (x) Lower carboxylic acids are highly soluble in water.
   - (y) Highly branched carboxylic acids are more acidic than unbranched acids.
   - (z) The reaction between an acid and alcohol is termed saponification.
3. Match the following:

(A) Acetic acid	(1) Soda lime	(M) $ClCH_2COOH$
(B) Formic acid	(2) Poisonous	(N) Dicarboxylic acid
(C) Decarboxylation	(3) Phosphorus	(O) Soap
(D) Hell-Volhard-Zelinsky reaction	(4) Kolbe's synthesis	(P) Fermentation of sugar

(E) Oxalic acid
(F) Electrolysis of CH_3COOK
(G) $CH_3COOC_2H_5 + NaOH$
(H) Formic acid + conc. H_2SO_4

(5) Saponification
(6) Vinegar
(7) Dehydration
(8) Red ants

(Q) Carbon monoxide
(R) Alkane
(S) Reducing acid
(T) Ethane

4. Write the final product in the following reactions:

(i) $CH_3COOH \xrightarrow[\text{Ether}]{LiAlH_4}$

(ii) $CH_3COOH \xrightarrow[H_2SO_4]{N_3H}$

(iii) $CH_3COONa \xrightarrow[\text{Heat}]{CH_3COCl}$

(iv) $CH_3COONa \xrightarrow[\text{Heat}]{\text{Soda lime}}$

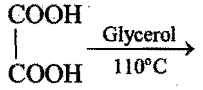
(v) $CH_3COOK \xrightarrow{\text{Electrolysis}}$

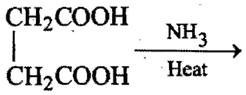
(vi) $(CH_3COO)_2Ca \xrightarrow{\text{Heat}}$

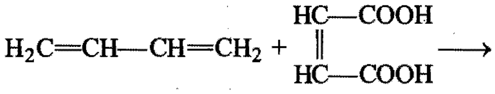
(vii) $(CH_3COO)_2Ca \xrightarrow[\text{Heat}]{(HCOO)_2Ca}$

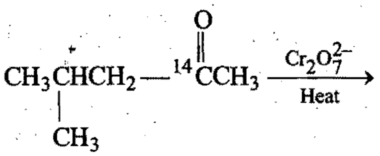
(viii) $CH_3COONH_4 \xrightarrow{\text{Heat}}$

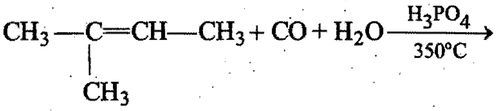
(ix) $NaOH + CO \xrightarrow[\text{8 to 10 atm.}]{210°C}$

(x)

$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow[110°C]{\text{Glycerol}}$

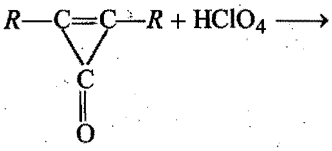
(xi)

$\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} \xrightarrow[\text{Heat}]{NH_3}$

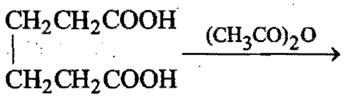
(xii)

$H_2C{=}CH{-}CH{=}CH_2 + \begin{matrix} HC{-}COOH \\ \| \\ HC{-}COOH \end{matrix} \longrightarrow$

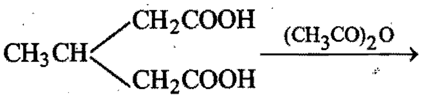
(xiii)

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2{-}{}^{14}\overset{\displaystyle O}{\overset{\|}{C}}CH_3 \xrightarrow[\text{Heat}]{Cr_2O_7^{2-}}$

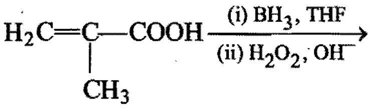
(xiv)

$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_3 + CO + H_2O \xrightarrow[350°C]{H_3PO_4}$

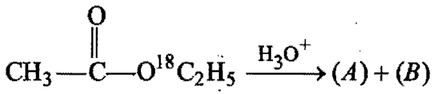
(xv) $HOOC{-}COOH + HOCH_2{-}CH_2OH \xrightarrow{\text{Heat}}$

(xvi)

$+ HClO_4 \longrightarrow$

(xvii)

$\begin{matrix} CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \end{matrix} \xrightarrow{(CH_3CO)_2O}$

(xviii)

$\xrightarrow{(CH_3CO)_2O}$

(xix)

$H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}COOH \xrightarrow[\text{(ii) } H_2O_2,\, OH^-]{\text{(i) } BH_3,\, THF}$ **[Roorkee 2001]**

(xx)

$CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O^{18}C_2H_5 \xrightarrow{H_3O^+} (A) + (B)$ **[IIT 2000]**

5. Complete the following equations by writing the missing (*A*), (*B*), (*C*), (*D*), etc.:

(i) $\underset{\text{Ethylene}}{H_2C{=}CH_2} \xrightarrow{HBr} (A) \xrightarrow{KCN} (B) \xrightarrow{H_2O/H^+} (C)$

(ii) $\underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{PCl_5} (A) \xrightarrow{KCN} (B) \xrightarrow{H_2O/H^+} (C)$

$\xrightarrow{NH_3} (D) \xrightarrow{\text{Heat}} (E)$

(iii) $\underset{\text{Methyl magnesium bromide}}{CH_3MgBr} \xrightarrow{CO_2} (A) \xrightarrow{H_2O} (B) \xrightarrow[\text{Ether}]{LiAlH_4} (C)$

(iv) $\underset{\text{Acetylene}}{HC{\equiv}CH} \xrightarrow[HgSO_4]{\text{Dil. } H_2SO_4} (A) \xrightarrow{[O]} (B) \xrightarrow{SOCl_2} (C)$

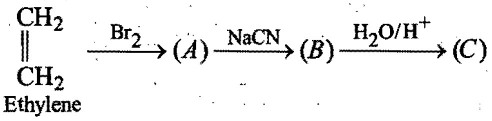
(v) $\underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} (A) \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} (B)$

$\xrightarrow{NaHCO_3} (C) \xrightarrow{\text{Soda lime}} (D)$

(vi) $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} (A) \xrightarrow{\text{Heat}} (B) \xrightarrow{KCN} (C)$

$\xrightarrow[H^+]{H_2O} (D)$

(vii) $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[(P)]{Cl_2} (A) \xrightarrow{NaCN} (B) \xrightarrow{H_2O/H^+} (C)$

(viii)

$\underset{\text{Ethylene}}{\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}} \xrightarrow{Br_2} (A) \xrightarrow{NaCN} (B) \xrightarrow{H_2O/H^+} (C)$

(ix) $CH_3CHO \xrightarrow{HCN} (A) \xrightarrow{H_2O/H^+} (B) \xrightarrow[H_2SO_4]{K_2Cr_2O_7} (C)$

(x) $CH_3COCl \xrightarrow{Pd/BaSO_4} (A) \xrightarrow{K_2CO_3} (B) \xrightarrow{\text{Heat}} (C)$

(xi) $CH_3CH_2COOH \xrightarrow{P/Br_2} (A) \xrightarrow[\text{(ii) } H^+]{\text{(i) Alc. KOH(excess)}} (B)$

(xii) $(A) \xrightarrow{PCl_5} (B) \xrightarrow{LiAlH_4} (C) \xrightarrow{HBr/H_2SO_4} (D)$

$\xrightarrow[\text{Ether}]{Na} CH_3CH_2CH_2CH_3$

(xiii) $HC{\equiv}CH \xrightarrow[\text{(ii) } 2CH_3I]{\text{(i) } 2NaNH_2} (A) \xrightarrow[H_2SO_4]{HgSO_4} (B) \xrightarrow{I_2/NaOH} (C)$

(xiv) $$\begin{tikzcd} CH_3CH_2MgBr + (A) \arrow[r] & CH_3CH_2CH_2CH_2OMgBr \arrow[d, "H_3O^+"] \\ & (B) \xrightarrow{KMnO_4} (C) \end{tikzcd}$$

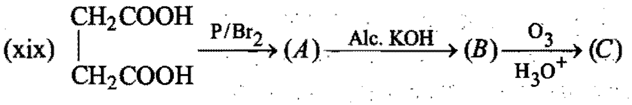
(xv) $CH_3COOH \xrightarrow{PBr_3/Br_2} (A) \xrightarrow{KCN} (B) \xrightarrow{H_3O^+} (C)$

(xvi) $H_2C{=}CHCH{=}CH_2 \xrightarrow{HBr} (A) \xrightarrow[\text{(ii) } CO_2/H_3O^+]{\text{(i) Mg/Ether}} (B)$

(xvii) $CH_3COOH \xrightarrow[\text{Excess}]{\text{Red P, } Br_2} (A) \xrightarrow[H_3O^+]{KOH} (B)$

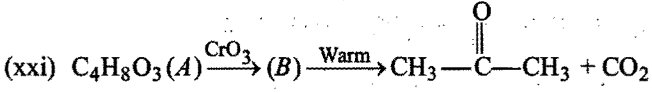
$\xrightarrow[260°C]{\text{Glycerol}} (C)$

(xviii) $C_8H_{10}(A) \xrightarrow[H_3O^+]{O_3} 2C_3H_5COOH\,(B)$


(xix) $\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} \xrightarrow{P/Br_2} (A) \xrightarrow{\text{Alc. KOH}} (B) \xrightarrow[H_3O^+]{O_3} (C)$

(xx) $CH_3COOH \xrightarrow{SOCl_2} (A) \xrightarrow[BaSO_4]{H_2/Pd} (B) \xrightarrow[\text{Heat}]{\text{Dil. NaOH}} (C)$

$\xrightarrow{Ag_2O} (D)$


(xxi) $C_4H_8O_3(A) \xrightarrow{CrO_3} (B) \xrightarrow{\text{Warm}} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + CO_2$

(xxii) $HC{\equiv}CH \xrightarrow{CH_3MgBr} CH_4 + (A) \xrightarrow{CO_2} (B) \xrightarrow{H^+} (C)$

$\xrightarrow[HgSO_4]{H_2SO_4} (D)$

(xxiii) $(B) \xleftarrow[H_2O]{HCrO_4} (A) \xrightarrow[\text{Pyridine}]{CrO_3} CH_3CHO$

[Roorkee 2000]

6. What happens when?

(i) Formic acid is heated with conc. H_2SO_4.
(ii) Dry chlorine is passed through acetic acid in presence of sunlight.
(iii) Oxalic acid is heated with glycerol.
(iv) Formic acid is reacted with ammoniacal silver nitrate solution.
(v) Acetic acid is heated with phosphorus pentoxide.
(vi) Formic acid is heated with Fehling's solution.
(vii) Ammonium acetate is dry distilled.
(viii) Acidified potassium permanganate is added to oxalic acid.
(ix) Oxalic acid is heated.
(x) Maleic acid is heated.
(xi) A carboxylic acid is treated with lithium aluminium hydride.
(xii) Acetic acid reacts with thionyl chloride.
(xiii) Tartaric acid is treated with hydrogen iodide.
(xiv) Lactic acid is heated.
(xv) Citric acid is refluxed with hydriodic acid.

❖ Short Answer Type

7. Give the structural formulae, common names and IUPAC names for the first six straight chain aliphatic carboxylic acids.

8. Define the term fatty acids. Give the common and IUPAC names for the following fatty acids:
(i) $CH_3(CH_2)_{14}COOH$,
(ii) $CH_3(CH_2)_{16}COOH$,
(iii) $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

9. Give the common and IUPAC names of the dicarboxylic acids, $HOOC(CH_2)_nCOOH$, $n = 0, 1, 2, 3, 4$ and 5.

10. How will you obtain formic acid from the following reagents?
(a) Formaldehyde, (b) Oxalic acid, (c) Carbon monoxide, (d) Acetic acid.

11. How will you obtain acetic acid from the following reagents?
(a) Methyl cyanide, (b) Methyl magnesium bromide, (c) Acetylene, (d) Malonic acid, (e) Ethyl alcohol.

12. Suggest five possible compounds from which $(CH_3)_2CHCOOH$ can be prepared in good yield by oxidation.

13. How would you distinguish between:
(a) solutions of acetic acid, formic acid and ethanol?
(b) calcium formate and calcium acetate?
(c) maleic acid and fumaric acid?
(d) acetic acid and acetone?
(e) acetic acid and acrylic acid?
(f) tartaric acid and citric acid?

14. Give two chemical tests and two uses of each of the following:
(a) Acetic acid.
(b) Formic acid.
(c) Oxalic acid.

15. How will you synthesise?
(i) Acetic acid from methyl iodide.
(ii) Iodoform from acetic acid.
(iii) Acetic acid from propionic acid.
(iv) Glycine from acetic acid.
(v) Butylamine from propionic acid.
(vi) Ethylamine from propionic acid.
(vii) α-Hydroxy propionic acid from acetaldehyde.
(viii) Acetamide from acetone.
(ix) Acetaldehyde from acetic acid.
(x) Methyl cyanide from acetic acid.
(xi) Crotonic acid from acetaldehyde.
(xii) Pyruvic acid from ethyl bromide.
(xiii) Succinic acid from ethyl bromide.
(xiv) Oxalic acid from methyl alcohol.

(xv) β-Hydroxy propionic acid from ethylene oxide.
(xvi) Tartaric acid from ethylene.
(xvii) Malonic acid from acetic acid.
(xviii) Lactic acid from acetic acid.

16. How are the following conversions made?
(i) —COOH to H
(ii) —CN to —COOH
(iii) $—CONH_2$ to $—NH_2$

17. What is the action of heat on the following?
(i) Oxalic acid, (ii) Ammonium oxalate,
(iii) Calcium formate, (iv) Calcium acetate,
(v) Sodium formate, (vi) Malonic acid,
(vii) Adipic acid, (viii) Succinic acid.

18. Arrange the following in order of increasing acidity:
(i) Propanoic acid, chloroethanoic acid, 3-bromopropanoic acid and trichloroacetic acid.
(ii) 2-Fluorobutanoic acid, 2-iodobutanoic acid, 2-bromobutanoic acid and butanoic acid.
(iii) Acetic acid, 2-methyl propanoic acid, 2,2-dimethyl propanoic acid.
(iv) Oxalic acid, malonic acid, succinic acid, glutaric acid.

19. Write short notes on the following:
(i) Decarboxylation of fatty acids.
(ii) Kolbe's synthesis.
(iii) Relative strength of the acids.
(iv) Koch reaction.
(v) Schmidt reaction.
(vi) Hunsdiecker's reaction.

20. Answer the following:
(i) Why 100% pure acetic acid is named glacial acetic acid?

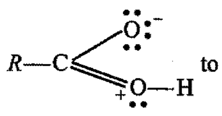
[Ans. The melting point of pure anhydrous acetic acid is 17°C. It is solid below this temperature and looks like 'icy', *i.e.*, glacial.]

(ii) What is vinegar and how is it made?

[Ans. Vinegar is 5% aqueous solution of acetic acid. It is formed by fermentation of sugars and starch. Ethanol is the intermediate product.]

(iii) Why the bond length of C=O in carboxylic acids is a bit longer than in aldehydes?

[Ans. Due to resonance, there is considerable contribution of the resonance form,



to the hybrid form, *i.e.*, there is some single bond character in C=O bond which makes it somewhat longer than in aldehydes.]

(iv) Why the C=O in *R*COOH is less reactive towards nucleophiles than in aldehydes and ketones?

[Ans. In *R*COOH, there is less positive charge on carbon atom of the C=O group. Thus, this carbon is less electrophilic in *R*COOH in comparison to aldehydes and ketones and so is less reactive towards nucleophiles.]

21. Account for the following:
(a) Carboxylic acids with five or fewer carbon atoms are water soluble but, higher ones are insoluble.

[Ans. The solubility of *R*COOH in water is due to hydrogen bonding of —COOH group and water. *R*-portion being lyophobic resists solubility. As *R* gets large, this factor prevails over the first factor and thus, higher acids become insoluble.]

(b) Highly branched carboxylic acids are less acidic than unbranched acids.

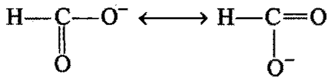
[Ans. The —COOH group of the branched acid is shielded from solvent molecules and cannot be stabilized by solvation as effectively as unbranched acid like the acetate anion.]

(c) Acetic acid can be halogenated in presence of phosphorus and chlorine but formic acid cannot be halogenated in the same way.

[Ans. This is HVZ reaction. It occurs only in those carboxylic acids which have α-hydrogen atoms. Acetic acid possesses three α-hydrogen atoms but formic acid does not have even a single α-hydrogen atom. Thus, formic acid does not undergo this reaction.]

(d) Carbon-oxygen bond lengths in formic acid are 1.23 Å and 1.36 Å but in sodium formate both carbon-oxygen bonds have same value, *i.e.*, 1.27 Å.

[Ans. The formate ion present in sodium formate is a resonance hybrid of the following two structures:



$$H—\underset{\underset{O}{\|}}{C}—O^- \longleftrightarrow H—\underset{\underset{O^-}{|}}{C}=O$$

Thus, in resonance hybrid the bond length of C—O are identical. In formic acid, no such resonance exists and thus, the bond lengths are different.]

(e) Formic acid is stronger than acetic acid.

[Ans. In acetic acid, methyl group is present which exerts +*I* effect and thus increases negative charge on the carboxylate ion and destabilise it. The loss of proton becomes comparatively difficult in comparison to formic acid. Hence, acetic acid is a weaker acid than formic acid.]

(f) Fluoroacetic acid is stronger than chloroacetic acid.

[Ans. Both fluorine and chlorine are electron withdrawing substituents. However, the capacity of fluorine is more than chlorine as it is more electronegative than chlorine. The fluoroacetate ion is more stabilised and thus, fluoroacetic acid has higher tendency to lose its proton. Hence, it is a stronger acid than chloroacetic acid.]

(g) Formic acid shows reducing properties.

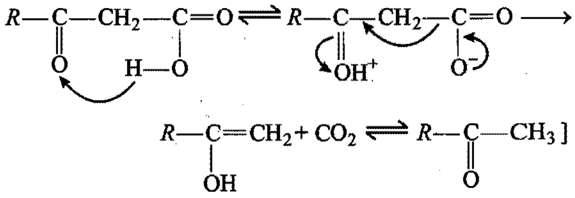
[Ans. Formic acid is easily oxidised to carbon dioxide and water and thus acts as a reducing agent.

$$HCOOH + [O] \longrightarrow H_2O + CO_2$$

It reduces Tollens' reagent, Fehling's solution and mercuric chloride solution.]

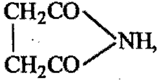
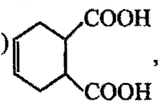
(h) β-Keto acids undergo decarboxylation easily.

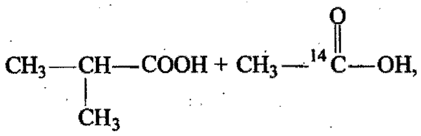
[Ans. β-Keto acids are unstable acids. These readily undergo decarboxylation through a cyclic transition state.



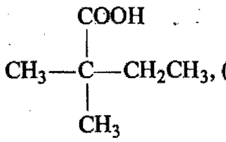
$$R—\underset{\underset{OH}{|}}{C}=CH_2 + CO_2 \rightleftharpoons R—\underset{\underset{O}{\|}}{C}—CH_3\ ]$$

ANSWERS

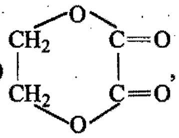
1. (a) carbon monoxide; (b) stronger; (c) reduces; (d) higher; (e) formic acid; (f) di; (g) pure or 100%; (h) acetic anhydride; (i) oxalic acid; (j) sodium formate; (k) sodium oxalate; (l) red; (m) ethyl alcohol; (n) butane; (o) carbon dioxide; (p) functional; (q) carboxylic acids; (r) Koch reaction; (s) increases; (t) intermolecular hydrogen bonding; (u) Grignard reagent; (v) acetic acid; (w) CH_3COCl; (x) potassium butyric acid; (y) alpha, phosphorus, halogen; (z) amides.
2. (a) True; (b) False—ethanoic acid; (c) True; (d) False—acetic acid does not show reducing properties; (e) False—poisonous in nature; (f) False—insoluble in acetic acid; (g) False; (h) True; (i) False; (j) True; (k) True; (l) True; (m) False—higher; (n) True; (o) False; (p) True; (q) False—stronger; (r) True; (s) False—formic acid does not form an anhydride; (t) True; (u) False—acetate ion is weaker base than methoxide ion; (v) True; (w) True; (x) True; (y) False—highly branched acids are less acidic than unbranched acids; (z) False—esterification.
3. (A—6—P); (B—8—S); (C—1—R); (D—3—M); (E—2—N); (F—4—T); (G—5—O); (H—7—Q).
4. (i) CH_3CH_2OH, (ii) CH_3NH_2, (iii) $(CH_3CO)_2O$, (iv) CH_4, (v) C_2H_6, (vi) CH_3COCH_3, (vii) CH_3CHO, (viii) CH_3CONH_2, (ix) HCOONa, (x) HCOOH, (xi)  (xii)  ,

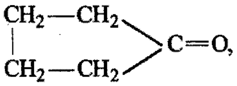
(xiii) 

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-COOH + CH_3-{}^{14}\overset{O}{\overset{\|}{C}}-OH,$$

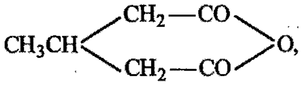
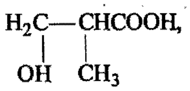
(xiv) 

$$CH_3-\underset{CH_3}{\underset{|}{\overset{COOH}{\overset{|}{C}}}}-CH_2CH_3,$$

(xv)  , (xvi) *R*COOH,

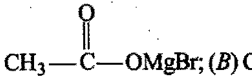
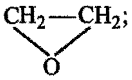
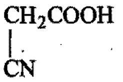
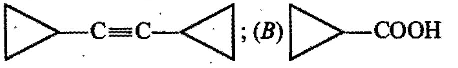
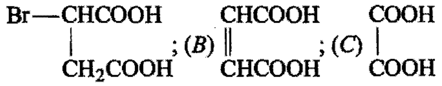
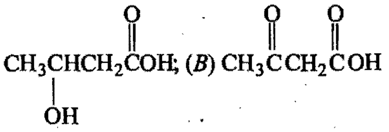
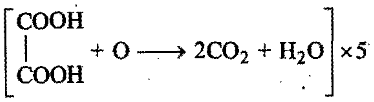
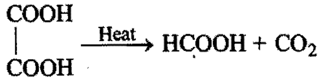
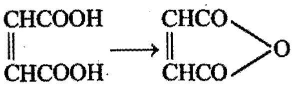
(xvii)  ,

Cyclo pentanone

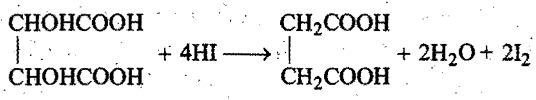
(xviii)  , (xix) 

$$\underset{OH}{\underset{|}{H_2C}}-\underset{CH_3}{\underset{|}{CHCOOH}},$$

(xx) (*A*) CH_3COOH; (*B*) $C_2H_5O^{18}H$

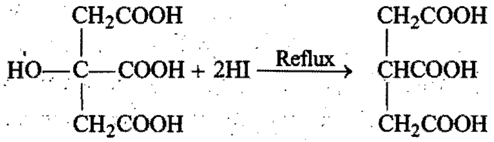
5. (i) (*A*) CH_3CH_2Br; (*B*) CH_3CH_2CN; (*C*) CH_3CH_2COOH
   (ii) (*A*) C_2H_5Cl; (*B*) C_2H_5CN; (*C*) C_2H_5COOH; (*D*) $C_2H_5COONH_4$; (*E*) $C_2H_5CONH_2$
   (iii) (*A*)  $CH_3-\overset{O}{\overset{\|}{C}}-OMgBr$; (*B*) CH_3COOH; (*C*) CH_3CH_2OH
   (iv) (*A*) CH_3CHO; (*B*) CH_3COOH; (*C*) CH_3COCl
   (v) (*A*) CH_3CHO; (*B*) CH_3COOH; (*C*) CH_3COONa; (*D*) CH_4
   (vi) (*A*) $(CH_3COO)_2Ca$; (*B*) CH_3COCH_3; (*C*) $(CH_3)_2C(OH)CN$; (*D*) $(CH_3)_2C(OH)COOH$
   (vii) (*A*) $ClCH_2COOH$; (*B*) $NCCH_2COOH$; (*C*) $CH_2(COOH)_2$ (Malonic acid)
   (viii) (*A*) $BrCH_2-CH_2Br$; (*B*) $NCCH_2-CH_2CN$; (*C*) $HOOCCH_2-CH_2COOH$ (Succinic acid)
   (ix) (*A*) $CH_3CH(OH)CN$; (*B*) $CH_3CHOHCOOH$; (*C*) $CH_3COCOOH$ (Pyruvic acid)
   (x) (*A*) CH_3CHO; (*B*) $CH_3CH(OH)CH_2CHO$; (*C*) $CH_3CH{=}CHCHO$ (Crotonaldehyde)
   (xi) (*A*) $CH_3CHBrCOOH$; (*B*) $H_2C{=}CHCOOH$
   (xii) (*A*) CH_3COOH; (*B*) CH_3COCl; (*C*) CH_3CH_2OH; (*D*) CH_3CH_2Br
   (xiii) (*A*) $CH_3C{\equiv}C-CH_3$; (*B*) $CH_3CH_2COCH_3$; (*C*) CH_3CH_2COOH
   (xiv) (*A*)  ; (*B*) $CH_3CH_2CH_2CH_2OH$; (*C*) $CH_3CH_2CH_2COOH$
   (xv) (*A*) $Br-CH_2-COOH$; (*B*)  $\underset{CN}{\underset{|}{CH_2COOH}}$; (*C*) $HOOC-CH_2COOH$
   (xvi) (*A*) $CH_3CH{=}CHCH_2Br$; (*B*) $CH_3CH{=}CHCH_2COOH$
   (xvii) (*A*) CBr_3-COOH; (*B*) $HOOC-COOH$; (*C*) $H_2C{=}CHCH_2OH$
   (xviii) (*A*) 
   (xix) (*A*)  $\begin{array}{l}Br-CHCOOH\\ \quad\ |\\ \quad CH_2COOH\end{array}$; (*B*) $\begin{array}{l}CHCOOH\\ \|\\ CHCOOH\end{array}$; (*C*) $\begin{array}{l}COOH\\ |\\ COOH\end{array}$
   (xx) (*A*) CH_3COCl; (*B*) CH_3CHO; (*C*) $CH_3CH{=}CHCHO$; (*D*) $CH_3CH{=}CHCOOH$
   (xxi) (*A*)  $CH_3\underset{OH}{\underset{|}{CH}}CH_2\overset{O}{\overset{\|}{C}}OH$; (*B*) $CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OH$
   (xxii) (*A*) $HC{\equiv}C-MgBr$; (*B*) $HC{\equiv}C-COOMgBr$; (*C*) $HC{\equiv}C-COOH$; (*D*) $OHC-CH_2COOH$
   (xxiii) (*A*) CH_3CH_2OH; (*B*) CH_3COOH
6. (i) $HCOOH \xrightarrow{H_2SO_4\,(conc.)} CO + H_2O$
   (ii) $CH_3COOH \xrightarrow[Sunlight]{Cl_2} CH_2ClCOOH$
   (iii) At 110°C, formic acid is formed. At 230°C, allyl alcohol is formed.
   (iv) $HCOOH + Ag(NH_3)_2NO_3 \longrightarrow Ag + 2NH_4NO_3 + CO_2$
   (v) $2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$
   (vi) $HCOOH + 2CuO \longrightarrow \underset{Red}{Cu_2O} + CO_2 + H_2O$
   (vii) $CH_3COONH_4 \xrightarrow{Heat} CH_3CONH_2 + H_2O$
   (viii) $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$
   
   $$\left[\begin{array}{l}COOH\\ |\\ COOH\end{array} + O \longrightarrow 2CO_2 + H_2O\right]\times 5$$
   (ix)  $\begin{array}{l}COOH\\ |\\ COOH\end{array} \xrightarrow{Heat} HCOOH + CO_2$
   (x) 
   (xi) $RCOOH + 4[H] \xrightarrow{LiAlH_4} RCH_2OH + H_2O$

(xii) $CH_3COOH \xrightarrow{SOCl_2} CH_3COCl$

(xiii) 

$$\begin{matrix} CHOHCOOH \\ | \\ CHOHCOOH \end{matrix} + 4HI \longrightarrow \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} + 2H_2O + 2I_2$$

(xiv) Lactide is formed.

(xv) 

$$HO-\overset{\displaystyle CH_2COOH}{\underset{\displaystyle CH_2COOH}{\overset{|}{\underset{|}{C}}}}-COOH + 2HI \xrightarrow{Reflux} \begin{matrix} CH_2COOH \\ | \\ CHCOOH \\ | \\ CH_2COOH \end{matrix}$$

Tricarballylic acid

7.

Formula	Common name	IUPAC name
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$CH_3CH_2CH_2CH_2COOH$	Valeric acid	Pentanoic acid
$CH_3CH_2CH_2CH_2CH_2COOH$	Caproic acid	Hexanoic acid.

8. Fatty acids are long chain aliphatic acids obtained by hydrolysis from naturally occurring oils and fats.
   (i) Palmitic or hexadecanoic acid
   (ii) Stearic or octadecanoic acid
   (iii) Oleic or *cis*-9-octadecanoic acid.

9.

Formula	Common name	IUPAC name
$HOOC—COOH$	Oxalic acid	Ethane-1,2-dioic acid
$HOOC—CH_2COOH$	Malonic acid	Propane-1,3-dioic acid
$HOOCCH_2CH_2COOH$	Succinic acid	Butane-1,4-dioic acid
$HOOC(CH_2)_3COOH$	Glutaric acid	Pentane-1,5-dioic acid
$HOOC(CH_2)_4COOH$	Adipic acid	Hexane-1,6-dioic acid
$HOOC(CH_2)_5COOH$	Pimelic acid	Heptane-1,7-dioic acid

10. See preparation of formic acid.

11. See preparation of acetic acid.

12. (a) $\underset{(i)}{(CH_3)_2CHCH_2OH} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} (CH_3)_2CHCHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7} (CH_3)_2CHCOOH$

(b) $\underset{(ii)}{(CH_3)_2CHCHO} \xrightarrow{[O]} (CH_3)_2CHCOOH$

(c) $\underset{(iii)}{(CH_3)_2CHCH{=}CHCH(CH_3)_2} \xrightarrow[Zn/H^+]{Ozonolysis} (CH_3)_2CHCHO \xrightarrow{[O]} (CH_3)_2CHCOOH$

(d) $\underset{(iv)}{(CH_3)_2CHC{\equiv}CCH(CH_3)_2} \xrightarrow[Cleavage]{Oxidative} (CH_3)_2CHCOOH$

(e) $\underset{(v)}{(CH_3)_2CHCOCH_3} \xrightarrow{NaOH/I_2} (CH_3)_2CHCOONa + CHI_3$

13. (a) Both formic and acetic acid solutions will give effervescences with $NaHCO_3$. Formic acid reduces Fehling's solution and Tollens' reagent while acetic acid do not give these tests. Ethanol neither reacts with $NaHCO_3$ nor with Fehling's solution and Tollen's reagent.

(b) Calcium formate on heating forms a gas with pungent smell. Calcium acetate on heating forms vapours of pleasant odour.

(c) Maleic acid on heating gives maleic anhydride. No anhydride is formed by fumaric acid.

(d) Acetic acid reacts with $NaHCO_3$ to give effervescence. Acetone gives iodoform test and yellow crystalline compound with 2,4-dinitrophenylhydrazine.

(e) Acrylic acid decolourises bromine water in CCl_4 and purple colour of dilute $KMnO_4$ solution. These tests are not given by acetic acid.

(f) Tartaric acid with Tollens' reagent gives silver mirror. Citric acid does not give this test.

15. (i) $CH_3I + KCN \longrightarrow CH_3CN \xrightarrow{H_2O/H^+} CH_3COOH$

(ii) $CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{Heat} CH_3COCH_3 \xrightarrow{NaOH/I_2} CHI_3$

(iii) $CH_3CH_2COOH \xrightarrow{NH_3} CH_3CH_2COONH_4 \xrightarrow{Heat} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$

$CH_3CHO \xrightarrow{[O]} CH_3COOH$

(iv) $CH_3COOH \xrightarrow[(P)]{Cl_2} CH_2ClCOOH \xrightarrow{NH_3} CH_2NH_2COOH$

(v) $CH_3CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2OH \xrightarrow{PCl_5} CH_3CH_2CH_2Cl \xrightarrow{KCN} CH_3CH_2CH_2CN \xrightarrow{Reduction} CH_3CH_2CH_2CH_2NH_2$

(vi) $CH_3CH_2COOH \xrightarrow{NH_3} CH_3CH_2COONH_4 \xrightarrow{Heat} C_2H_5CONH_2 \xrightarrow[KOH]{Br_2} C_2H_5NH_2$

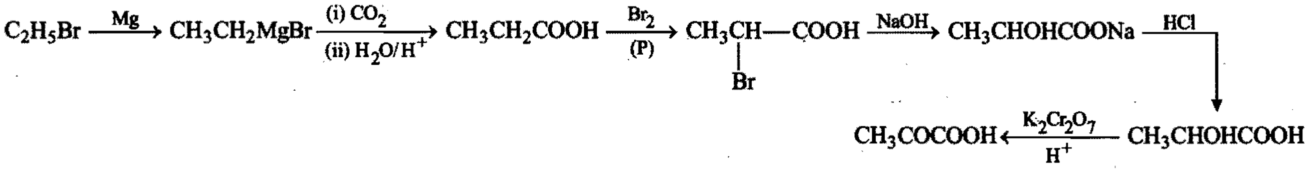
(vii) $CH_3CHO \xrightarrow{HCN} CH_3CH(OH)CN \xrightarrow[H^+]{H_2O} CH_3CHOHCOOH$

(viii) $CH_3COCH_3 \xrightarrow[NaOH]{I_2} CH_3COONa \xrightarrow{H^+} CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow{Heat} CH_3CONH_2$

(ix) $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{[O]} CH_3CHO$

(x) $CH_3COOH \longrightarrow CH_3CONH_2$ (as in viii) $\xrightarrow[Heat]{P_2O_5} CH_3CN$

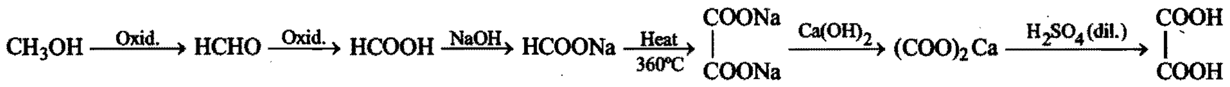
(xi) $2CH_3CHO \xrightarrow{Dil.\ NaOH} CH_3CHOHCH_2CHO \xrightarrow{Heat} CH_3CH{=}CHCHO \xrightarrow{AgNO_3} CH_3CH{=}CHCOOH$

(xii) 

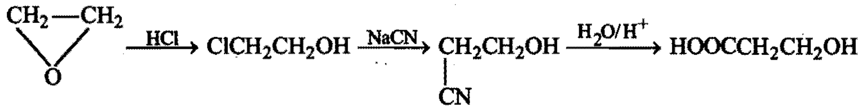
$$C_2H_5Br \xrightarrow{Mg} CH_3CH_2MgBr \xrightarrow[(ii)\ H_2O/H^+]{(i)\ CO_2} CH_3CH_2COOH \xrightarrow[(P)]{Br_2} CH_3\underset{\displaystyle Br}{\underset{|}{C}}H-COOH \xrightarrow{NaOH} CH_3CHOHCOONa \xrightarrow{HCl}$$

$$CH_3COCOOH \xleftarrow[H^+]{K_2Cr_2O_7} CH_3CHOHCOOH$$

(xiii) $C_2H_5Br \xrightarrow{Alc.\ KOH} C_2H_4 \xrightarrow{Br_2} C_2H_4Br_2 \xrightarrow{KCN} C_2H_4(CN)_2 \xrightarrow{H_2O/H^+} C_2H_4(COOH)_2$

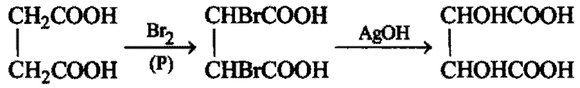
(xiv) 

$$CH_3OH \xrightarrow{Oxid.} HCHO \xrightarrow{Oxid.} HCOOH \xrightarrow{NaOH} HCOONa \xrightarrow[360°C]{Heat} \begin{matrix}COONa\\ |\\ COONa\end{matrix} \xrightarrow{Ca(OH)_2} (COO)_2Ca \xrightarrow{H_2SO_4(dil.)} \begin{matrix}COOH\\ |\\ COOH\end{matrix}$$

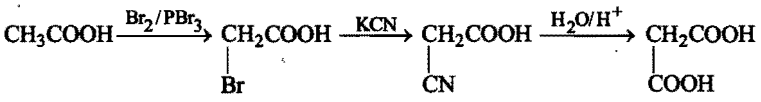
(xv) 

$$\xrightarrow{HCl} ClCH_2CH_2OH \xrightarrow{NaCN} \underset{\displaystyle CN}{\underset{|}{C}}H_2CH_2OH \xrightarrow{H_2O/H^+} HOOCCH_2CH_2OH$$

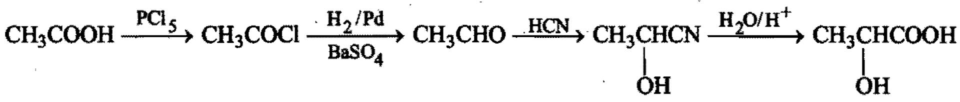
(xvi) C_2H_4 to succinic acid as in (xiii).



$$\begin{matrix}CH_2COOH\\ |\\ CH_2COOH\end{matrix} \xrightarrow[(P)]{Br_2} \begin{matrix}CHBrCOOH\\ |\\ CHBrCOOH\end{matrix} \xrightarrow{AgOH} \begin{matrix}CHOHCOOH\\ |\\ CHOHCOOH\end{matrix}$$

(xvii) 

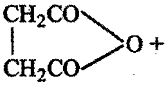
$$CH_3COOH \xrightarrow{Br_2/PBr_3} \begin{matrix}CH_2COOH\\ |\\ Br\end{matrix} \xrightarrow{KCN} \begin{matrix}CH_2COOH\\ |\\ CN\end{matrix} \xrightarrow{H_2O/H^+} \begin{matrix}CH_2COOH\\ |\\ COOH\end{matrix}$$

(xviii) 

$$CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow[BaSO_4]{H_2/Pd} CH_3CHO \xrightarrow{HCN} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCN \xrightarrow{H_2O/H^+} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCOOH$$

16. (i) Decarboxylation with soda lime, (ii) Hydrolysis in presence of acid, (iii) Hofmann bromide reaction with Br_2 and NaOH.

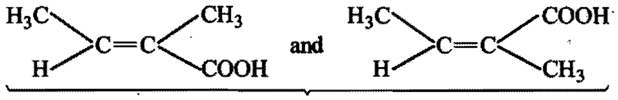
17. (i) $HCOOH + CO_2$, (ii) Oxamide + $2H_2O$, (iii) $HCHO + CaCO_3$, (iv) $CH_3CHO + CaCO_3$, (v) $(COO)_2Na_2 + H_2$, (vi) $CH_3COOH + CO_2$,

(vii) Cyclopentanone + CO_2 + H_2O, (viii)  + H_2O

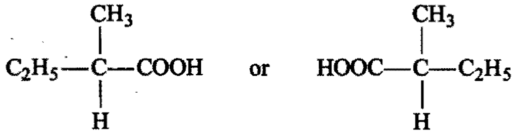
18. (i) $CH_3CH_2COOH < BrCH_2CH_2COOH < ClCH_2COOH < Cl_3CCOOH$
 (ii) $CH_3CH_2CH_2COOH < CH_3CH_2CHICOOH < CH_3CH_2CHBrCOOH < CH_3CH_2CHFCOOH$
 (iii) $(CH_3)_3C{\cdot}COOH < (CH_3)_2CHCOOH < CH_3COOH$
 (iv) $HOOCCH_2CH_2CH_2COOH < HOOCCH_2CH_2COOH < HOOCCH_2COOH < HOOC—COOH$

PROBLEMS BASED ON STRUCTURE AND PROPERTIES

1. Compound (*A*) $C_5H_8O_2$ liberated carbon dioxide on reaction with sodium bicarbonate. It exists in two forms neither of which is optically active. It yields compound (*B*) $C_5H_{10}O_2$ on hydrogenation. Compound (*B*) can be separated into two enantiomorphs. Write the structural formulae of (*A*) and (*B*) giving reason.

[Ans. 

(*A*) Geometrical isomers

(*B*) 

$$C_2H_5-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-COOH \quad \text{or} \quad HOOC-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-C_2H_5$$

One asymmetric carbon atom is present.]

2. An unsaturated dicarboxylic acid (*A*), $C_6H_8O_4$ loses CO_2 on heating and gives another unsaturated acid (*B*), $C_5H_8O_2$. Upon catalytic reduction (*B*) affords pentanoic acid. Assign structures to (*A*) and (*B*).
[Ans. (*A*) $CH_3CH{=}CH{\cdot}CH(COOH)_2$; (*B*) $CH_3CH{=}CH{\cdot}CH_2COOH$]

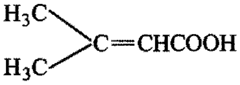
3. An organic acid (A), $C_5H_{10}O_2$ reacts with Br_2 in the presence of phosphorus to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometric isomerism and on decarboxylation gives an alkene (D) which on ozonolysis gives (E) and (F). Compound (E) gives a positive Schiff's test but (F) does not. Give the structures of (A) to (F) with reasons.

[**Ans.** $\underset{(A)}{R{-}CH_2COOH} \xrightarrow{\text{P and } Br_2} \underset{(B)}{R\overset{*}{C}HBrCOOH}$, where R is C_3H_7

It has one asymmetric carbon atom.

$$C_3H_7CHBrCOOH \longrightarrow \underset{(C)}{C_3H_6{=}CHCOOH}$$

Since, (C) has no geometrical isomer, it should have structure



(C)

Decarboxylation of (C) gives, $\underset{(D)}{(CH_3)_2C{=}CH_2}$

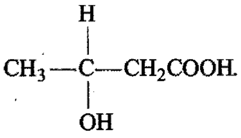
$$\Big\downarrow \text{Ozonolysis}$$

$$\underset{\substack{\text{Acetone}\\(F)}}{(CH_3)_2CO} \quad + \quad \underset{\substack{\text{Formaldehyde}\\(E)}}{HCHO} \quad]$$

does not give Schiff's test gives Schiff's test

4. An acidic compound (A), $C_4H_8O_3$ loses its optical activity on strong heating yielding (B), $C_4H_6O_2$ which reacts readily with $KMnO_4$. (B) forms a derivative (C) with $SOCl_2$, which on reaction with $(CH_3)_2NH$ gives (D). The compound (A) on oxidation with dilute chromic acid gives an unstable compound (E) which decarboxylates readily to give (F), C_3H_6O. The compound (F) gives a hydrocarbon (G) on treatment with amalgamated Zn and HCl. Give the structures of (A) to (G) with proper reasoning.

[**Ans.** Compound (A) is a hydroxy compound and is optically active.



$$CH_3{-}\overset{H}{\underset{OH}{\overset{|}{\underset{|}{C}}}}{-}CH_2COOH$$

On heating it gives an unsaturated compound which reacts with $KMnO_4$.

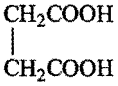
$$\underset{(A)}{CH_3CHOHCH_2COOH} \xrightarrow{\text{Heat}} \underset{(B)\,C_4H_6O_2}{CH_3CH{=}CHCOOH} \xrightarrow{KMnO_4} CH_3CHOHCHOHCOOH$$

$$\underset{(B)}{CH_3CH{=}CHCOOH} \xrightarrow{SOCl_2} \underset{(C)}{CH_3CH{=}CHCOCl} \xrightarrow{(CH_3)_2NH} \underset{(D)}{CH_3CH{=}CHCON(CH_3)_2}$$

$$\underset{(A)}{CH_3CHOHCH_2COOH} \xrightarrow[\text{acid}]{\text{Dil. chromic}} \underset{\substack{(E)\\\text{Unstable}}}{CH_3COCH_2COOH} \longrightarrow \underset{(F)}{CH_3COCH_3} \xrightarrow[HCl]{Zn/Hg} \underset{(G)}{CH_3CH_2CH_3}\ ]$$

5. An acid (A) contains carbon = 40.7%, hydrogen = 5.1 % and its silver salt contains 65.1 % silver. The ethyl ester of (A) has V.D. of 87. What structure (A) may have? How would you distinguish between isomers?

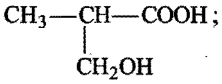
[**Ans.** (A) may have two structures



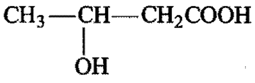
$$\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}\ ; \quad CH_3CH(COOH)_2$$]

6. Give the structures of the four optically active structural isomers of $C_4H_8O_3$ (A to D) and evolve CO_2 with aq. $NaHCO_3$. Find the structure of (A), the isomer that reacts with $LiAlH_4$ to give an achiral product and (B) gives an iodoform test.

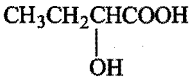
[**Ans.** (A)



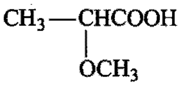
$CH_3{-}\underset{CH_2OH}{\underset{|}{CH}}{-}COOH$; (B)



$CH_3{-}\underset{OH}{\underset{|}{CH}}{-}CH_2COOH$; (C)



$CH_3CH_2\underset{OH}{\underset{|}{C}}HCOOH$; (D)



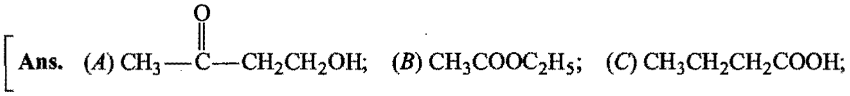
$CH_3{-}\underset{OCH_3}{\underset{|}{C}}HCOOH$]

7. Give the various structures of $C_4H_8O_2$:

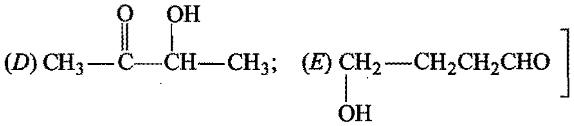
(A) that can give iodoform test and gives white turbidity only on heating with Lucas reagent.

(B) that can be hydrolysed to give acetic acid and alcohol.

(*C*) that can be decarboxylated to propane.
(*D*) that can give iodoform test and reduces Tollens' reagent.
(*E*) that can reduce Tollens' reagent but does not give iodoform test.

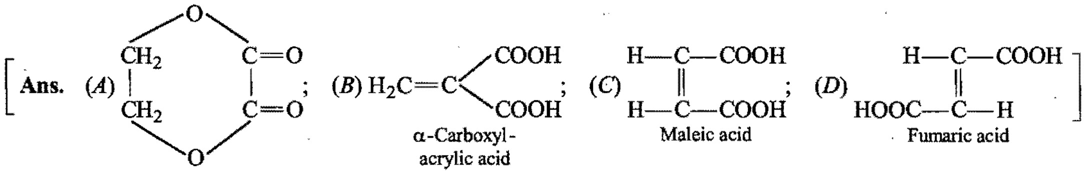


[**Ans.** (*A*) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2OH$; (*B*) $CH_3COOC_2H_5$; (*C*) $CH_3CH_2CH_2COOH$;



(*D*) $CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH}-CH_3$; (*E*) $\underset{\underset{OH}{|}}{CH_2}-CH_2CH_2CHO$]

8. Molecular formula $C_4H_4O_4$ can have various structures:
(i) a cyclic ester (*A*).
(ii) a dibasic acid (*B*) that on heating is converted into acrylic acid.
(iii) a dibasic acid (*C*) that forms meso tartaric acid with alkaline $KMnO_4$.
(iv) a dibasic acid (*D*) that forms racemic mixture of tartaric acid with alkaline $KMnO_4$.
Assign structures to (*A*), (*B*), (*C*) and (*D*).



(Glycol oxalate) α-Carboxyl-acrylic acid Maleic acid Fumaric acid

9. A mixture of an acid anhydride (*A*) and a monobasic acid (*B*) on heating produces another monobasic acid (*C*) of equivalent weight 74 and an anhydride (*D*). The acids and anhydrides remain in equilibrium. The anhydride (*D*) contains two identical fluoro alkyl groups. The acid (*B*) contains a trifluoro methyl group and has an equivalent weight of 128. Give the structures of (*A*) to (*D*) with proper reasoning (Atomic weight of fluorine = 19).

Solution : Acid anhydride (*A*) + Monobasic acid (*B*) ⇌ Monobasic acid (*C*) + Anhydride (*D*)

(CF$_3$ group) (Two CF$_3$ groups)

Eq. wt. = 128 Eq. wt. = 74

$$\text{Probable formula of acid } (B) = CF_3(CH_2)_n COOH$$

$$\text{Equivalent weight of } (B) = \frac{\text{Molecular weight}}{\text{Basicity}}$$

$$128 = \frac{57+12+14n+12+32+1}{1}$$

$$n = 1$$

$$\therefore \qquad (B) = CF_3CH_2COOH \text{ and } (D) = (CF_3CH_2CO)_2O$$

Similarly, molecular formula of acid (*C*) can be calculated to be CH_3CH_2COOH. The reaction, therefore, can be given as,

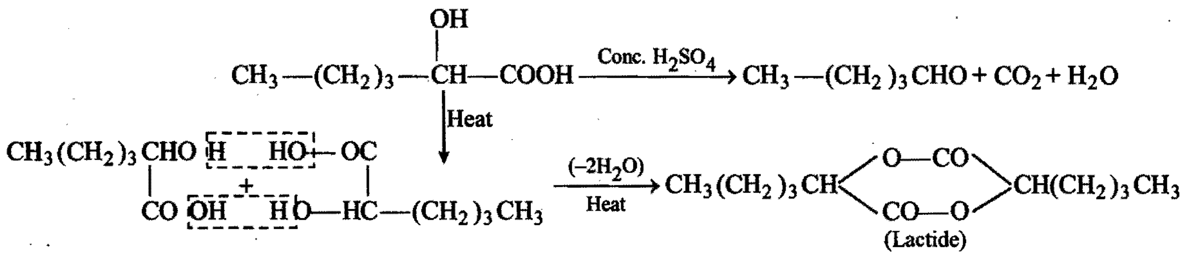
$$\underset{(A)}{(CH_3CH_2CO)_2O} + \underset{(B)}{F_3CCH_2COOH} \rightleftharpoons \underset{(C)}{CH_3CH_2COOH} + \underset{(D)}{(F_3CCH_2CO)_2O}$$

10. An organic compound (*A*) $C_6H_{12}O_3$ on treatment with concentrated H_2SO_4 gives CO, H_2O and (*B*). Compound (*B*) can be prepared by passing vapours of 1-pentanol over heated copper at 570 K. Compound (*A*) on heating gives (*C*), $C_{12}H_{20}O_4$. Give the structures of (*A*) to (*C*) with proper reasoning.

Solution : Compound (*B*) must be pentanol because it is prepared by passing vapours of 1-pentanol over heated copper.

$$\underset{\text{Pentan-1-ol}}{CH_3(CH_2)_3CH_2OH} \xrightarrow[570\text{ K}]{Cu} \underset{\text{Pentanal}}{CH_3(CH_2)_3-CHO} + H_2O$$

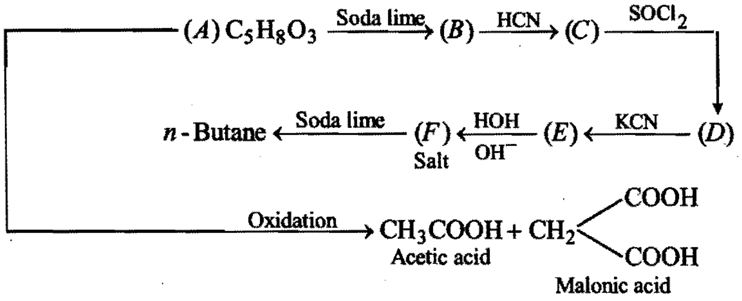
Compound (*A*) gives CO_2 and H_2O on treatment with conc. H_2SO_4. Thus, compound (*A*) must be α-hydroxy acid.



$$CH_3-(CH_2)_3-\overset{OH}{\overset{|}{C}}H-COOH \xrightarrow{\text{Conc. } H_2SO_4} CH_3-(CH_2)_3CHO + CO_2 + H_2O$$

11. An organic compound (*A*) $C_5H_8O_3$ on heating with soda lime gives (*B*), which reacts with HCN to give (*C*). The compound (*C*) reacts with thionyl chloride to produce (*D*) which on reaction with KCN gives compound (*E*). Alkaline hydrolysis of (*E*) gives a salt (*F*), which on heating with soda lime produces *n*-butane. Careful oxidation of (*A*) with dichromate gives acetic acid and malonic acid. Give the structures of (*A*) to (*F*) with proper reasoning.

Solution :

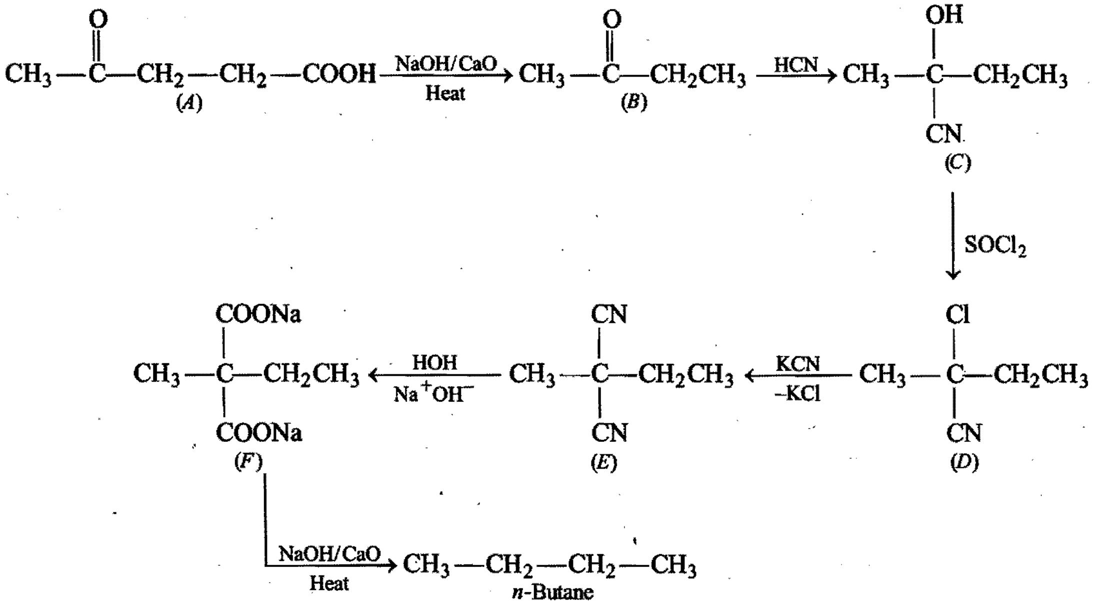


The given informations conclude about different products.

(i) Soda lime treatment of (*A*) confirms the presence of carboxylic group in it.

(ii) Final product is *n*-butane, thus compound (*A*) must be a straight chain compound.

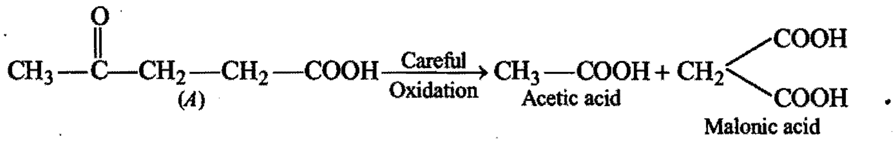
(iii) Careful oxidation of compound (*A*) gives acetic acid and malonic acid. It shows that oxidisable group (keto group) should be present at (carbon number C_2).



$$\underset{(A)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-COOH} \xrightarrow[\text{Heat}]{NaOH/CaO} \underset{(B)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3} \xrightarrow{HCN} \underset{(C)}{CH_3-\overset{OH}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-CH_2CH_3}$$

$$\underset{(C)}{CH_3-\overset{OH}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-CH_2CH_3} \xrightarrow{SOCl_2} \underset{(D)}{CH_3-\overset{Cl}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-CH_2CH_3} \xrightarrow[-KCl]{KCN} \underset{(E)}{CH_3-\overset{CN}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-CH_2CH_3} \xrightarrow[Na^+OH^-]{HOH} \underset{(F)}{CH_3-\overset{COONa}{\overset{|}{\underset{COONa}{\underset{|}{C}}}}-CH_2CH_3}$$

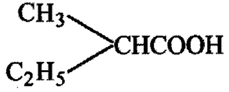
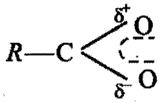
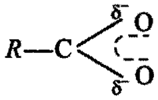
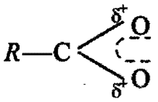
$$(F) \xrightarrow[\text{Heat}]{NaOH/CaO} \underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3}$$



$$\underset{(A)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-COOH} \xrightarrow[\text{Oxidation}]{\text{Careful}} \underset{\text{Acetic acid}}{CH_3-COOH} + \underset{\text{Malonic acid}}{CH_2\begin{cases}COOH\\COOH\end{cases}}$$

OBJECTIVE QUESTIONS

Set I : This set contains the questions with a single correct answer.

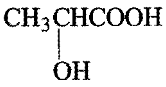
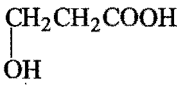
1. Which of the following is not a fatty acid?
   (a) Stearic acid ☐ (b) Palmitic acid ☐
   (c) Propionic acid ☐ (d) Phenyl acetic acid ☐
2. Lemon is sour due to: **[MHCET 2007]**
   (a) citric acid ☐ (b) tartaric acid ☐
   (c) oxalic acid ☐ (d) acetic acid ☐
3. Which of the following acids is present in vinegar?
   (a) Hydrochloric acid ☐ (b) Acetic acid ☐
   (c) Tartaric acid ☐ (d) Citric acid ☐
4. The general formula $C_nH_{2n}O_2$ could be for open chain: **[AIEEE 2003]**
   (a) diols ☐ (b) diketones ☐
   (c) carboxylic acids ☐ (d) dialdehydes ☐
5. Monocarboxylic acids (saturated) are regarded as .... oxidation products of paraffins.
   (a) first ☐ (b) second ☐
   (c) third ☐ (d) fourth ☐
6. Monocarboxylic acids show functional isomerism with:
   (a) esters ☐ (b) alcohols ☐
   (c) ethers ☐ (d) aldehydes ☐
7. Acetic acid is obtained when:
   (a) methyl alcohol is oxidised with $KMnO_4$ ☐
   (b) calcium acetate is distilled in presence of calcium formate ☐
   (c) acetaldehyde is oxidised with $K_2Cr_2O_7$ and H_2SO_4 ☐
   (d) glycerol is heated with H_2SO_4 ☐
8. Formic acid is obtained when:
   (a) calcium acetate is heated with conc. H_2SO_4 ☐
   (b) glycerol is heated with oxalic acid ☐
   (c) acetaldehyde is oxidised with $K_2Cr_2O_7$ and H_2SO_4 ☐
   (d) calcium formate is heated with calcium acetate ☐
9. Which of the following is isobutyric acid?
   (a) $CH_3CH_2CH_2COOH$ ☐
   (b) $(CH_3)_2CHCOOH$ ☐
   (c) $CH_3CH_2CH_2CH_2COOH$ ☐
   (d)  $(CH_3)(C_2H_5)CHCOOH$ ☐
10. The higher boiling points of carboxylic acids are due to:
    (a) their acidic nature ☐
    (b) intermolecular hydrogen bonding ☐
    (c) their dimerisation ☐
    (d) both (b) and (c) ☐
11. Carboxylic acids do not give the characteristic properties of:
    (a) $>C{=}O$ group ☐ (b) —COOH group ☐
    (c) alkyl group ☐ (d) none of these ☐
12. The acidic nature of the carboxylic acids is due to:
    (a) high degree of ionisation of the acid ☐
    (b) greater resonance stabilization of the acid ☐
    (c) greater resonance stabilization of the carboxylate ion ☐
    (d) all of the above ☐
13. Formic acid is not a representative member of the carboxylic acids because:
    (a) it is the first member of the series ☐
    (b) it does not contain an alkyl group ☐
    (c) it is a gas ☐
    (d) it contains an aldehydic group while the other acids do not have the aldehydic group ☐
14. Which of the following will not undergo HVZ reaction?
    (a) 2,2-Dimethyl propanoic acid ☐
    (b) Propanoic acid ☐
    (c) Acetic acid ☐
    (d) 2-Methyl propanoic acid ☐
15. The IUPAC name of caproic acid is:
    (a) pentanoic acid ☐ (b) hexanoic acid ☐
    (c) heptanoic acid ☐ (d) octanoic acid ☐
16. The reaction of CH_3MgBr on dry ice followed by acid hydrolysis gives:
    (a) acetic acid ☐ (b) formic acid ☐
    (c) acetone ☐ (d) acetaldehyde ☐
17. The acidic character of fatty acids...........with an increase in molecular mass.
    (a) sometimes increases sometimes decreases ☐
    (b) decreases ☐
    (c) increases ☐
    (d) none of the above ☐
18. Malonic acid on heating gives acetic acid while succinic acid on heating gives:
    (a) butyric acid ☐ (b) propionic acid ☐
    (c) succinic anhydride ☐ (d) oxalic acid ☐
19. Which of the following best represents the structure of the carboxylate ion?
    (a)  ☐ (b)  ☐
    (c)  ☐ (d) None of these ☐
20. Some carboxylic acids and their IUPAC names are given below. Which of the following is not correctly matched ? **[PMT (Kerala) 2010]**
    (a) Formic acid — Methanoic acid ☐
    (b) Acetic acid — Ethanoic acid ☐
    (c) *Iso*-butyric acid — 2-Methyl butanoic acid ☐
    (d) *n*-Butyric acid — Butanoic acid ☐
    (e) Malonic acid — Propanedioic acid ☐
21. Formic acid and formaldehyde can be distinguished by treating with:
    (a) Benedict's solution ☐ (b) Tollens' reagent ☐
    (c) Fehling's solution ☐ (d) $NaHCO_3$ ☐
22. Which of the following has the highest boiling point?
    (a) $CH_3OCH_2CH_3$ ☐ (b) $CH_3CH_2CH_2OH$ ☐
    (c) CH_3COOH ☐ (d) $CH_3CH_2CH_2CH_3$ ☐

23. Amongst the acids (*a*) $HC{\equiv}CCOOH$, (*b*) $H_2C{=}CHCOOH$ and (*c*) CH_3CH_2COOH, the acid strength follows the sequence:
(a) $(a) > (b) > (c)$ ☐ (b) $(a) < (b) < (c)$ ☐
(c) $(a) = (b) = (c)$ ☐ (d) $(a) = (b) < (c)$ ☐

24. Which of the following compounds is produced when α-chloroacetic acid is heated with Ag powder?
(a) Acetic acid ☐ (b) Acetone ☐
(c) Maleic acid ☐ (d) Succinic acid ☐

25. $CH_3CH_2COOH \xrightarrow[\text{Red P}]{Cl_2} (A) \xrightarrow{\text{Alc. KOH}} (B)$

The compound (*B*) is: **[BHU (Mains) 2008]**

(a) 
$CH_3\underset{\displaystyle OH}{CH}COOH$ ☐ (b) 
$\underset{\displaystyle OH}{CH_2}CH_2COOH$ ☐

(c) $H_2C{=}CHCOOH$ ☐ (d) $ClCH_2CH_2COOH$ ☐

26. —OH group in alcohol is neutral, while it is acidic in carboxylic acid because:
(a) alcohol has alkyl group with +*I* effect ☐
(b) carboxylic acid is an electrovalent compound ☐
(c) alcohol is a covalent compound ☐
(d) in carboxylic acid, —OH group is joined to the electron withdrawing carbonyl group ☐

27. Acetic acid exists in a dimer state in benzene due to:
(a) condensation reaction ☐
(b) hydrogen bonding ☐
(c) presence of carbonyl group ☐
(d) presence of α-hydrogen ☐

28. Which of the following acids is the strongest? **[MGIMS (Med.) 2007]**
(a) CH_3COOH ☐ (b) $CH_2ClCOOH$ ☐
(c) $CHCl_2COOH$ ☐ (d) CCl_3COOH ☐

29. Which of the following is the strongest acid?
(a) $HCOOH$ (pK_a 3.77) ☐
(b) C_6H_5COOH (pK_a 4.22) ☐
(c) CH_3COOH (pK_a 4.71) ☐
(d) CH_3CH_2COOH (pK_a 4.88) ☐

30. Which one of the following is a strong reducing agent?
(a) Ethanoic acid ☐ (b) Benzoic acid ☐
(c) Methanoic acid ☐ (d) Chloroacetic acid ☐

31. When sucrose is heated with conc. HNO_3 in presence of V_2O_5, the product formed is:
(a) sucrose nitrate ☐ (b) formic acid ☐
(c) citric acid ☐ (d) oxalic acid ☐

32. The weakest acid among the following is:
(a) CH_3COOH ☐ (b) $ClCH_2COOH$ ☐
(c) $Cl_2CHCOOH$ ☐ (d) $Cl_3C{\cdot}COOH$ ☐

33. Formic acid:
(a) is immiscible with water ☐
(b) reduces ammoniacal silver nitrate ☐
(c) is a weak acid, nearly three and a half times weaker than acetic acid ☐
(d) is prepared by heating potassium formate ☐

34. Which of the following reduces carboxylic acid directly to primary alcohols?
(a) $LiAlH_4$ ☐ (b) $Na + C_2H_5OH$ ☐
(c) $NaBH_4$ ☐ (d) H_2 ☐

35. In the reaction,

$$C_2H_5OH \xrightarrow{PI_3} (A) \xrightarrow{KCN} (B) \xrightarrow{\text{Hydrolysis}} (C)$$

The product (*C*) is:
(a) acetic acid ☐ (b) formic acid ☐
(c) oxalic acid ☐ (d) propionic acid ☐

36. Pyroligneous acid contains:
(a) 2% acetic acid ☐ (b) 50% acetic acid ☐
(c) 10% acetic acid ☐ (d) 20% acetic acid ☐

37. When sodium formate is heated at 360°C, main product is: **[JIPMER (Med.) 2008]**
(a) sodium oxalate and H_2 ☐
(b) oxalic acid and H_2 ☐
(c) sodium oxalate ☐
(d) CO_2 and caustic soda ☐

38. Sodium acetate + acetyl chloride gives:
(a) CH_3COOH ☐ (b) sodium formate ☐
(c) acetic anhydride ☐ (d) acetone ☐

39. Fermentation of ethyl alcohol into acetic acid is done by:
(a) zymase ☐
(b) diastase ☐
(c) maltase ☐
(d) *Bacterium Mycoderma aceti* ☐

40. When sodium formate is heated with soda lime, it forms: **[VITEEE 2008]**
(a) H_2 ☐ (b) CO ☐
(c) CO_2 ☐ (d) water vapour ☐

41. Methyl magnesium bromide on reaction with SO_2 followed by hydrolysis gives : **[AMU (Engg.) 2010]**
(a) methyl sulphonic acid ☐
(b) methane sulphinic acid ☐
(c) dithio acetic acid ☐
(d) ethanethiol ☐

42. In the following reaction,

$$RCH_2COOH \xrightarrow{Br_2/P} X \xrightarrow{\text{Excess } NH_3} Y$$

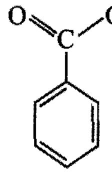
the major amounts of *X* and *Y* are: **[UPSEE (Engg.) 2008]**
(a) $RCHBrCONH_2$; $RCH(NH_2)COOH$ ☐
(b) $RCHBrCOOH$; RCH_2CONH_2 ☐
(c) RCH_2COBr; RCH_2COONH_4 ☐
(d) $RCHBrCOOH$; $RCH(NH_2)COOH$ ☐

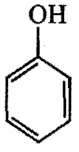
43. Which one of the following would be expected to be most highly ionised in water?
(a) $CH_2ClCH_2CH_2COOH$ ☐
(b) $CH_3CHClCH_2COOH$ ☐
(c) $CH_3CH_2CHClCOOH$ ☐
(d) $CH_3CH_2CCl_2COOH$ ☐

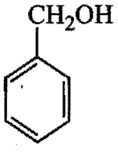
44. Mercuric chloride is reduced to mercurous chloride by:
(a) acetic acid ☐ (b) carbon tetrachloride ☐
(c) formic acid ☐ (d) ammonia ☐

45. Which is the correct order of acidity from weakest to strongest acid for these compounds :

CF_3CH_2OH ,
(I)


(II)


(III)


(IV)

[PMT (Kerala) 2010]

(a) I < IV < III < II ☐ (b) IV < I < III < II ☐
(c) III < IV < I < II ☐ (d) II < III < I < IV ☐
(e) II < III < IV < I ☐

46. Which one of the following is used to remove ink and rust stains on cloth?
(a) Oxalic acid ☐ (b) Alcohol ☐
(c) Ether ☐ (d) Kerosene ☐

47. Oxalic acid on treatment with conc. H_2SO_4 gives: **[AFMC 2010]**
(a) CO only ☐ (b) CO_2 only ☐
(c) $CO_2 + H_2O$ ☐ (d) $H_2O + CO + CO_2$ ☐

48. Which of the following is used in synthetic lemonade?
(a) Tartaric acid ☐ (b) Acetic acid ☐
(c) Citric acid ☐ (d) Oxalic acid ☐

49. The reaction,

$$RCOOAg + Br_2 \xrightarrow{CCl_4} RBr + AgBr + CO_2$$

is called:
(a) HVZ reaction ☐ (b) Hunsdiecker reaction ☐
(c) Hofmann's reaction ☐ (d) Carbylamine reaction ☐

50. $RCOOH + N_3H \xrightarrow{H_2SO_4(\text{conc.})} RNH_2 + CO_2 + N_2$
The above reaction is called:
(a) HVZ reaction ☐
(b) Hunsdiecker reaction ☐
(c) Schmidt reaction ☐
(d) decarboxylation reaction ☐

51. Acetic acid does not form acetyl chloride with: **[AFMC 2007]**
(a) PCl_5 ☐ (b) PCl_3 ☐
(c) $SOCl_2$ ☐ (d) Cl_2 ☐

52. The product (*C*) in the following reactions is:

$$RCOOH \xrightarrow{NH_3} (A) \xrightarrow{\text{Heat}} (B) \xrightarrow[\text{Heat}]{P_2O_5} (C)$$

(a) RNH_2 ☐ (b) RCN ☐
(c) RNC ☐ (d) $RCONH_2$ ☐

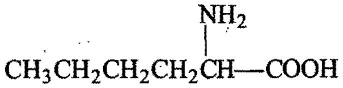
53. The compound insoluble in acetic acid is:
(a) calcium oxide ☐ (b) calcium carbonate ☐
(c) calcium oxalate ☐ (d) calcium hydroxide ☐

54. Which of the following cannot reduce Fehling's solution? **[BHU (Screening) 2008]**
(a) Formic acid ☐ (b) Acetic acid ☐
(c) Formaldehyde ☐ (d) Acetaldehyde ☐

55. The carboxylic acid which reduces Tollens' reagent is: **[VMMC 2007]**
(a) $CH_3CH_2CH_2COOH$ ☐ (b) CH_3CH_2COOH ☐
(c) CH_3COOH ☐ (d) HCOOH ☐

56. What is the main reason for the fact that carboxylic acids can undergo ionisation?
(a) Absence of alpha-hydrogen ☐
(b) Resonance stabilization of the carboxylate ion ☐
(c) High reactivity of alpha-hydrogen ☐
(d) Hydrogen bonding ☐

57. $CH_3CH_2CH_2CH_2CH_2COOH \longrightarrow$


$CH_3CH_2CH_2CH_2\overset{\overset{NH_2}{|}}{C}H\text{—}COOH$

the reagents used in the conversion are: **[DPMT 2008]**
(a) (i) Red P, Br_2/(ii) NH_3 (excess) ☐
(b) (i) PBr_3/(ii) NH_3 ☐
(c) (i) PBr_3, NaCN/(ii) $LiAlH_4$ ☐
(d) none of the above ☐

58. Between CH_3COOH and HCOOH, the HCOOH will be:
(a) less acidic ☐ (b) equally acidic ☐
(c) more acidic ☐ (d) non-acidic ☐

59. What are A, B, C in the following reactions?

(i) $(CH_3CO_2)_2Ca \xrightarrow{\Delta} A$

(ii) $CH_3CO_2H \xrightarrow[\text{Red P}]{\text{HI}} B$

(iii) $2CH_3CO_2H \xrightarrow{P_4O_{10}} C$ **[EAMCET 2009]**

	A	*B*	*C*	
(a)	C_2H_6	CH_3COCH_3	$(CH_3CO)_2O$	☐
(b)	$(CH_3CO)_2O$	C_2H_6	CH_3COCH_3	☐
(c)	CH_3COCH_3	$(CH_3CO)_2O$	C_2H_6	☐
(d)	CH_3COCH_3	C_2H_6	$(CH_3CO)_2O$	☐

60. Adipic acid is a:
(a) dibasic acid ☐ (b) tribasic acid ☐
(c) monobasic acid ☐ (d) tetrabasic acid ☐

61. Hydrated oxalic acid contains:
(a) two water molecules ☐ (b) three water molecules ☐
(c) four water molecules ☐ (d) five water molecules ☐

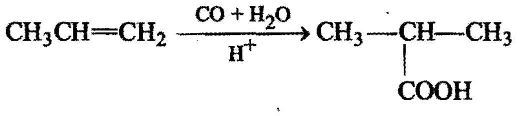
62. Lactic acid is:
(a) propionic acid ☐
(b) α-hydroxy propionic acid ☐
(c) β-hydroxy propionic acid ☐
(d) none of the above ☐

63. Which of the following compounds does not react with NaOH? **[CPMT 2004]**
(a) CH_3COOH ☐ (b) CH_3CONH_2 ☐
(c) C_6H_5OH ☐ (d) CH_3CH_2OH ☐

64. Tamarind contains:
(a) tartaric acid ☐ (b) lactic acid ☐
(c) citric acid ☐ (d) succinic acid ☐

65. Which is a tribasic acid?
(a) Succinic acid ☐ (b) Tartaric acid ☐
(c) Citric acid ☐ (d) Valeric acid ☐

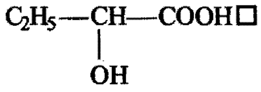
66. Which of the following gives smell of burnt sugar on charring?
(a) Oxalic acid ☐ (b) Tartaric acid ☐
(c) Malonic acid ☐ (d) Succinic acid ☐

67. 

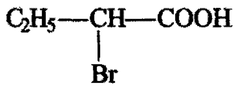
$CH_3CH{=}CH_2 \xrightarrow[H^+]{CO + H_2O} CH_3{-}\underset{\underset{COOH}{|}}{CH}{-}CH_3$

is known as: [PMT (MP) 2002]
(a) Wurtz reaction ☐
(b) Clemmensen reduction ☐
(c) Koch reaction ☐
(d) Kolbe's reaction ☐

68. Which of the following will not give HVZ reaction? [DPMT 2002]

(a) 

$C_2H_5{-}\underset{\underset{OH}{|}}{CH}{-}COOH$ ☐ (b) CH_3CBr_2COOH ☐

(c) 

$C_2H_5{-}\underset{\underset{Br}{|}}{CH}{-}COOH$ ☐ (d) $(CH_3)_2CHCOOH$ ☐

69. Identify *A* and *B* in the following reaction:

$$CH_3CH_3 \xleftarrow{B} CH_3COOH \xrightarrow{A} CH_3CH_2OH$$

[AMU (Engg.) 2008]

	A	*B*	
(a)	HI + Red P	$LiAlH_4$	☐
(b)	Ni/Δ	$LiAlH_4$	☐
(c)	Pd-$BaSO_4$	Zn + HCl	☐
(d)	$LiAlH_4$	HI + Red P	☐

70. $CH_3COOH \xrightarrow{P/Br_2} CH_2BrCOOH$. The reaction is called: [JIPMER 2004]
(a) Schotten-Baumann reaction ☐
(b) Hell-Volhard-Zelinsky reaction ☐
(c) Finkelstein reaction ☐
(d) none of the above ☐

71. When lactic acid is oxidised by Fenton's reagent, the product formed is:
(a) acetic acid ☐ (b) oxalic acid ☐
(c) pyruvic acid ☐ (d) maleic acid ☐

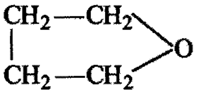
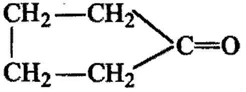
72. Rochelle's salt is:
(a) sod. pot. tartrate ☐ (b) sodium tartrate ☐
(c) potassium tartrate ☐ (d) calcium tartrate ☐

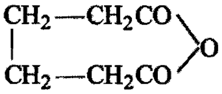
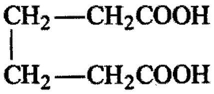
73. Nickel formate is best used as a catalyst in:
(a) preservation of fruits ☐
(b) esterification ☐
(c) dyeing wool and cotton fabrics ☐
(d) hydrogenation of oils ☐

74. Butyric acid undergoes mild oxidation with dilute hydrogen peroxide at:
(a) α-position ☐
(b) β-position ☐
(c) γ-position ☐
(d) simultaneously at α, β and γ-positions ☐

75. Acetic acid reacts with chlorine in the presence of catalyst, anhydrous $FeCl_3$ to give:
(a) acetyl chloride ☐ (b) methyl chloride ☐
(c) trichloroacetic acid ☐ (d) chloral hydrate ☐

76. Which of the following products is formed when adipic acid is heated? [CPMT 2008]

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

77. Which salt of citric acid is used as antacid and laxative?
(a) Iron ☐ (b) Magnesium ☐
(c) Calcium ☐ (d) Sodium ☐

78. Which acid is used as a standard substance in volumetric titrations?
(a) Formic acid ☐ (b) Acetic acid ☐
(c) Oxalic acid ☐ (d) Tartaric acid ☐

79. Cream of tartar, used for making baking powder is:
(a) sodium tartrate ☐
(b) potassium acid tartrate ☐
(c) sodium potassium tartrate ☐
(d) potassium antimonyl tartrate ☐

80. Vinegar contains: [JIPMER 2003]
(a) 100% acetic acid ☐ (b) 10–20% acetic acid ☐
(c) 1 % acetic acid ☐ (d) 7–8% acetic acid ☐

81. Tartaric acid on treatment with resorcinol and conc. H_2SO_4 gives:
(a) violet colour ☐ (b) blue colour ☐
(c) green colour ☐ (d) no colour ☐

82. Acids form sodium salt, with the evolution of carbon dioxide on treatment with:
(a) sodium carbonate ☐ (b) sodium hydroxide ☐
(c) soda lime ☐ (d) sodium metal ☐

83. Choose the weakest acid among the following : [PET (Kerala) 2010]
(a) F_3CCOOH ☐ (b) FCH_2COOH ☐
(c) $(CH_3)_2CHCOOH$ ☐ (d) CH_3CH_2COOH ☐
(e) CH_3COOH ☐

84. Anhydrous formic acid is prepared by:
(a) heating NaOH with CO at 210°C under pressure ☐
(b) heating glycerol with oxalic acid at high temperature ☐
(c) catalytic oxidation of ethane in presence of a catalyst ☐
(d) heating lead formate in a current of hydrogen sulphide ☐

85. By heating a mixture of ethylene, carbon monoxide and steam at high temperature under pressure in presence of a catalyst gives:

(a) formic acid ☐ (b) acetic acid ☐
(c) propionic acid ☐ (d) oxalic acid ☐

86. Cyanogen on hydrolysis with dil. HCl gives:
(a) formic acid ☐ (b) acetic acid ☐
(c) glycol ☐ (d) oxalic acid ☐

87. Maleic acid on catalytic reduction gives:
(a) oxalic acid ☐ (b) malonic acid ☐
(c) succinic acid ☐ (d) tartaric acid ☐

88. By the oxidation of benzene with air in presence of V_2O_5 catalyst heated to 400–450°C yields:
(a) acetic acid ☐ (b) succinic acid ☐
(c) malic acid ☐ (d) maleic anhydride ☐

89. Ammonium succinate on strong heating gives:
(a) succinic acid ☐ (b) succinic anhydride ☐
(c) succinimide ☐ (d) tartaric acid ☐

90. Acetic acid dissolved in benzene shows a molecular mass of:
(a) 30 ☐ (b) 60 ☐
(c) 120 ☐ (d) 240 ☐

91. $CH_3COOH + CH_2{=}C{=}O \longrightarrow (X)$
(X) is most probably:
(a) $(CH_3CO)_2O$ ☐ (b) $CH_3COOCH_2CH_3$ ☐
(c) $CH_3CH_2COOCH_3$ ☐ (d) $(COOH)_2$ ☐

92. An aqueous solution of formic acid cannot be fractionated to get anhydrous acid because:
(a) it explodes on warming ☐
(b) its boiling point is about the same as that of water ☐
(c) it decomposes in aqueous medium ☐
(d) it polymerises on warming ☐

93. Action of formic acid on Tollens' reagent shows:
(a) acidic nature of formic acid ☐
(b) basic nature of formic acid ☐
(c) that formic acid is a reducing agent ☐
(d) that formic acid is an oxidising agent ☐

94. Propionic acid when reacted with bromide in the presence of phosphorus forms:
(a) $CH_2(Br)CH_2COOH$☐ (b) CH_3CH_2COBr ☐
(c) $CH_3CH(Br)COOH$ ☐ (d) $CH_3CH(Br)COBr$ ☐

95. Formic acid can be distinguished from acetic acid by its reaction with: [BHU 2006]
(a) Tollens' reagent ☐ (b) $NaHCO_3$ ☐
(c) NaOH ☐ (d) none of these ☐

96. A compound undergoes the following sequence of reactions:

$$\underset{}{C_3H_5N} \xrightarrow{\text{Hydrolysis}} \underset{(A)}{C_3H_6O_2} \xrightarrow{Cl_2/P}$$

$$\underset{(B)}{C_3H_5O_2Cl} \xrightarrow{NH_3} \underset{(C)}{C_3H_7NO_2}$$ [DCE 2000]

The compound (C) is:
(a) 1-nitropropane ☐
(b) 2-aminopropionic acid ☐
(c) 2-nitropropane ☐
(d) 2-hydroxypropanamide ☐

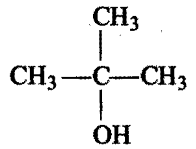
97. Maleic acid and fumaric acid:
(a) have identical melting point ☐
(b) form the same ester with methanol ☐
(c) have identical solubility in water ☐
(d) form the same anhydride on heating ☐

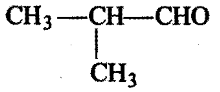
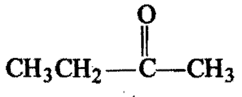
98. Which of the following is most effective for the hydrolysis of an ester?
(a) Dilute alkali ☐ (b) Dilute acid ☐
(c) Water ☐ (d) Acid or alkali ☐

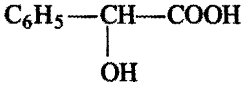
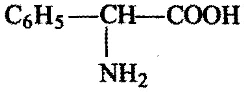
99. An unsubstituted amide is converted into the acid and nitrogen by:
(a) HCl ☐ (b) HNO_2 ☐
(c) NaOH ☐ (d) P_4O_{10} ☐

100. Which of the following reactions is expected to readily give a hydrocarbon product in good yield?
(a) $RCOOK \xrightarrow{\text{Electrolysis}}$ ☐
(b) $RCOOAg \xrightarrow{Br_2}$ ☐
(c) $CH_3CH_3 \xrightarrow[h\nu]{Cl_2}$ ☐
(d) $(CH_3)_3C{-}Cl \xrightarrow{C_2H_5OH}$ ☐

101. Which of the following methods cannot be used for the preparation of an ester?
(a) $RCOOH + R'OH + H^+$ ☐
(b) $RCOCl + R'OH$ + Pyridine ☐
(c) $RCOOH + R'OH + OH^-$ ☐
(d) $(RCO)_2O + R'OH$ + Pyridine ☐

102. Best starting material to synthesize 2-methyl-2-butenoic acid is:
(a) 
$CH_3{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OH}{|}}{C}}{-}CH_3$ ☐ (b) $CH_3CH_2CH_2CHO$ ☐

(c) 
$CH_3{-}\underset{\underset{\large CH_3}{|}}{CH}{-}CHO$ ☐ (d) 
$CH_3CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3$ ☐

103. Which of the following carboxylic acids undergoes decarboxylation easily?
(a) $C_6H_5CO{-}CH_2COOH$ ☐
(b) $C_6H_5COCOOH$ ☐
(c) 
$C_6H_5{-}\underset{\underset{\large OH}{|}}{CH}{-}COOH$ ☐
(d) 
$C_6H_5{-}\underset{\underset{\large NH_2}{|}}{CH}{-}COOH$ ☐

104. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to:

(a) ionization of benzoic acid ☐
(b) dimerisation of benzoic acid ☐
(c) trimerisation of benzoic acid ☐
(d) solvation of benzoic acid ☐

105. When propionic acid is treated with aqueous $NaHCO_3$, CO_2 is liberated. The 'C' of CO_2 comes from:
(a) methyl group ☐ (b) carboxylic acid group ☐
(c) methylene group ☐ (d) bicarbonate ☐

106. Propionic acid with Br_2/P yields a dibromoproduct. Its structure would be: **[CBSE (Med.) 2009]**
(a) CH_2BrCH_2COBr ☐ (b) $CH_2BrCHBrCOOH$ ☐
(c) $CHBr_2CH_2COOH$ ☐ (d) CH_3CBr_2COOH ☐

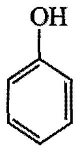
107. Which of the following orders of relative strength of acids is correct? **[CPMT 2000; CBSE (Med.) 2007]**
(a) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$ ☐
(b) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$ ☐
(c) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$ ☐
(d) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$ ☐

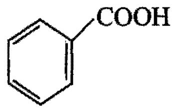
108. HCOOH reacts with concentrated H_2SO_4 to produce: **[UGET (Med.) 2001]**
(a) CO ☐ (b) CO_2 ☐
(c) NO ☐ (d) NO_2 ☐

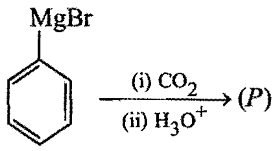
109. Carboxylic acids readily dissolve in aqueous sodium bicarbonate, liberating carbondioxide. Which one of the following is correct? **[UGET (Med.) 2008]**
(a) The conjugate base of the carboxylic acid is more stable than the free carboxylic acid ☐
(b) Free carboxylic acid and its conjugate base are of comparable stability ☐
(c) The free carboxylic acid is more stable than its conjugate base ☐
(d) The conjugated acid of the carboxylic acid is more stable than the free carboxylic acid ☐

110. Lactic acid on oxidation by alkaline potassium permanganate gives: **[CET (Tamil Nadu) 2001]**
(a) tartaric acid ☐ (b) pyruvic acid ☐
(c) cinnamic acid ☐ (d) propanoic acid ☐

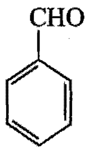
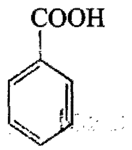
111. Which of the following is the weakest acid? **[CPMT 2001]**

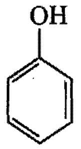
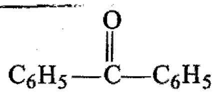
(a)  ☐ (b) CH_3COOH ☐

(c) HCOOH ☐ (d)  ☐

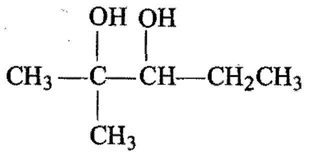
112. 

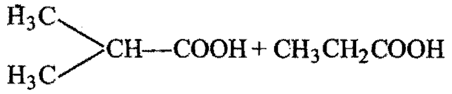
In the above reaction, product '*P*' is: **[CBSE (Med.) 2002]**

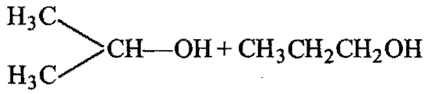
(a)  ☐ (b)  ☐

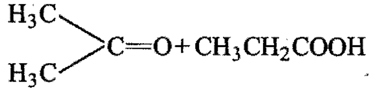
(c)  ☐ (d)  $C_6H_5-\overset{\overset{\large O}{\|}}{C}-C_6H_5$ ☐

113. On vigorous oxidation by permanganate solution, $(CH_3)_2C{=}CH-CH_2CH_3$ gives: **[AIEEE 2002]**

(a)  $CH_3-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large OH}{|}}{C}}-\overset{\overset{\large OH}{|}}{CH}-CH_2CH_3$ ☐

(b)  $(H_3C)_2CH-COOH + CH_3CH_2COOH$ ☐

(c)  $(H_3C)_2CH-OH + CH_3CH_2CH_2OH$ ☐

(d)  $(H_3C)_2C{=}O + CH_3CH_2COOH$ ☐

114. Which of the following acids has the smallest dissociation constant? **[IIT (S) 2002]**
(a) $CH_3CHFCOOH$ ☐ (b) FCH_2CH_2COOH ☐
(c) $BrCH_2CH_2COOH$ ☐ (d) $CH_3CHBrCOOH$ ☐

115. Identify the correct order of boiling points of the following compounds: **[IIT(S) 2002]**
$\underset{1}{CH_3CH_2CH_2CH_2OH}$; $\underset{2}{CH_3CH_2CH_2CHO}$;
$\underset{3}{CH_3CH_2CH_2COOH}$
(a) $1 > 2 > 3$ ☐ (b) $3 > 1 > 2$ ☐
(c) $1 > 3 > 2$ ☐ (d) $3 > 2 > 1$ ☐

116. Which gives lactic acid on hydrolysis after reacting with HCN? **[UPSEAT 2003]**
(a) HCHO ☐ (b) CH_3CHO ☐
(c) C_6H_5CHO ☐ (d) CH_3COCH_3 ☐

117. When $H_2C{=}CH-COOH$ is reduced with $LiAlH_4$, the compound obtained will be: **[AIEEE 2003; JCECE (Med.) 2008]**
(a) CH_3CH_2COOH ☐ (b) CH_3CH_2CHO ☐
(c) $CH_3CH_2CH_2OH$ ☐ (d) $H_2C{=}CHCH_2OH$ ☐

118. Ethyl isocyanide on hydrolysis in acidic medium gives: **[AIEEE 2003]**
(a) ethanoic acid and ammonium salt ☐
(b) propanoic acid and ammonium salt ☐
(c) ethylamine and methanoic acid ☐
(d) methylamine and ethanoic acid ☐

119. The correct order of acidic strength of carboxylic acid is: **[DCE 2009]**

(a) acetic acid < benzoic acid < formic acid ☐
(b) formic acid < benzoic acid < acetic acid ☐
(c) formic acid < acetic acid < benzoic acid ☐
(d) acetic acid < formic acid < benzoic acid ☐

120. Which among the following is the strongest acid? **[DPMT 2004]**

(a) HOCl ☐ (b) $HClO_2$ ☐
(c) $HClO_3$ ☐ (d) $HClO_4$ ☐

121. When CH_3COOH reacts with $CH_3—MgX$: **[AMU (Med.) 2004]**

(a) CH_3COX is formed ☐
(b) hydrocarbon is formed ☐
(c) acetone is formed ☐
(d) alcohol is formed ☐

122. Among the following acids, which has the lowest pK_a value? **[AIEEE 2005]**

(a) CH_3COOH ☐ (b) HCOOH ☐
(c) $(CH_3)_2CH—COOH$ ☐ (d) CH_3CH_2COOH ☐

123. Products of the following reaction,

$$CH_3—C{\equiv}CCH_2CH_3 \xrightarrow[\text{(ii) Hydrolysis}]{\text{(i) } O_3} \text{? are:}$$

[CBSE (Med.) 2005]

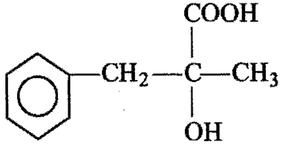
(a) $CH_3COOH + CO_2$ ☐
(b) $CH_3COOH + HOOCCH_2CH_3$ ☐
(c) $CH_3CHO + CH_3CH_2CHO$ ☐
(d) $CH_3COOH + CH_3COCH_3$ ☐

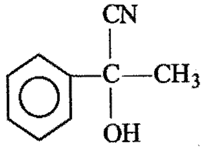
124. A set of reactions yielded a product (*D*):

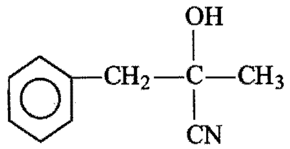
$$CH_3COOH \xrightarrow{SOCl_2} (A) \xrightarrow[\text{anhyd. } AlCl_3]{\text{Benzene}}$$

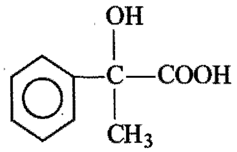
$$(B) \xrightarrow{HCN} (C) \xrightarrow{HOH} (D)$$

The structure of (*D*) would be: **[CBSE (Med.) 2005]**

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

125. Identify *X* and *Y* in the following sequence of reactions respectively:

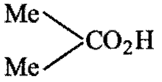
$$CH_3CHO \xrightarrow{HNO_3} X \xrightarrow[\Delta]{P_4O_{10}} Y$$

[EAMCET (Med.) 2005]

(a) C_2H_5OH and C_2H_4 ☐
(b) CH_3COOH and $(CH_3CO)_2O$ ☐
(c) CH_3COOH and CH_3COOCH_3 ☐
(d) C_2H_5OH and CH_3COOH ☐

126. The correct order of increasing acid strength of the compounds:

(*A*) CH_3CO_2H (*B*) $MeOCH_2CO_2H$ (*C*) CF_3CO_2H

(*D*)  is: **[AIEEE 2006]**

(a) $B < D < A < C$ ☐ (b) $D < A < C < B$ ☐
(c) $D < A < B < C$ ☐ (d) $A < D < C < B$ ☐

127. The *d* (+) lactic acid is obtained from: **[CET (Gujarat) 2006]**

(a) fermentation of cane sugar ☐
(b) green vegetables ☐
(c) muscles ☐
(d) fermentation of milk sugar ☐

128. An acid reacts with isotopically labelled methanol to produce: **[PMT (HP) 2006]**

(a) methyl acetate having the labelled oxygen ☐
(b) water having all the labelled oxygen ☐
(c) both methyl acetate and water contain isotopic oxygen ☐
(d) no esterification ☐

129. Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl because HCl: **[AIEEE 2008]**

(a) oxidises oxalic acid to carbon dioxide and water ☐
(b) reduces permanganate to Mn^{2+} ☐
(c) gets oxidised by oxalic acid to chlorine ☐
(d) furnishes H^+ ions in addition to those from oxalic acid ☐

130. When acetic acid is treated with P_2O_5, the product is: **[AMU (Med.) 2006]**

(a) ester ☐ (b) ether ☐
(c) alcohol ☐ (d) anhydride ☐

131. When acetyl chloride reacts with sodium propionate, the product formed is: **[DPMT 2009]**

(a) acetic propionic anhydride ☐
(b) acetic anhydride ☐
(c) *n*-propyl acetate ☐
(d) pent-2,4-dione ☐

132. In the reaction

$$CH_3CH_2COONH_4 \xrightarrow{P_2O_5} (A) \xrightarrow{H^+/H_2O} (B)$$

(*A*) and (*B*) are: **[DPMT (Med.) 2007]**

(a) $CH_3CH_2CONH_2, CH_3CH_2COO^-$ ☐
(b) $CH_3CH_2COONH_2, CH_3CH_2COOH$ ☐
(c) $CH_3CH_2CN, CH_3CH_2COO^-$ ☐
(d) CH_3CH_2CN, CH_3CH_2COOH ☐

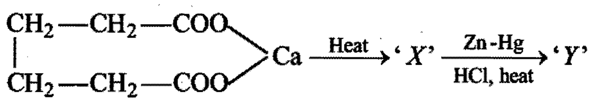
133. Arrange the following carboxylic acids in the decreasing order of their reactivities:
(i) CH_3COOH (ii) $ClCH_2COOH$ (iii) $Cl_2CHCOOH$
(iv) Cl_3CCOOH [CET (J & K) 2007]
(a) (ii) > (iv) > (i) > (iii) ☐ (b) (ii) > (i) > (iii) > (iv) ☐
(c) (iv) > (iii) > (ii) > (i) ☐ (d) (i) > (ii) > (iii) > (iv) ☐

134. Corrosive sublimate ($HgCl_2$) can be used to distinguish between: [CET (MH) 2007]
(a) formic acid and acetic acid ☐
(b) acetaldehyde and butanone ☐
(c) formaldehyde and propanone ☐
(d) all of the above ☐

135. Monocarboxylic acids react with alcohols in presence of an acid catalyst to form: [CET (J & K) 2007]
(a) acid chlorides ☐ (b) acid amides ☐
(c) esters ☐ (d) ethers ☐

136. Which of the following is not the functional isomer of monocarboxylic acid? [PET (MP) 2007]
(a) Amide ☐ (b) Ester ☐
(c) Hydroxy aldehyde ☐ (d) Hydroxy ketone ☐

137. Identify the product '*Y*' in the following reaction sequence:



$$\begin{matrix} CH_2-CH_2-COO \\ | \\ CH_2-CH_2-COO \end{matrix}\!\!>Ca \xrightarrow{\text{Heat}} \text{'}X\text{'} \xrightarrow[\text{HCl, heat}]{\text{Zn-Hg}} \text{'}Y\text{'}$$

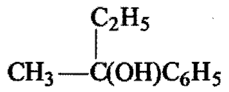
[CET (Pb) Engg. 2007]
(a) pentane ☐ (b) cyclobutane ☐
(c) cyclopentane ☐ (d) cyclopentanone ☐

138. In a set of the given reaction, acetic acid yielded a product *C*.

$$CH_3COOH + PCl_5 \longrightarrow A$$

$$A \xrightarrow[\text{Anhy. } AlCl_3]{C_6H_6} B \xrightarrow[\text{ether}]{C_2H_5MgBr} C$$

The product *C* would be:
[UPSEE (Engg.) 2007; JCECE (Med.) 2008]

(a) $CH_3CH(OH)C_6H_5$ ☐ (b)  $CH_3-\overset{\overset{\large C_2H_5}{|}}{C}(OH)C_6H_5$ ☐
(c) $CH_3CH(OH)C_2H_5$ ☐ (d) $CH_3COC_6H_5$ ☐

139. $C_6H_5{}^{14}COOH$ on heating with Na_2CO_3 releases: [CPMT 2007]
(a) CO_2 ☐ (b) $^{14}CO_2$ ☐
(c) CO ☐ (d) none of these ☐

140. $CH_3CHI_2 \xrightarrow{KCN} \xrightarrow[\Delta]{H_2O}$?;
here the end product would be: [MGIMS (Med.) 2007]
(a) 2-cyanopropionic acid ☐
(b) ethane-1,1-dicarboxylic acid ☐
(c) 2-methyl ethanoic acid ☐
(d) propionic acid ☐

Set II : This set contains questions with two or more correct answers.

141. The acids, which do not contain a —COOH group are: [BHU (Mains) 2007]
(a) picric acid ☐ (b) lactic acid ☐
(c) carbolic acid ☐ (d) propanoic acid ☐

142. Which of the following acids are dicarboxylic acids?
(a) Succinic acid ☐ (b) Glutaric acid ☐
(c) Lactic acid ☐ (d) Cinnamic acid ☐

143. Formic acid gives the test of:
(a) aldehydic group ☐ (b) ketonic group ☐
(c) carboxylic group ☐ (d) alcoholic group ☐

144. Optical activity is expected for:
(a) 2-methyl propanoic acid ☐
(b) 2-chloropropanoic acid ☐
(c) methyl-2-methylpropanoate ☐
(d) methyl-2-chloropropanoate ☐

145. Which of the following compounds will give ethyl alcohol on reduction with $LiAlH_4$?
(a) $(CH_3CO)_2O$ ☐ (b) CH_3COCl ☐
(c) CH_3CONH_2 ☐ (d) $CH_3COOC_2H_5$ ☐

146. Which of the following reagents can be used to test carboxylic group?
(a) $NaHCO_3$ ☐
(b) $FeCl_3$ ☐
(c) Alcohol in presence of conc. H_2SO_4 ☐
(d) Ceric ammonium nitrate ☐

147. Oxalic acid is used:
(a) for removing ink stains ☐
(b) for the lab preparation of formic acid and allyl alcohol ☐
(c) in making beverages ☐
(d) as a mordant in dyeing and calico-printing ☐

148. Which of the following acids are unsaturated one?
(a) Stearic acid ☐ (b) Acrylic acid ☐
(c) Oleic acid ☐ (d) Crotonic acid ☐

149. Reaction of *R*—COOH with N_3H gives RNH_2 as the main product. The intermediates involved in this reaction are:
(a) $RNHNH_2$ ☐ (b) $RCON_3$ ☐
(c) $RNCO$ ☐ (d) $RCONH_2$ ☐

150. Formic acid and acetic acid can be distinguished by the action of:
(a) conc. H_2SO_4 ☐ (b) Tollens' reagent ☐
(c) Fehling's solution ☐ (d) sodium salt on heating ☐

151. Acetic acid is obtained by the strong oxidation of:
(a) ethyl acetate ☐ (b) ethyl methyl ketone ☐
(c) ethyl alcohol ☐ (d) dimethyl ketone ☐

ASSERTION-REASON TYPE QUESTIONS

Following questions consist of Assertion (A) and Reason (R). Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are **correct** and (R) is the correct explanation of (A).

(b) If both (A) and (R) are **correct but** (R) is not correct explanation of (A).

(c) If (A) is **correct** but (R) is **incorrect.**

(d) If (A) is **incorrect** but (R) is **correct.**

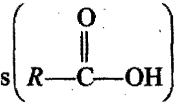
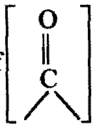
1. (A) Acetic acid does not give haloform reaction.
(R) Acetic acid has no α-hydrogen.

2. (A) Acetoacetic ester $CH_3COCH_2COOC_2H_5$ gives iodoform test.
(R) It has CH_3CO^- group attached to methylene group.

3. (A) Formic acid reduces mercuric chloride.
(R) Formic acid has reducing aldehydic group.

4. (A) $(CH_3)_3C—COOH$ does not give HVZ reaction.
(R) It does not have any α-hydrogen.

5. (A) Formic acid is a weaker acid than acetic acid.
(R) pK_a of formic acid is less than acetic acid.

6. (A) Carboxylic acids 
$\left(R—\overset{\overset{\large O}{\|}}{C}—OH \right)$ have a carbonyl group but it does not give the test of carbonyl group.
(R) Due to resonance double, the bond character of  group is greatly reduced.

7. (A) The pK_a value of acetic acid is lower than that of phenol.
(R) Phenoxide ion is more resonance stabilized. [AIIMS 2004]

8. (A) $HClO_4$ is a stronger acid than $HClO_3$.
(R) Oxidation state of Cl in $HClO_4$ is + VII and in $HClO_3$ it is + V. [AIIMS 2004]

9. (A) The molecular weight of acetic acid determined by depression in freezing point method in benzene and water was found to be different.
(R) Water is polar and benzene is non-polar. [AIIMS 2005]

ANSWERS

OBJECTIVE QUESTIONS

1. (d)	2. (a)	3. (b)	4. (c)	5. (c)	6. (a)	7. (c)	8. (b)	9. (b)	10. (d)
11. (a)	12. (c)	13. (d)	14. (a)	15. (b)	16. (a)	17. (b)	18. (c)	19. (b)	20. (c)
21. (d)	22. (c)	23. (a)	24. (d)	25. (c)	26. (d)	27. (b)	28. (d)	29. (a)	30. (c)
31. (d)	32. (a)	33. (b)	34. (a)	35. (d)	36. (c)	37. (a)	38. (c)	39. (d)	40. (a)
41. (b)	42. (d)	43. (d)	44. (c)	45. (b)	46. (a)	47. (d)	48. (c)	49. (b)	50. (c)
51. (d)	52. (b)	53. (c)	54. (b)	55. (d)	56. (b)	57. (a)	58. (c)	59. (d)	60. (a)
61. (a)	62. (b)	63. (d)	64. (a)	65. (c)	66. (b)	67. (c)	68. (b)	69. (d)	70. (b)
71. (c)	72. (a)	73. (d)	74. (b)	75. (c)	76. (b)	77. (b)	78. (c)	79. (b)	80. (d)
81. (b)	82. (a)	83. (c)	84. (d)	85. (c)	86. (d)	87. (c)	88. (d)	89. (c)	90. (c)
91. (a)	92. (b)	93. (c)	94. (c)	95. (a)	96. (b)	97. (c)	98. (a)	99. (b)	100. (a)
101. (c)	102. (d)	103. (a)	104. (b)	105. (d)	106. (d)	107. (a)	108. (a)	109. (a)	110. (b)
111. (b)	112. (b)	113. (d)	114. (c)	115. (b)	116. (b)	117. (d)	118. (c)	119. (a)	120. (d)
121. (b)	122. (b)	123. (b)	124. (d)	125. (b)	126. (c)	127. (c)	128. (a)	129. (b)	130. (d)
131. (a)	132. (d)	133. (c)	134. (a)	135. (c)	136. (a)	137. (c)	138. (b)	139. (a)	140. (d)
141. (a,c)	142. (a,b)	143. (a,c)	144. (b,d)	145. (a,b)	146. (a,b,c)	147. (a,b,d)	148. (b,c,d)	149. (b,c)	150. (a,b,c,d)
151. (b,c,d)									

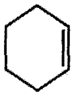
ASSERTION-REASON TYPE QUESTIONS

1. (c)	2. (d)	3. (a)	4. (a)	5. (d)	6. (a)	7. (b)	8. (b)	9. (a)

BRAIN STORMING PROBLEMS

1. Two isomeric compounds (*A*) and (*B*) have molecular formula C_6H_{10}. Oxidation of (*A*) gives mixture of butanoic and acetic acids, whereas compound (*B*) gives hexa-1,6-dioic acid. What are (*A*) and (*B*)?

[**Ans.** (*A*) : $CH_3CH_2CH_2C \equiv C-CH_3$; (*B*) :

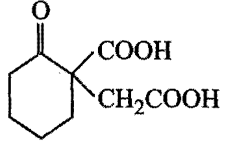


Cyclohexene]

[**Hint :** Compound (*A*) must be an alkyne because it gives mixture of two acids on oxidation. Compound (*B*) should be cycloalkene because it gives dioic acid on oxidation.]

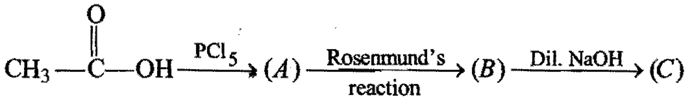
2. Complete the following reactions:

(i)



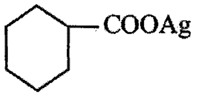
$\xrightarrow{\Delta}$ .... + CO_2

(ii)



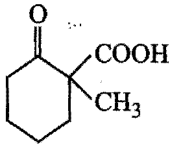
$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{PCl_5} (A) \xrightarrow[\text{reaction}]{\text{Rosenmund's}} (B) \xrightarrow{\text{Dil. NaOH}} (C)$

(iii)



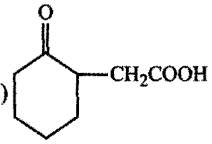
$\xrightarrow[\Delta]{Br_2}$ .... + CO_2 + AgBr

(iv)

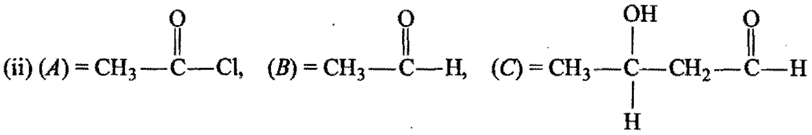


$\xrightarrow{\Delta}$ .... + CO_2

[**Ans.** (i)

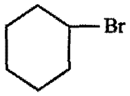


(ii)

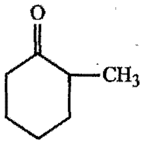


$(A) = CH_3-\overset{\overset{O}{\|}}{C}-Cl$, $(B) = CH_3-\overset{\overset{O}{\|}}{C}-H$, $(C) = CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-H$

(iii)

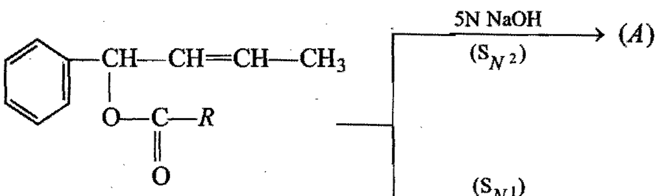


(iv)

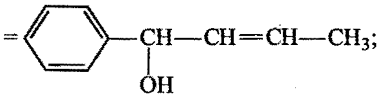


]

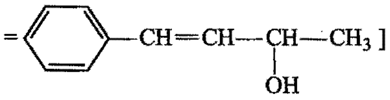
3. Complete the following reactions:



[**Ans.** (*A*) =



(*B*) =



]

4. Arrange the following in decreasing order of acid catalysed esterification:
CH_3CH_2COOH, $(CH_3)_2CHCOOH$, $(CH_3)_3CCOOH$
[**Ans.** $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$]

5. Arrange the following esters in the decreasing order of alkaline hydrolysis:

(i) $HCOOCH_3, CH_3COOCH_3, (CH_3)_3C—COOCH_3, (CH_3)_2CHCOOCH_3$

(ii) $CH_3COOCH_3, CH_3COOC(CH_3)_3, CH_3COOCH(CH_3)_2, CH_3COOC_2H_5$

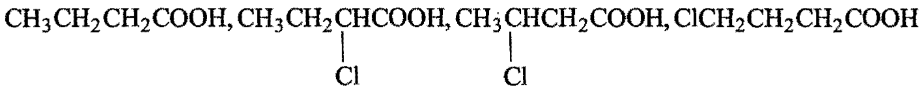
[Ans. (i) $HCOOCH_3 > CH_3COOCH_3 > (CH_3)_2CHCOOCH_3 > (CH_3)_3C—COOCH_3$

(ii) $CH_3COOCH_3 > CH_3COOC_2H_5 > CH_3COOCH(CH_3)_2 > CH_3COOC(CH_3)_3$]

[Hint : Greater is the steric hindrance either on alcoholic portion or on the acid portion, more difficult will be the hydrolysis.]

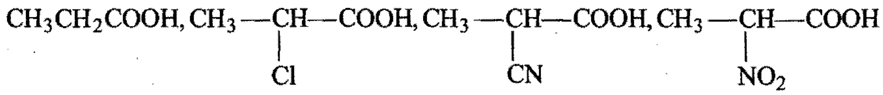
6. Arrange the following in decreasing order of acidic character:

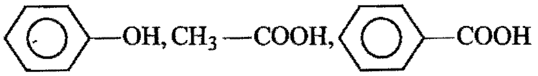
(i) $HCOOH, CH_3COOH, C_2H_5COOH, C_6H_5COOH, (CH_3)_2CHCOOH, CH_2ClCOOH$

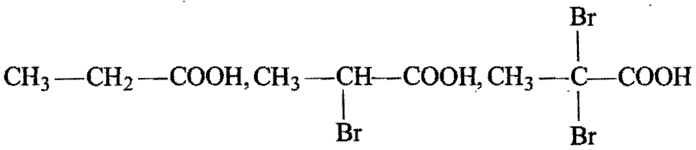
(ii) 
$CH_3CH_2CH_2COOH, CH_3CH_2\underset{Cl}{\underset{|}{CH}}COOH, CH_3\underset{Cl}{\underset{|}{CH}}CH_2COOH, ClCH_2CH_2CH_2COOH$

(iii) $CH_3COOH, CH_2ClCOOH, CHCl_2COOH, CCl_3—COOH$

(iv) $CH_2BrCOOH, CH_2ClCOOH, CH_2FCOOH, CH_2ICOOH$

(v) 
$CH_3CH_2COOH, CH_3—\underset{Cl}{\underset{|}{CH}}—COOH, CH_3—\underset{CN}{\underset{|}{CH}}—COOH, CH_3—\underset{NO_2}{\underset{|}{CH}}—COOH$

(vi) 

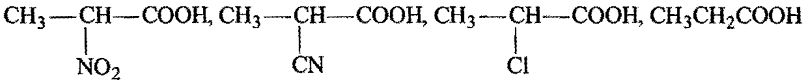
(vii) 
$CH_3—CH_2—COOH, CH_3—\underset{Br}{\underset{|}{CH}}—COOH, CH_3—\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}—COOH$

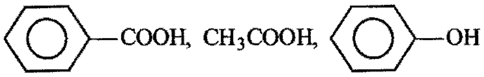
[Ans. (i) $CH_2ClCOOH, HCOOH, C_6H_5COOH, CH_3COOH, C_2H_5COOH, (CH_3)_2CHCOOH$

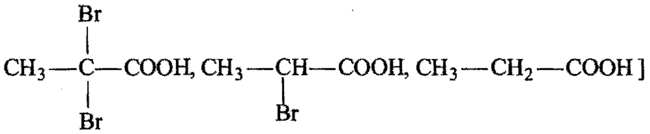
(ii) $CH_3CH_2CHClCOOH, CH_3CHClCH_2COOH, CH_2ClCH_2CH_2COOH, CH_3CH_2CH_2COOH$

(iii) $CCl_3COOH, CHCl_2COOH, CH_2ClCOOH, CH_3COOH$

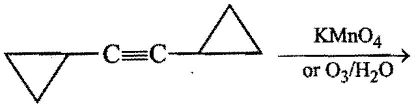
(iv) $FCH_2COOH, ClCH_2COOH, BrCH_2COOH, ICH_2COOH$

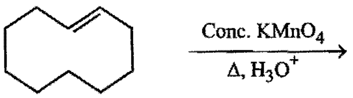
(v) 
$CH_3—\underset{NO_2}{\underset{|}{CH}}—COOH, CH_3—\underset{CN}{\underset{|}{CH}}—COOH, CH_3—\underset{Cl}{\underset{|}{CH}}—COOH, CH_3CH_2COOH$

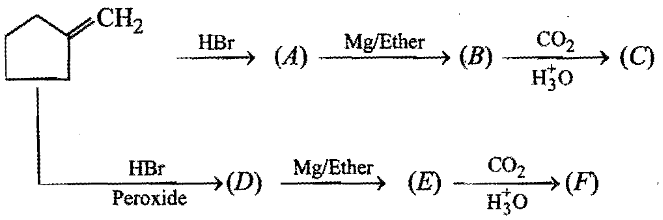
(vi) 

(vii) 
$CH_3—\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}—COOH, CH_3—\underset{Br}{\underset{|}{CH}}—COOH, CH_3—CH_2—COOH$]

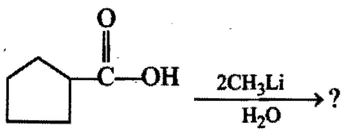
7. Complete the following reactions:

(i) 

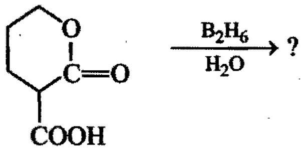
(ii) 

(iii) 

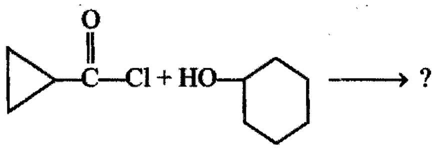
(iv)



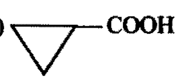
(v)



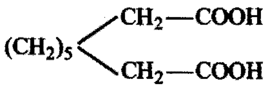
(vi)



[Ans. (i)



(ii)



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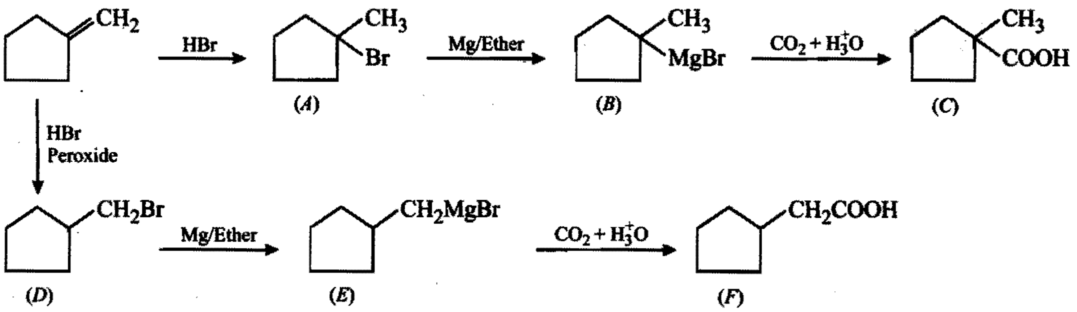

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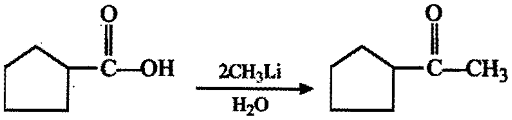
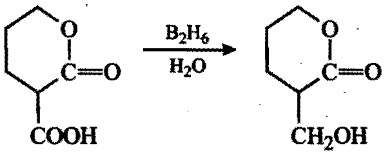
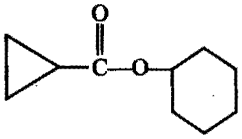


(v)



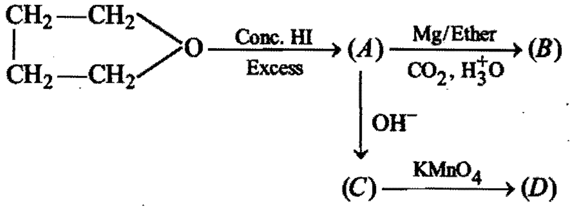
Carboxylic group is reduced in preference to ester group present in the same molecule.

(vi)

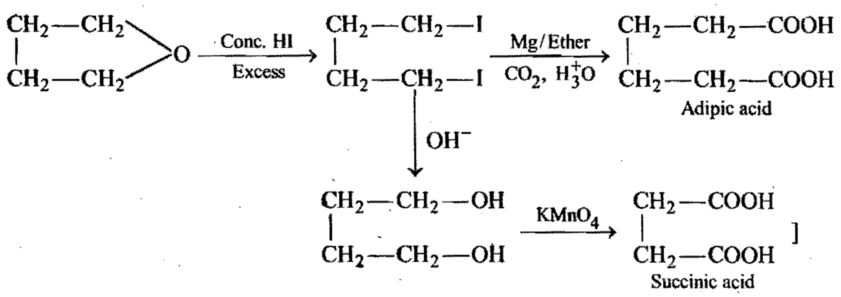


]

8. Complete the following chain of reactions:

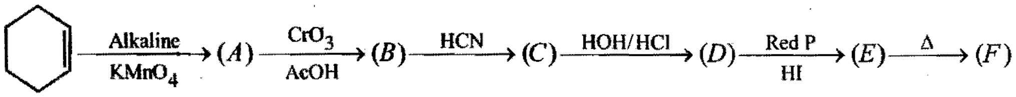


[Ans.

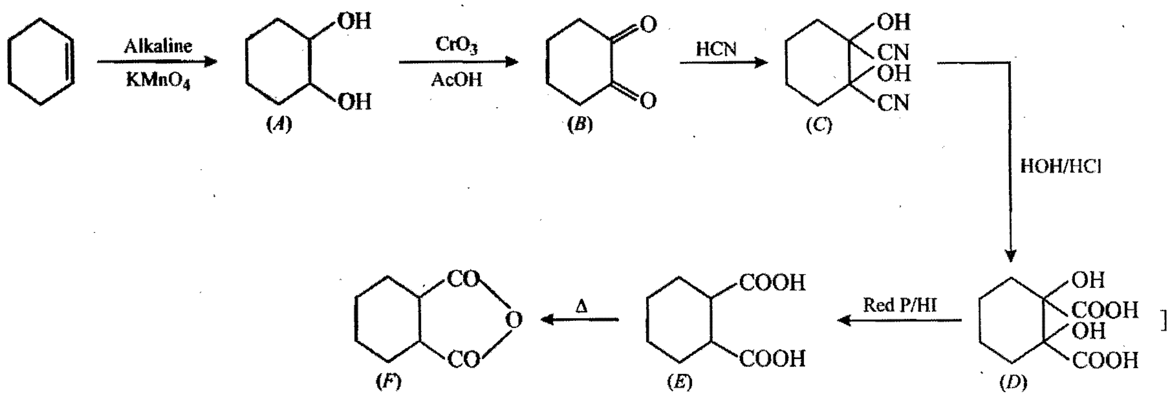


]

9. **Identify (*A*) to (*F*) in the following series of reactions:**



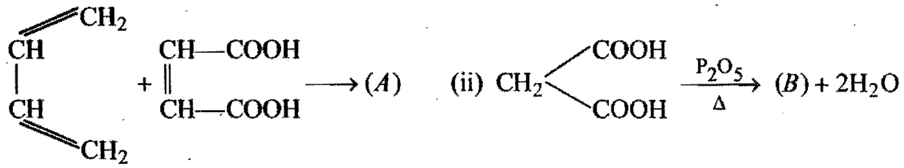
[Ans.



]

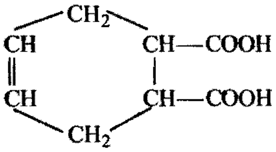
10. **What are (*A*) and (*B*) in the following reactions?**

(i)



(ii) $CH_2(COOH)_2 \xrightarrow[\Delta]{P_2O_5} (B) + 2H_2O$

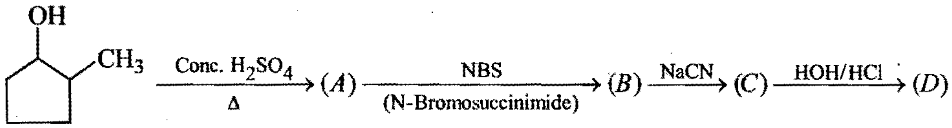
[Ans. (i) (*A*):



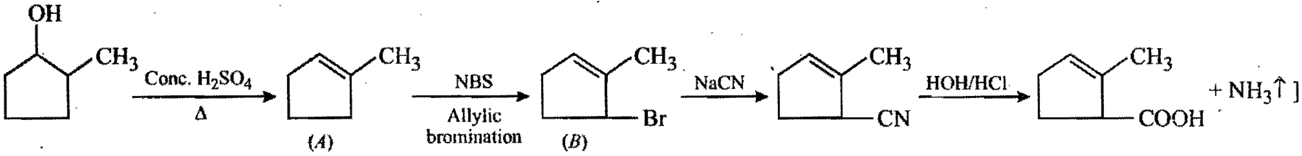
This product is formed as a result of Diels Alder reaction.

(ii) (*B*) : O=C=C=C=O (carbon suboxide)]

11. **Complete the following reactions:**

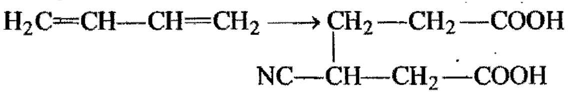


[Ans.



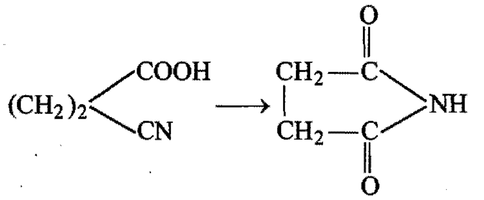
12. **How can you achieve the following interconversions?**

(a)

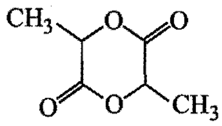


$H_2C{=}CH{-}CH{=}CH_2 \longrightarrow CH_2{-}CH_2{-}COOH$ with $NC{-}CH{-}CH_2{-}COOH$ joined below

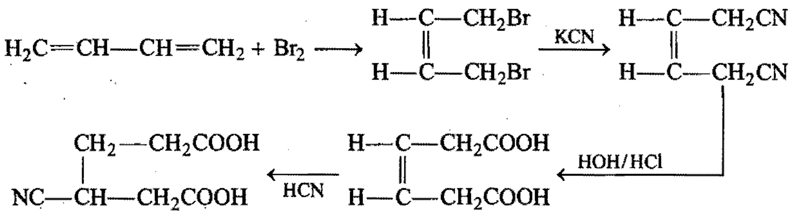
(b)



(c) $CH_3CH_2COOH \longrightarrow$

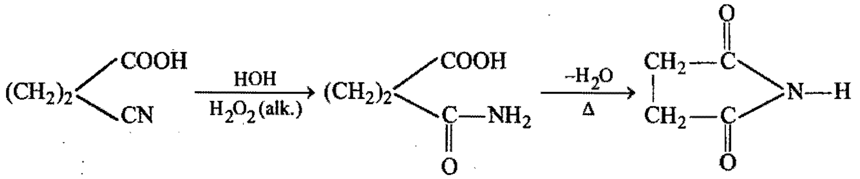


[**Ans.** (a)



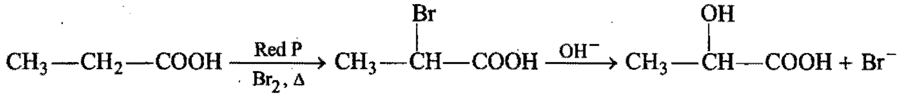
$$H_2C{=}CH{-}CH{=}CH_2 + Br_2 \longrightarrow \begin{matrix} H{-}C{-}CH_2Br \\ \| \\ H{-}C{-}CH_2Br \end{matrix} \xrightarrow{KCN} \begin{matrix} H{-}C{-}CH_2CN \\ \| \\ H{-}C{-}CH_2CN \end{matrix} \xrightarrow{HOH/HCl} \begin{matrix} H{-}C{-}CH_2COOH \\ \| \\ H{-}C{-}CH_2COOH \end{matrix} \xrightarrow{HCN} \begin{matrix} CH_2{-}CH_2COOH \\ | \\ NC{-}CH{-}CH_2COOH \end{matrix}$$

(b)

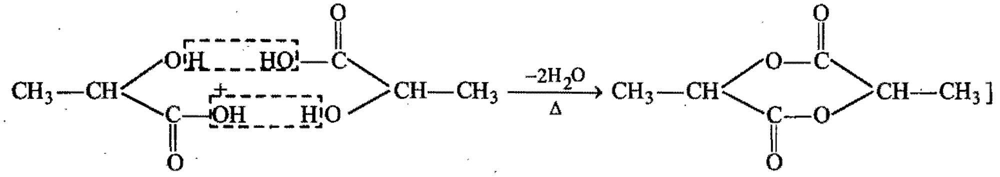


Succinimide

(c)



$$CH_3{-}CH_2{-}COOH \xrightarrow[Br_2,\,\Delta]{Red\ P} CH_3{-}\overset{Br}{\overset{|}{C}H}{-}COOH \xrightarrow{OH^-} CH_3{-}\overset{OH}{\overset{|}{C}H}{-}COOH + Br^-$$

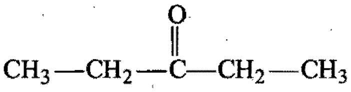


Lactic acid

Lactide

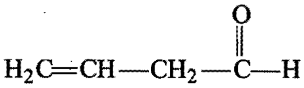
13. Give the star mark to the hydrogen which is most acidic in the following compounds:

(a)



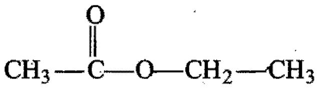
$CH_3{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_3$

(b)



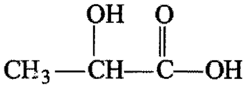
$H_2C{=}CH{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}H$

(c)



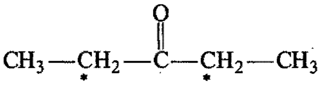
$CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_3$

(d)



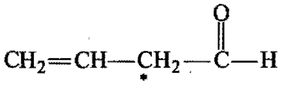
$CH_3{-}\overset{OH}{\overset{|}{C}H}{-}\overset{O}{\overset{\|}{C}}{-}OH$

[**Ans.** (a) Hydrogen of methylene group will be most acidic.



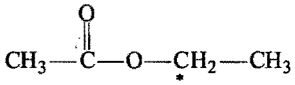
$CH_3{-}\underset{*}{C}H_2{-}\overset{O}{\overset{\|}{C}}{-}\underset{*}{C}H_2{-}CH_3$

(b) In this compound, allylic hydrogen will be most acidic.



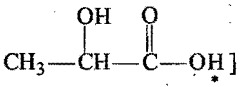
$CH_2{=}CH{-}\underset{*}{C}H_2{-}\overset{O}{\overset{\|}{C}}{-}H$

(c) Hydrogen of methylene group will be most acidic.



$CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{*}{C}H_2{-}CH_3$

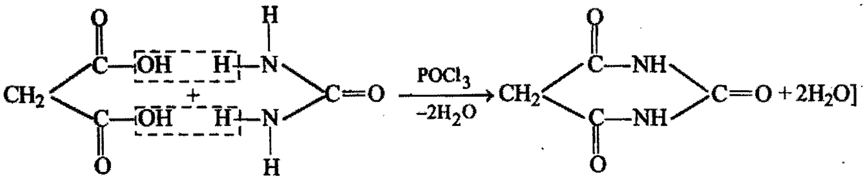
(d) Hydrogen of carboxylic group will be most acidic.



$CH_3{-}\overset{OH}{\overset{|}{C}H}{-}\overset{O}{\overset{\|}{C}}{-}O\underset{*}{H}$]

14. **What happens when malonic acid is heated with urea in presence of $POCl_3$?**

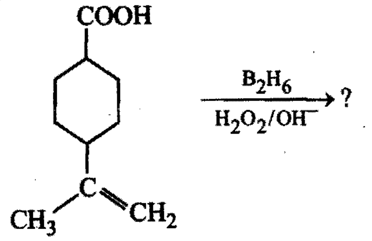
[Ans.



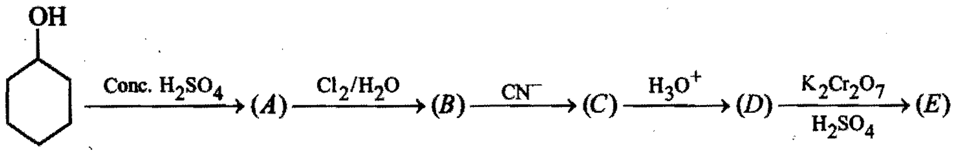
Barbituric acid (Malonyl urea)

15. **Complete the following reactions:**

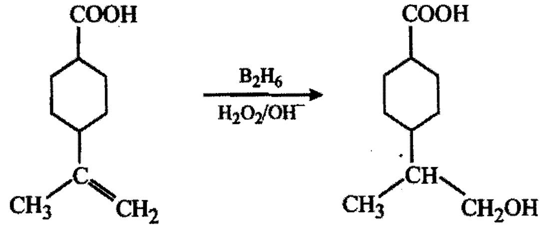
(i)



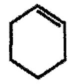
(ii)



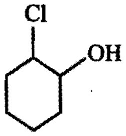
[Ans. (i)



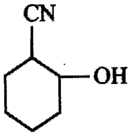
(ii) (A) =



(B) =



(C) =



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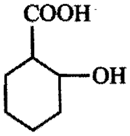
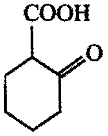


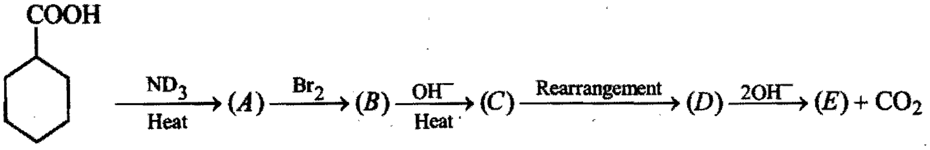
(E) =



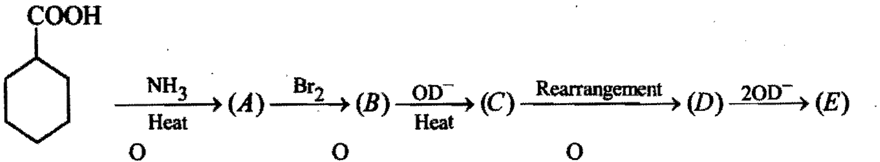
]

16. **Complete the following reactions:**

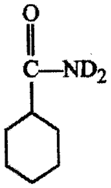
(i)



(ii)



[Ans. (i) (A) =



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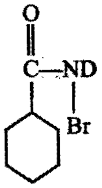
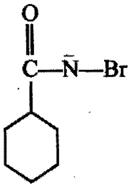


(C) =



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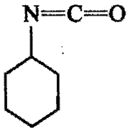

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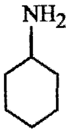

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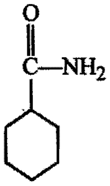

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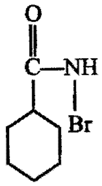

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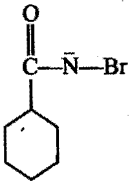
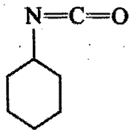
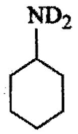


(D) =



(E) =



]

17. The compound which does not give a crystalline product on reaction with either sodium bisulphite or 2,4-DNP but reduces ammoniacal silver nitrate solution is:

(a) C_6H_5CHO ☐ (b) $C_6H_5CH_2OH$ ☐

(c) $H—\overset{\overset{O}{\|}}{C}—OH$ ☐ (d) CH_3CHO ☐

18. The reaction of tartaric acid with Fenton's reagent results in the formation of :

(a) dihydroxy maleic acid ☐
(b) succinic acid ☐
(c) lactic acid ☐
(d) crotonic acid ☐

19.

$$\begin{tikzcd} CH_3—CH_2—COOH \arrow[r, "N_3H"', "H_2SO_4"'] \arrow[d, "\Delta", "Br_2/P"'] & (A)\text{(by reaction } R_1) \\ (B)\text{(by reaction } R_2) & \end{tikzcd}$$

which is the correct alternate?

(a) (*A*) $CH_3CH_2NH_2$, (*B*) $CH_3—\underset{\underset{Br}{|}}{CH}—COOH$ ☐
$R_1 \rightarrow$ Schmidt reaction; $R_2 \rightarrow$ HVZ reaction

(b) (*A*) $CH_3CH_2CONH_2$, (*B*) CH_3CH_2COBr ☐
$R_1 \rightarrow$ HVZ reaction; $R_2 \rightarrow$ Schmidt reaction

(c) (*A*) $CH_3CH_2NH_2$, (*B*) CH_3CH_2COBr ☐
$R_1 \rightarrow$ HVZ reaction; $R_2 \rightarrow$ Schmidt reaction

(d) None is correct ☐

20. $\underset{(A)}{C_4H_6O_4} \xrightarrow{\Delta} \underset{(B)}{C_3H_6O_2} \xrightarrow[\Delta]{\text{Soda lime}} C_2H_6$

The compound [*A*] is:

(a) $CH_3—CH(COOH)_2$ ☐

(b) $\begin{matrix} CH_2—COOH \\ | \\ CH_2—COOH \end{matrix}$ ☐

(c) both are correct ☐

(d) none is correct ☐

21. Which one of the following undergoes decarboxylation most readily?

(a) $CH_3\overset{\overset{O}{\|}}{C}COOH$ ☐ (b) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2COOH$ ☐

(c) $CH_3\overset{\overset{O}{\|}}{C}CH_2COOH$ ☐ (d) $CH_3\overset{\overset{O}{\|}}{C}(CH_2)_3COOH$ ☐

22. Malonic acid on heating gives.........while on decarboxylation gives ....

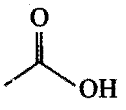
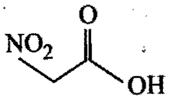
(a) acetic acid, ethane ☐
(b) propanoic acid, methane ☐
(c) propanoic acid, ethane ☐
(d) acetic acid, methane ☐

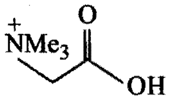
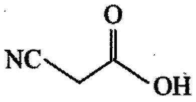
23. Predict the product '*C*' in the following chain of the reactions:

$$CH_3CH_2COOH \xrightarrow{\text{Red P/Br}_2} (A) \xrightarrow{KCN} (B) \xrightarrow[\Delta]{HOH/H^+} (C)$$

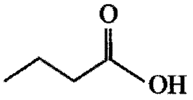
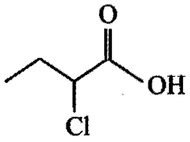
(a) propanoic acid ☐ (b) malonic acid ☐
(c) acetic acid ☐ (d) α-methyl malonic acid ☐

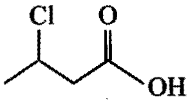
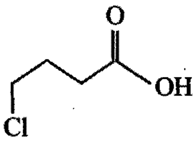
24. Which of the following has the highest pK_a value?

(a)  ☐ (b)  ☐

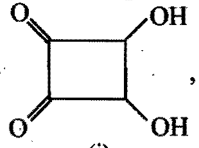
(c)  ☐ (d)  ☐

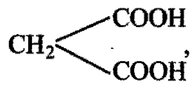
25. Which of the following is the most acidic?

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

26. Consider the following compounds, which of these will release CO_2 with 5% $NaHCO_3$?


(i)


(ii)

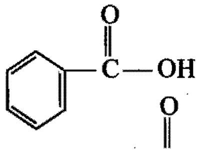
$CH_3—\overset{\overset{O}{\|}}{C}—COOH$
(iii)

(a) (i), (ii) and (iii) ☐ (b) (i) and (iii) ☐
(c) (ii) and (iii) ☐ (d) (i) and (ii) ☐

27. Which of the following has the lowest pK_a value?

(a) $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—OH$ ☐

(b) $CH_2=CH—\overset{\overset{O}{\|}}{C}—OH$ ☐

(c)  ☐

(d) $H—C\equiv C—\overset{\overset{O}{\|}}{C}—OH$ ☐

[**Hint:** In ($H—C\equiv C—\overset{\overset{O}{\|}}{C}—OH$); the carboxylic group is attached to $C\equiv$]

28. The compound *X*, in the reaction,

$$X \xrightarrow{CH_3MgI} Y \xrightarrow{\text{Hydrolysis}} Mg(OH)I + CH_3COOH$$

is:

(a) HCHO ☐ (b) CH_3CHO ☐
(c) $(CH_3)_2CO$ ☐ (d) CO_2 ☐

29. The most suitable reagent for laboratory preparation of acetyl chloride from acetic acid is:

(a) PCl_5 ☐ (b) HCl ☐

(c) $SOCl_2$ ☐ (d) PCl_3 ☐

[**Hint:** $CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2\uparrow + HCl\uparrow$

Byproducts in above reaction are in gaseous state hence, they can be separated easily.]

30. When propanoic acid is treated with aqueous $NaHCO_3$, CO_2 is liberated. The carbon of carbon dioxide comes from:

(a) methyl group ☐ (b) carboxylic group ☐

(c) methylene group ☐ (d) bicarbonate ☐

[**Hint:** $CH_3—CH_2—\overset{*}{C}OOH + NaHCO_3 \longrightarrow$

$CH_3—CH_2—\overset{*}{C}OONa + H_2O + CO_2\uparrow$

Thus, carbon of carbon dioxide comes from sodium bicarbonate.]

31. Decarboxylation of carboxylic acid takes place:

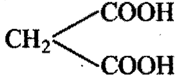
(a) in soda lime treatment ☐

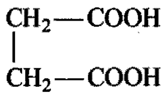
(b) in quick lime treatment ☐

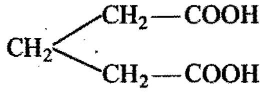
(c) in Kolbe's electrolysis ☐

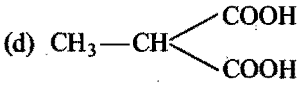
(d) in all of the above ☐

32. A dibasic organic acid (A) on heating gives (B). The compound (B) on soda lime treatment gives the lowest alkane which can be prepared by Wurtz synthesis. The compound (A) is:

(a) 
$CH_2(COOH)_2$ ☐

(b) 
$CH_2—COOH \,|\, CH_2—COOH$ ☐

(c) 
$CH_2(CH_2—COOH)_2$ ☐

(d) 
$CH_3—CH(COOH)_2$ ☐

33. 0.759 g of a silver salt of a dibasic organic acid on ignition left 0.463 g metallic silver. The equivalent weight of acid is:

(a) 70 ☐ (b) 108 ☐

(c) 60 ☐ (d) 50 ☐

[**Hint:** Equivalent weight of acid

$$= \frac{\text{Mass of silver salt}}{\text{Mass of silver residue}} \times 108 - 107]$$

34. The reagent, which distinguishes formic acid from acetic acid is:

(a) 2,4-dinitrophenyl hydrazine ☐

(b) $HgCl_2$ ☐

(c) C_2H_5ONa ☐

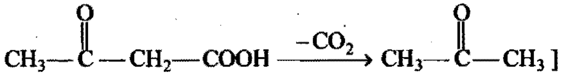
(d) Hg_2Cl_2 ☐

35. Which of the following compounds easily undergoes decarboxylation?

(a) CCl_3COOH ☐ (b) β-Keto carboxylic acid ☐

(c) HCOOH ☐ (d) CH_3COOH ☐

[**Hint:** β-Keto acids are most easily decarboxylated.


$$CH_3—\overset{O}{\overset{\|}{C}}—CH_2—COOH \xrightarrow{-CO_2} CH_3—\overset{O}{\overset{\|}{C}}—CH_3\,]$$

36. (A), (B) and (C) are three dicarboxylic acids such that:

$(A) \xrightarrow{\Delta}$ carboxylic acid $+ CO_2\uparrow$

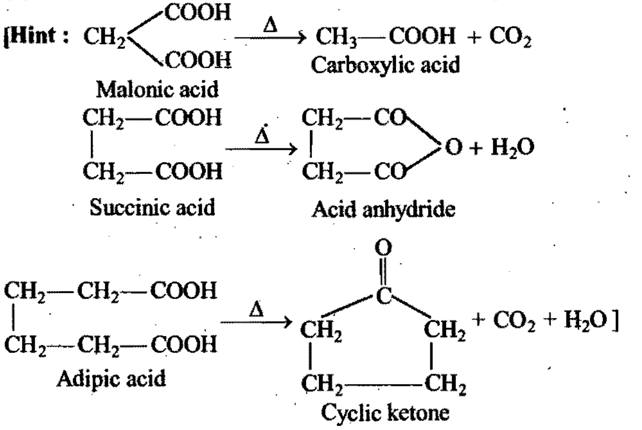
$(B) \xrightarrow{\Delta}$ acid anhydride $+ H_2O\uparrow$

$(C) \xrightarrow{\Delta}$ cyclic ketone $+ H_2O + CO_2\uparrow$

then:

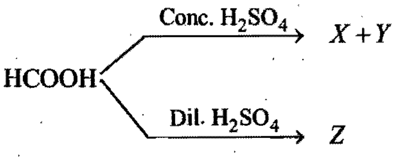
	(A)	(B)	(C)
(a)	adipic acid	malonic acid	succinic acid ☐
(b)	malonic acid	adipic acid	succinic acid ☐
(c)	adipic acid	succinic acid	malonic acid ☐
(d)	malonic acid	succinic acid	adipic acid ☐

[**Hint:**



$$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3—COOH + CO_2$$

$$\text{Adipic acid} \xrightarrow{\Delta} \text{Cyclic ketone} + CO_2 + H_2O\,]$$

37. 
$$HCOOH \begin{cases} \xrightarrow{\text{Conc. } H_2SO_4} X + Y \\ \xrightarrow{\text{Dil. } H_2SO_4} Z \end{cases}$$

Products X, Y and Z are respectively:

(a) $CO, H_2O, \begin{array}{l}COOH\\|\\COOH\end{array}$ ☐ (b) $\begin{array}{l}COOH\\|\\COOH\end{array}, CO, H_2O$ ☐

(c) $CO_2, H_2, \begin{array}{l}COOH\\|\\COOH\end{array}$ ☐ (d) $\begin{array}{l}COOH\\|\\COOH\end{array}, CO_2, H_2$ ☐

[**Hint:** $HCOOH \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CO(g) + H_2O(g)$

$$2HCOOH + [O] \xrightarrow{\text{Dil. } H_2SO_4} \begin{array}{l}COOH\\|\\COOH\end{array} + H_2O]$$

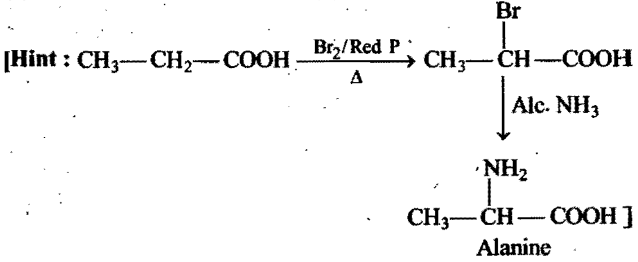
38. $CH_3CH_2COOH \xrightarrow[\Delta]{Br_2/\text{Red P}} (A) \xrightarrow{\text{Alc. } NH_3} (B)$

The final product (B) in above reaction is:

(a) alanine ☐ (b) pyruvic acid ☐

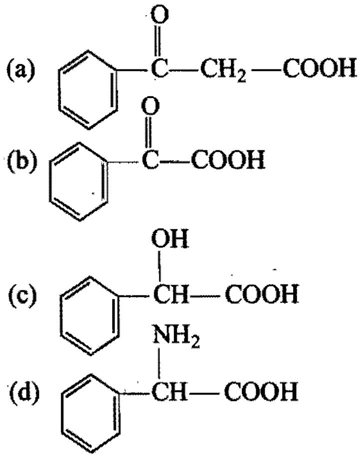
(c) citric acid ☐ (d) lactic acid ☐

[**Hint:**



$$CH_3—CH_2—COOH \xrightarrow[\Delta]{Br_2/\text{Red P}} CH_3—\underset{}{\overset{Br}{\overset{|}{C}}}H—COOH \xrightarrow{\text{Alc. } NH_3} CH_3—\overset{NH_2}{\overset{|}{C}}H—COOH\,]$$

39. Which of the following carboxylic acids undergoes decarboxylation most easily?



(a) ☐
(b) ☐
(c) ☐
(d) ☐

40. Arrange the following carboxylic acids in order of decreasing acidity:

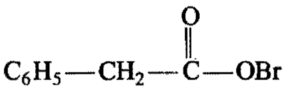
Oxalic acid	Malonic acid	Succinic acid
(I)	(II)	(III)

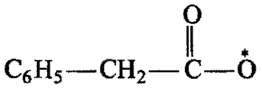
(a) I > II > III ☐ (b) III > II > I ☐
(c) II > III > I ☐ (d) II > I > III ☐

41. The intermediate(s) formed during the reaction

$$C_6H_5CH_2COOAg + Br_2 \xrightarrow{CCl_4} C_6H_5CH_2Br,$$

is (are):

(a)  $C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-OBr$ ☐

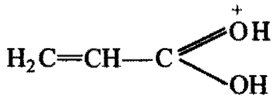
(b)  $C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-\dot{O}$ ☐

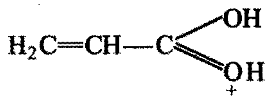
(c) $C_6H_5-\dot{C}H_2$ ☐

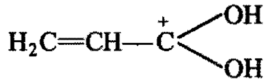
(d) $\dot{Br}$ ☐

42. Which of the following intermediate species is/are formed in the reaction of acrylic acid with HBr to give β-bromopropanoic acid?

$$H_2C=CH-COOH \xrightarrow{HBr} BrCH_2-CH_2-COOH$$

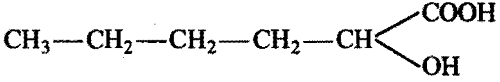
(a)  ☐

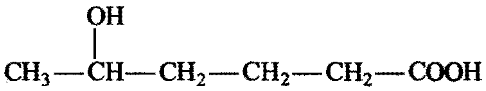
(b)  ☐

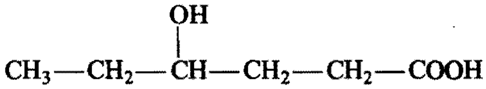
(c)  ☐

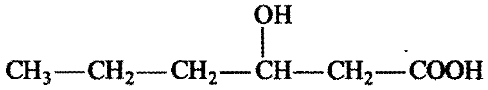
(d)  ☐

43. Which of the following will give cyclic products upon being heated or being treated by an acid?

(a)  ☐

(b)  $CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CH_2-CH_2-COOH$ ☐

(c)  $CH_3-CH_2-\overset{OH}{\overset{|}{C}H}-CH_2-CH_2-COOH$ ☐

(d)  $CH_3-CH_2-CH_2-\overset{OH}{\overset{|}{C}H}-CH_2-COOH$ ☐

44. What types of isomerism are exhibited by hexanoic acid?

(a) Chain isomerism ☐
(b) Position isomerism ☐
(c) Functional group isomerism ☐
(d) Metamerism ☐

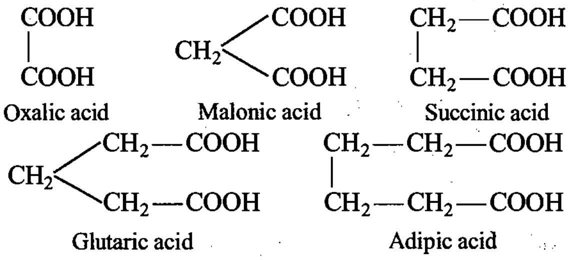
ANSWERS : BRAIN STORMING PROBLEMS

17. (c)	**18.** (a)	**19.** (a)	**20.** (a)	**21.** (c)	**22.** (d)	**23.** (a)	**24.** (a)	**25.** (b)	**26.** (c)
27. (d)	**28.** (d)	**29.** (c)	**30.** (d)	**31.** (d)	**32.** (d)	**33.** (a)	**34.** (b)	**35.** (b)	**36.** (d)
37. (a)	**38.** (a)	**39.** (a)	**40.** (a)	**41.** (a,b,c,d)	**42.** (a,b,c,d)	**43.** (a,b,c)	**44.** (a,c)		

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Dicarboxylic acids have two carboxylic groups, *e.g.*,


Oxalic acid Malonic acid Succinic acid

Glutaric acid Adipic acid

Acidity of dicarboxylic acid depends upon the stability of intermediate ion and upon the distance between two carboxylic groups. Shorter the distance between two carboxylic groups, greater is the acidic character. Melting point of these acids depends on the symmetry. Greater the symmetry, higher will be the melting point.

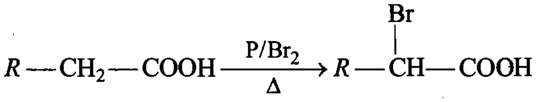
Dicarboxylic acids on heating give monocarboxylic acid, alkanes, cyclic ketones depending on the conditions.

Answer the following questions:

1. Which of the following is the most acidic?
   (a) Oxalic acid (b) Malonic acid
   (c) Succinic acid (d) Adipic acid
2. Which of the following dicarboxylic acids is used in the manufacture of nylon-6?
   (a) Succinic acid (b) Glutaric acid
   (c) Adipic acid (d) Oxalic acid
3. Which of the following has highest melting point?
   (a) Maleic acid (b) Fumaric acid
   (c) Succinic acid (d) Oxalic acid
4. Which of the following dicarboxylic acids, will give monocarboxylic acid on heating ?
   (a) Malonic acid (b) Succinic acid
   (c) Glutaric acid (d) Adipic acid
5. Sodium adipate on electrolysis gives:
   (a) but-2-ene (b) but-1-ene
   (c) cyclobutane (d) cyclobutene

Passage 2

Carboxylic acids having atleast one α-hydrogen react with Cl_2 or Br_2 in the presence of phosphorus (or a phosphorus halide) to give α-halo acids. This reaction is known as Hell-Volhard-Zelinsky reaction (HVZ reaction),



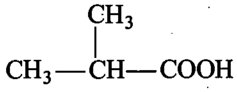
$$R-CH_2-COOH \xrightarrow[\Delta]{P/Br_2} R-\underset{}{\overset{Br}{\overset{|}{C}}}H-COOH$$

The HVZ reaction is limited to the formation of α-chloro and α-bromo acids and it is sometimes awkward to carry out. The reagents (X_2 and P) are noxious and the reaction time is often long and the conditions of reaction are harsh.

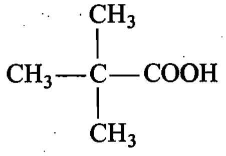
Answer the following questions:

1. Which of the following carboxylic acids will not give HVZ reaction?

(a) CH_3-COOH

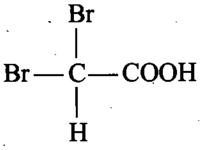
(b) 
$CH_3-CH(CH_3)-COOH$

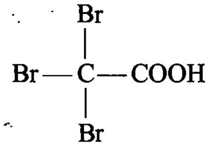
(c) CH_3-CH_2-COOH

(d) 
$CH_3-C(CH_3)_2-COOH$

2. Which of the following will be obtained when acetic acid is subjected to HVZ reaction?

(a) $BrCH_2COOH$

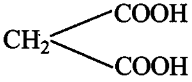
(b) 
$Br_2CH-COOH$

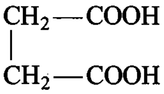
(c) 
$Br_3C-COOH$

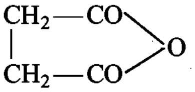
(d) All of these

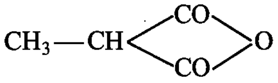
3. $CH_3-COOH \xrightarrow{Br_2/P} (A) \xrightarrow{NaCN} (B) \xrightarrow{HOH/H^+} (C)$

The product (*C*) will be:

(a) 

(b) 

(c) 

(d) 

4. $\underset{(A)}{R-CH_2-CH_2-OH} \longrightarrow \underset{(B)}{R-CH_2-CH_2-COOH}$

In above conversion, the reactant (*A*) follows the sequence of reactions with three reagents.

(a) $PBr_3, KCN, H_3\overset{+}{O}$ (b) $PBr_3, H_3\overset{+}{O}, KCN$

(c) HCN, PBr_3, KCN (d) $H_3\overset{+}{O}, KCN, PBr_3$

5. $CH_3CH_2COOH \xrightarrow{Red\ P + Br_2} (A) \xrightarrow{Alc.\ -KOH} (B)$. The product (*B*) is:
   (a) 2-ketopropanoic acid
   (b) acrylic acid
   (c) 2-hydroxy propanoic acid
   (d) 2-amino propanoic acid

Passage 3

Variety of products are obtained when dicarboxylic acids are heated. The nature of products depends on the carbon chain length separating the two carboxylic groups.

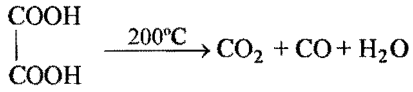
(I) 1,2 and 1,3-dibasic acids on heating give monocarboxylic acid.

(II) 1,4 and 1,5-dibasic acids on heating give cyclic anhydride.

(III) 1,6 and 1,7-dibasic acids give cyclic ketones.

Indicate whether the following reactions are right or wrong:

1.

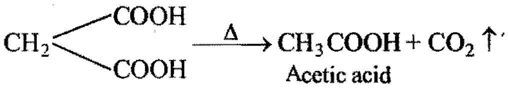


$$\underset{COOH}{\overset{COOH}{|}} \xrightarrow{200^\circ C} CO_2 + CO + H_2O$$

Oxalic acid

(a) Right (b) Wrong

2.

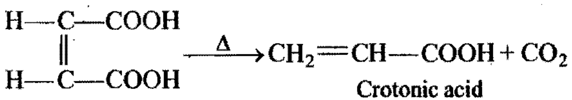


Malonic acid

Acetic acid

(a) Right (b) Wrong

3.



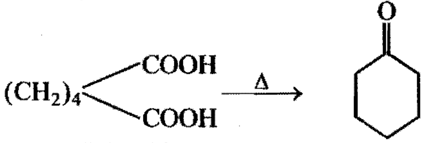
$$\begin{matrix} H—C—COOH \\ \| \\ H—C—COOH \end{matrix} \xrightarrow{\Delta} CH_2{=}CH—COOH + CO_2$$

Maleic acid

Crotonic acid

(a) Right (b) Wrong

4.

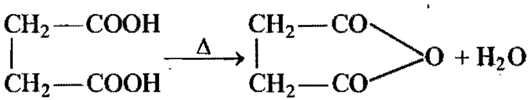


Adipic acid

Cyclohexanone

(a) Right (b) Wrong

5.



Succinic acid

Succinic anhydride

(a) Right (b) Wrong

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

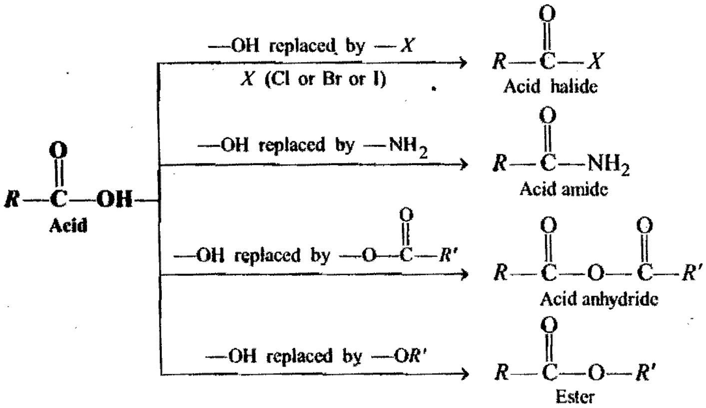
Passage 1	1. (a)	2. (c)	3. (b)	4. (a)	5. (c)
Passage 2	1. (d)	2. (d)	3. (a)	4. (a)	5. (b)
Passage 3	1. (a)	2. (a)	3. (b)	4. (b)	5. (a)

13

ACID DERIVATIVES

13.1 DERIVATIVES OF CARBOXYLIC ACIDS

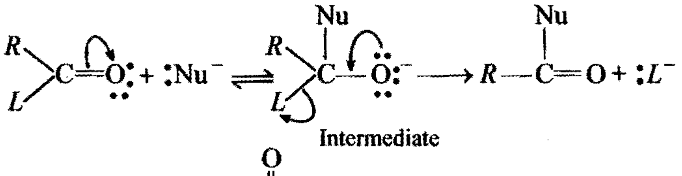
The classes of compounds obtained from carboxylic acids by the replacement of —OH group of the —COOH group with —X, —NH_2, —OOCR or —OR are termed as acid derivatives.

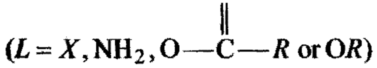


(where R and R' may be either same or different)

The acid derivatives undergo hydrolysis and form the parent acid. ($R-\overset{\overset{O}{\|}}{C}-$) group is common to these derivatives and is known as acyl group and hence these derivatives are also termed as acyl derivatives.

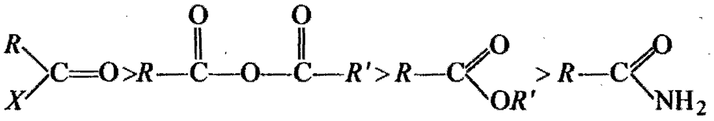
Acyl derivatives are characterized by **nucleophilic substitution reactions.**





$$(L = X, NH_2, O-\overset{\overset{O}{\|}}{C}-R \text{ or } OR)$$

The relative reactivities of various acyl compounds have been found to be in the following order:



$$\underset{X}{\overset{R}{>}}C{=}O > R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R' > R-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OR'} > R-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow NH_2}$$

Out of acid halides, the acid chlorides are more important ones.

The overall order of reactivity can be accounted for in terms of the following three factors:

(i) Basicity of the leaving group, (ii) Resonance effect and (iii) Inductive effect.

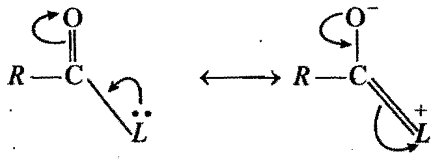
(i) Basicity of the leaving group : Weaker bases are good leaving groups. Hence, the acyl derivatives with weaker bases as leaving groups can easily rupture the bond and are more reactive. Chloride ion is the weakest base while —NH_2 is the strongest base. Thus, acyl chlorides are most reactive and amides are least reactive.

The correct order of basicity of the leaving group and their tendency of leave is:

$$H_2\bar{N}: > :\bar{O}R > RCO\bar{O}: > :Cl^-$$

(Basicity decreases and **Reactivity** increases)

(ii) Resonance effect : The leaving group in each case has an atom with lone pair of electrons adjacent to the carbonyl group. The compound exists, therefore, as a resonance hybrid.



This makes the molecule more stable. The greater the stabilization, the smaller is the reactivity of the acyl compound. However, acyl chlorides are least affected by resonance. Due to lower stabilization, the acid chlorides are more reactive as the loss of —Cl is easier. Greater stabilization is achieved by resonance in esters and amides and thus, they are less reactive.

(iii) **Inductive effect** : Higher the $-I$ effect, more reactive is the acyl compound. Inductive effect of oxygen in ester is greater than nitrogen in amide, hence ester is more reactive than an amide.

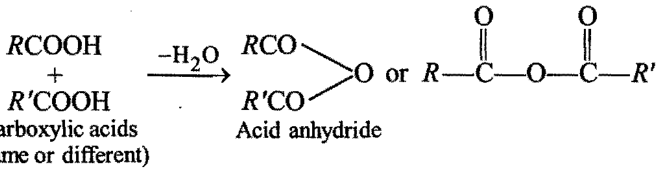
13.2 NOMENCLATURE

1. Acid chlorides : Acid chlorides (acyl chlorides) have the general formula, $RCOCl$. The common names are derived by changing the suffix, '-ic acid', of the trivial names of the corresponding acids by 'yl chloride'.

In IUPAC system, these are named after the name of alkane by replacing the ending 'e' by 'oyl chloride'.

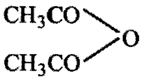
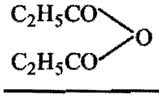
Formula	Common name	IUPAC name
$HCOCl$ (Unstable)	Formyl chloride	Methanoyl chloride
CH_3COCl	Acetyl chloride	Ethanoyl chloride
C_2H_5COCl	Propionyl chloride	Propanoyl chloride
C_3H_7COCl	Butyryl chloride	Butanoyl chloride

2. Acid anhydrides : The acid anhydrides may be regarded as being derived from acid(s) with the elimination of one molecule of water from two molecules of the same or different acids.

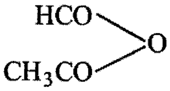


$$\underset{\text{(Same or different)}}{\underset{\text{Carboxylic acids}}{RCOOH + R'COOH}} \xrightarrow{-H_2O} \underset{\text{Acid anhydride}}{(RCO)(R'CO)O} \text{ or } R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R'$$

Anhydrides are named by replacing the word 'acid' in the name of the acid by 'anhydride' in both common and IUPAC names.

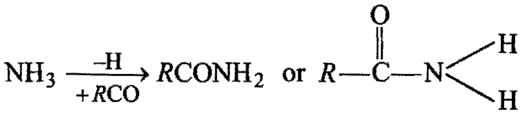
Formula	Common name	IUPAC name
 $(CH_3CO)_2O$	Acetic anhydride	Ethanoic anhydride
 $(C_2H_5CO)_2O$	Propionic anhydride	Propanoic anhydride

When both acyl groups are similar the anhydride is called symmetrical or simple anhydride and when they are different (derived from two molecules of different acids) are called unsymmetrical or mixed anhydrides. Formic anhydride is unknown but the mixed acetic formic anhydride,



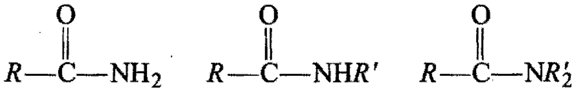
$HCO-O-COCH_3$ (Ethanoic methanoic anhydride), is known.

3. Acid amides : Acid amides have general formula, $RCONH_2$. The —$CONH_2$ group is called the amide group. Primary acid amide may be regarded as acyl derivatives of ammonia obtained by replacement of hydrogen atom by acyl group.



$$NH_3 \xrightarrow[+RCO]{-H} RCONH_2 \text{ or } R-\overset{O}{\overset{\|}{C}}-N\begin{matrix}H\\H\end{matrix}$$

They are further classified as primary (1°), secondary (2°) and tertiary (3°) according as the —OH part of the —COOH group is replaced by —NH_2, —NHR' and —NR'_2 groups respectively. Thus,

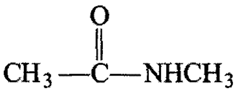


$$\underset{1^\circ \text{ acid amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} \quad \underset{2^\circ \text{ acid amide}}{R-\overset{O}{\overset{\|}{C}}-NHR'} \quad \underset{3^\circ \text{ acid amide}}{R-\overset{O}{\overset{\|}{C}}-NR'_2}$$

In common name system, name of the primary amides are derived from the names of corresponding acids by replacing the suffix '-ic acid' by 'amide'. IUPAC names are derived by replacing 'e' of the parent hydrocarbon by 'amide'.

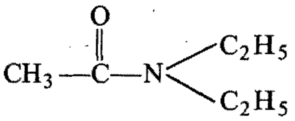
Formula	Common name	IUPAC name
$HCONH_2$	Formamide	Methanamide
CH_3CONH_2	Acetamide	Ethanamide
$C_2H_5CONH_2$	Propionamide	Propanamide
$C_3H_7CONH_2$	Butyramide	Butanamide

Secondary and tertiary amides are named by adding the name of the substituent present on the nitrogen atom before the name of the parent (or primary) amide. The letter 'N' is normally written before the name of the substituent to indicate that the substituent is attached to the nitrogen atom. In tertiary amides, the letter N is repeated twice. For example,



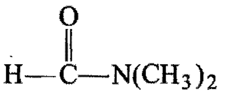
$CH_3-\overset{O}{\overset{\|}{C}}-NHCH_3$

N-Methyl ethanamide



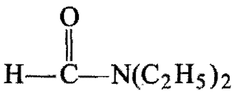
$CH_3-\overset{O}{\overset{\|}{C}}-N(C_2H_5)_2$

N,N-Diethyl ethanamide



$H-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$

N,N-Dimethyl methanamide



$H-\overset{O}{\overset{\|}{C}}-N(C_2H_5)_2$

N,N-Diethyl methanamide

4. Esters :

$$\underset{\text{Organic acid}}{CH_3COOH} + \underset{\text{Alcohol}}{HOC_2H_5} \rightleftharpoons \underset{\text{Organic ester}}{CH_3COOC_2H_5} + H_2O$$

$$\underset{\text{Inorganic acid}}{H_2SO_4} + \underset{\text{Alcohol}}{HOC_2H_5} \rightleftharpoons \underset{\text{Inorganic ester}}{C_2H_5HSO_4} + H_2O$$

An ester, therefore, may be defined as an alkyl derivative of an acid (organic or inorganic) whose hydrogen atom has been replaced by an alkyl group.

Organic esters are represented by general formula, *RCOOR′*, where *R* and *R′* may be same or different. Organic esters are named by first naming the alkyl group of the alcohol followed by the name of the acid and changing the suffix '-ic acid' by '-ate'.

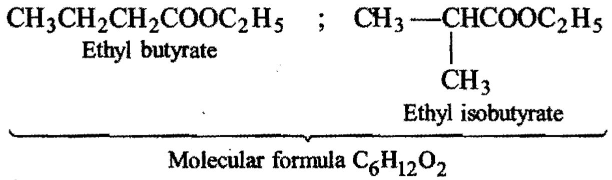
Formula	**Common name**	**IUPAC name**
$HCOOCH_3$	Methyl formate	Methyl methanoate
CH_3COOCH_3	Methyl acetate	Methyl ethanoate
$CH_3COOC_2H_5$	Ethyl acetate	Ethyl ethanoate
$C_2H_5COOC_2H_5$	Ethyl propionate	Ethyl propanoate

Organic esters show the following types of isomerism:

(i) **Functional isomerism :** Esters are isomeric with fatty acids.

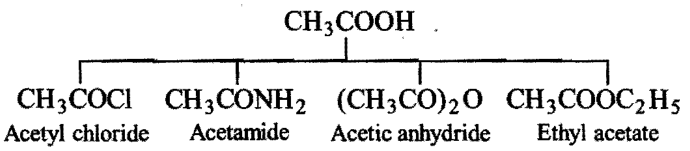
$$\underbrace{\underset{\text{Ethyl formate}}{HCOOC_2H_5} \quad ; \quad \underset{\text{Propionic acid}}{C_2H_5COOH}}_{\text{Molecular formula } C_3H_6O_2}$$

(ii) **Chain isomerism :**



$$\underbrace{\underset{\text{Ethyl butyrate}}{CH_3CH_2CH_2COOC_2H_5} \quad ; \quad \underset{\text{Ethyl isobutyrate}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOC_2H_5}}_{\text{Molecular formula } C_6H_{12}O_2}$$

Acid Derivatives of Acetic Acid



Acetyl chloride, acetamide, acetic anhydride and ethyl acetate are the acid derivatives of acetic acid. These are the typical compounds of their homologous series and thus, the chemistry of these four compounds has only been discussed here.

13.3 ACETYL CHLORIDE OR ETHANOYL CHLORIDE, CH_3COCl

Acetyl chloride is the most important acyl chloride or acid chloride. The first member of the series, formyl chloride (HCOCl) is an unstable compound and readily break up into carbon monoxide and hydrogen chloride.

Methods of Preparation

1. Acetyl chloride is prepared by heating glacial acetic acid with phosphorus trichloride, phosphorus pentachloride or thionyl chloride. Thionyl chloride is the better reagent because the byproducts of the reaction are the gases SO_2 and HCl, which are easily separated.

$$\underset{\text{Ethanoic acid}}{3CH_3COOH} + PCl_3 \xrightarrow{\text{Heat}} \underset{\text{Ethanoyl chloride}}{3CH_3COCl} + H_3PO_3$$

$$CH_3COOH + PCl_5 \xrightarrow{\text{Heat}} CH_3COCl + POCl_3 + HCl$$

$$\underset{\substack{\text{Acetic acid}\\\text{(Glacial)}}}{CH_3COOH} + \underset{\substack{\text{Thionyl}\\\text{Chloride}}}{SOCl_2} \xrightarrow{\text{Heat}} \underset{\substack{\text{Acetyl}\\\text{chloride}}}{CH_3COCl} + SO_2 + HCl$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2\uparrow + HCl\uparrow$$

In laboratory, acetyl chloride is also prepared by this method.

Fluorides, bromides and iodides can also be prepared but they offer no advantage over the less expensive acyl chlorides.

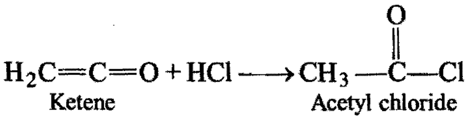
2. **Industrial method :** Acetyl chloride is prepared on a large scale by distilling anhydrous sodium acetate or calcium acetate with phosphorus trichloride, phosphorus oxychloride or sulphuryl chloride.

$$3CH_3COONa + PCl_3 \xrightarrow{\text{Heat}} 3CH_3COCl + Na_3PO_3$$

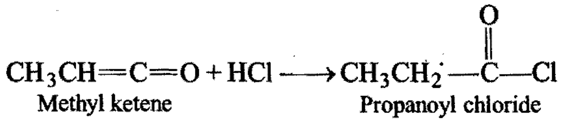
$$\underset{\text{Sodium acetate}}{2CH_3COONa} + POCl_3 \xrightarrow{\text{Heat}} \underset{\text{Acetyl chloride}}{2CH_3COCl} + NaPO_3 + NaCl$$

$$\underset{\substack{\text{Calcium}\\\text{acetate}}}{(CH_3COO)_2Ca} + \underset{\substack{\text{Sulphuryl}\\\text{chloride}}}{SO_2Cl_2} \xrightarrow{\text{Heat}} \underset{\substack{\text{Acetyl}\\\text{chloride}}}{2CH_3COCl} + CaSO_4$$

3. **From ketenes :** By addition of HCl.



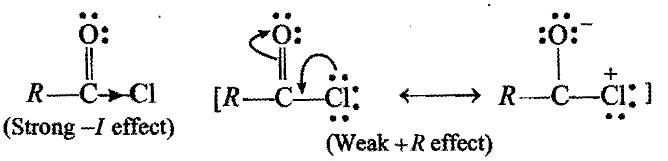
$$\underset{\text{Ketene}}{H_2C{=}C{=}O} + HCl \longrightarrow \underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl}$$



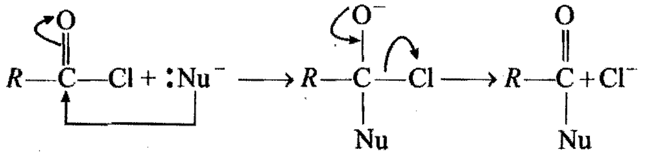
$$\underset{\text{Methyl ketene}}{CH_3CH{=}C{=}O} + HCl \longrightarrow \underset{\text{Propanoyl chloride}}{CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-Cl}$$

Physical properties : Acetyl chloride is a colourless lachrymatory (tear producing) liquid with a pungent odour. It boils at 52°C. It fumes in moist air due to the formation of hydrogen chloride. It is soluble in ether, acetone and acetic acid. They are incapable of forming the H-bond and thus have lower boiling points than parent carboxylic acids.

Chemical properties : Among the different acid derivatives, acyl chlorides are the most reactive. In acyl chlorides, the carbonyl group $\left(-\overset{\overset{\displaystyle O}{\|}}{C}-\right)$ is attached to highly electronegative chlorine atom. Due to strong electron withdrawing effect of chlorine atom (*–I* effect), the electron density on the carbonyl carbon is reduced further and at the same time, it has a weak electron releasing resonance effect (+*R* effect).



As a result of combined influence of both these effects, the acyl carbon atom becomes sufficiently electron deficient. Hence, acyl chlorides readily undergo a number of **nucleophilic substitution reactions** in which the attacking nucleophile can easily attack the electron deficient carbon atom.



$$R\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!Cl + :Nu^- \longrightarrow R\!-\!\underset{\underset{\displaystyle Nu}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}\!-\!Cl \longrightarrow R\!-\!\underset{\underset{\displaystyle Nu}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}} + Cl^-$$

$$Cl^- + H^+ \longrightarrow HCl$$

Compounds which contain strong electron donor group with a replaceable hydrogen atom, (*e.g.*, —OH, —NH_2, —NH*R*, etc.) readily react with acetyl chloride with the result that their hydrogen atom is replaced by acetyl group, CH_3—CO. This is known as **acetylation.**

Some of the important reactions of acetyl chloride are given below:

(i) Hydrolysis : Acetyl chloride readily reacts with water when chlorine atom is replaced by —OH group to form acetic acid.

$$\underset{\text{Acetyl chloride}}{CH_3CO\boxed{Cl + H}OH} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + HCl$$

An aqueous solution of aliphatic acid chlorides gives white precipitate with $AgNO_3$ solution.

$$RCOCl + HOH + AgNO_3 \longrightarrow R\text{—}COOH + HNO_3 + \underset{\text{(White ppt.)}}{AgCl}$$

(ii) Action with alcohols (Alcoholysis) : Acetyl chloride reacts with an alcohol in presence of pyridine base when the —Cl is replaced by alkoxy group (—O*R*) to form an ester.

$$CH_3CO\boxed{Cl + H}\underset{\text{Alcohol}}{OC_2H_5} \xrightarrow{\text{Base}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$

Thioalcohols are acetylated to thioesters.

$$CH_3CO\boxed{Cl + H}\underset{\text{Ethyl thioalcohol}}{SC_2H_5} \longrightarrow \underset{\text{Ethyl thioacetate}}{CH_3COSC_2H_5}$$

(iii) Action with ammonia : Acetyl chloride reacts with ammonia when —Cl is replaced by an amino group (—NH_2) to form an amide (1°).

$$CH_3CO\boxed{Cl + H}NH_2 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + HCl$$

(iv) Action with primary and secondary amines : Acetyl chloride reacts with primary and secondary amines and forms substituted amides (2° and 3°) respectively.

$$CH_3CO\boxed{Cl + H}\underset{\text{Ethylamine}}{NHC_2H_5} \longrightarrow \underset{N\text{-Ethyl acetamide}}{CH_3CONHC_2H_5} + HCl$$

$$CH_3CO\boxed{Cl + H}\underset{\text{Diethylamine}}{N(C_2H_5)_2} \longrightarrow \underset{NN\text{-Diethyl acetamide}}{CH_3CON(C_2H_5)_2} + HCl$$

(v) Action with hydroxylamine and hydrazine : Corresponding acetyl derivatives are formed.

$$CH_3COCl + \underset{\text{Hydroxyl-amine}}{H_2NOH} \longrightarrow \underset{\substack{\text{Acetyl hydroxylamine}\\\text{(Hydroxamic acid)}}}{CH_3CONHOH} + HCl$$

$$CH_3COCl + \underset{\text{Hydrazine}}{H_2NNH_2} \longrightarrow \underset{\substack{\text{Acetyl hydrazine}\\\text{(Hydrazides)}}}{CH_3CONHNH_2} + HCl$$

(vi) Reduction : (a) Acetyl chloride on reduction with hydrogen in presence of palladium over barium sulphate and partially poisoned with a small amount of sulphur or quinoline, as catalyst (to avoid further reduction of aldehydes to alcohols) to form acetaldehyde **(Rosenmund's reduction).**

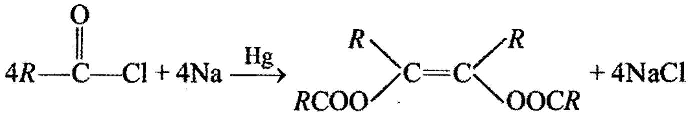
$$CH_3COCl + H_2 \xrightarrow[\text{S or quinoline}]{Pd/BaSO_4} CH_3CHO + HCl$$

(b) When reduced with $LiAlH_4$ or $NaBH_4$, it gives ethyl alcohol.

$$CH_3COCl + 2H_2 \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

(c) Acid chlorides are reduced to aldehydes by LiH or lithium tri-*tert*.-butoxy aluminium hydride.

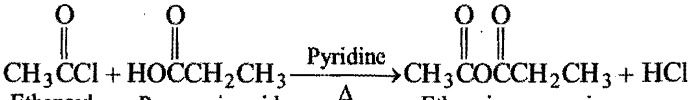
(d) Acid chlorides are reduced to esters of an enediol by Na-Hg in an inert solvent.



$$4R\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!Cl + 4Na \xrightarrow{Hg} (R)(RCOO)C{=}C(R)(OOCR) + 4NaCl$$

(vii) Action with salts of carboxylic acids : It reacts with sodium salts of carboxylic acids to form anhydrides.

$$CH_3COCl + \underset{\text{Sodium acetate}}{NaOOCCH_3} \longrightarrow \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NaCl$$

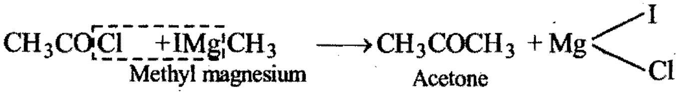


$$\underset{\substack{\text{Ethanoyl}\\\text{chloride}}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}Cl} + \underset{\text{Propanoic acid}}{HO\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3} \xrightarrow[\Delta]{\text{Pyridine}} \underset{\substack{\text{Ethanoic propanoic}\\\text{anhydride}}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}O\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3} + HCl$$

(viii) Friedel-Crafts reaction : It reacts with benzene in the presence of anhydrous aluminium chloride to form acetophenone.

$$CH_3COCl + \underset{\text{Benzene}}{C_6H_6} \xrightarrow{\text{Anhyd. }AlCl_3} \underset{\text{Acetophenone}}{CH_3COC_6H_5} + HCl$$

(ix) Action with Grignard reagent : (a) With calculated amount of Grignard reagent, ketones are formed.



$$CH_3CO\boxed{Cl + IMg}\underset{\substack{\text{Methyl magnesium}\\\text{iodide}}}{CH_3} \longrightarrow \underset{\text{Acetone}}{CH_3COCH_3} + Mg\begin{matrix} \diagup I \\ \diagdown Cl \end{matrix}$$

(b) With excess of Grignard reagent, tertiary alcohol is obtained.

(c) With dialkyl cadmium (less reactive than Grignard reagent), ketones are formed.

$$\underset{\text{Acyl chloride}}{2RCOCl} + \underset{\substack{\text{Dialkyl}\\\text{cadmium}}}{R'_2Cd} \xrightarrow[\text{Ether}]{\text{Dry}} \underset{\text{Ketone}}{2RCOR'} + CdCl_2$$

$$\underset{\text{Ethanoyl chloride}}{2CH_3COCl} + \underset{\substack{\text{Dimethyl}\\\text{cadmium}}}{(CH_3)_2Cd} \xrightarrow[\text{Ether}]{\text{Dry}} \underset{\text{Propanone}}{2CH_3COCH_3} + CdCl_2$$

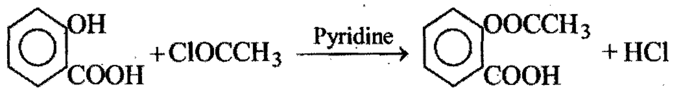
(x) Action with diethyl ether : Acetyl chloride reacts with diethyl ether in presence of anhydrous zinc chloride to form ester and ethyl chloride.

$$CH_3COCl + \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} \xrightarrow[\Delta]{ZnCl_2} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Ethyl chloride}}{C_2H_5Cl}$$

(xi) Action with potassium cyanide : Chlorine is replaced by —CN group. The cyanide thus formed yields α-keto acid (pyruvic acid) on hydrolysis.

$$CH_3COCl + KCN \longrightarrow \underset{\text{Acetyl cyanide}}{CH_3COCN} \xrightarrow[H^+]{H_2O} \underset{\text{Pyruvic acid}}{CH_3COCOOH}$$

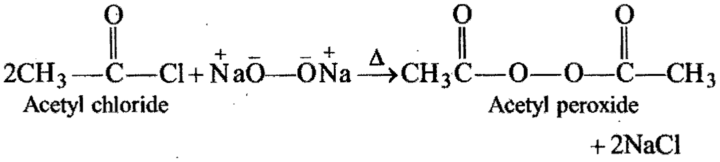
(xii) Action with salicylic acid : Aspirin is formed.



Salicylic acid

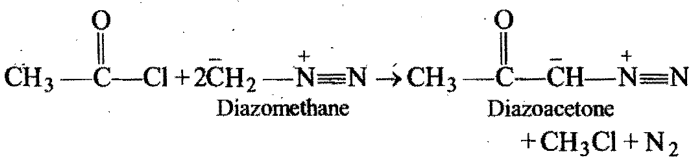
Acetyl salicylic acid (Aspirin)

(xiii) Peroxide formation : Acetyl chloride reacts with sodium peroxide ($\overset{+}{N}a\overset{-}{O}—\overset{-}{O}\overset{+}{N}a$), to form acetyl peroxide.



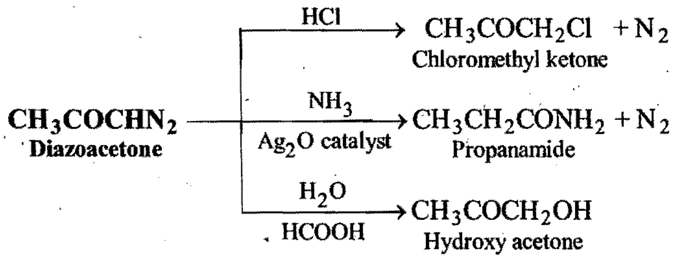
$$\underset{\text{Acetyl chloride}}{2CH_3—\overset{\overset{O}{\|}}{C}—Cl} + \overset{+}{N}a\overset{-}{O}—\overset{-}{O}\overset{+}{N}a \xrightarrow{\Delta} \underset{\text{Acetyl peroxide}}{CH_3\overset{\overset{O}{\|}}{C}—O—O—\overset{\overset{O}{\|}}{C}—CH_3} + 2NaCl$$

(xiv) Action with diazomethane : Acetyl chloride readily reacts with diazomethane (CH_2N_2) to form diazoketone. Diazomethane (CH_2N_2) is used in the **Arndt-Eistert Synthesis** to convert a carboxylic acid into the next higher homologue.



$$CH_3—\overset{\overset{O}{\|}}{C}—Cl + \underset{\text{Diazomethane}}{2\overset{-}{C}H_2—\overset{+}{N}{\equiv}N} \rightarrow \underset{\text{Diazoacetone}}{CH_3—\overset{\overset{O}{\|}}{C}—\overset{-}{C}H—\overset{+}{N}{\equiv}N} + CH_3Cl + N_2$$

Diazoketone gives different compounds as follows:

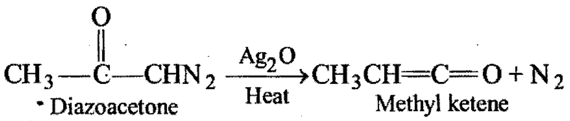


$$\underset{\text{Diazoacetone}}{\mathbf{CH_3COCHN_2}} \xrightarrow{HCl} \underset{\text{Chloromethyl ketone}}{CH_3COCH_2Cl} + N_2$$

$$\xrightarrow[\text{Ag}_2\text{O catalyst}]{NH_3} \underset{\text{Propanamide}}{CH_3CH_2CONH_2} + N_2$$

$$\xrightarrow[HCOOH]{H_2O} \underset{\text{Hydroxy acetone}}{CH_3COCH_2OH}$$

This diazoacetone loses nitrogen to form a ketene by rearrangement when warmed in the presence of silver oxide as catalyst.



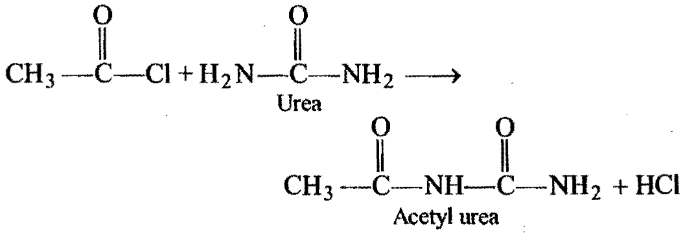
$$\underset{\text{Diazoacetone}}{CH_3—\overset{\overset{O}{\|}}{C}—CHN_2} \xrightarrow[\text{Heat}]{Ag_2O} \underset{\text{Methyl ketene}}{CH_3CH{=}C{=}O} + N_2$$

This rearrangement of diazoketone is called **Wolff rearrangement.**

When the rearrangement of diazoketone is carried out in the presence of water, a carboxylic acid is formed.

$$\underset{\text{Ketene}}{CH_3—CH{=}C{=}O} + H_2O \xrightarrow{\text{Heat}} \underset{\text{Carboxylic acid}}{CH_3CH_2COOH}$$

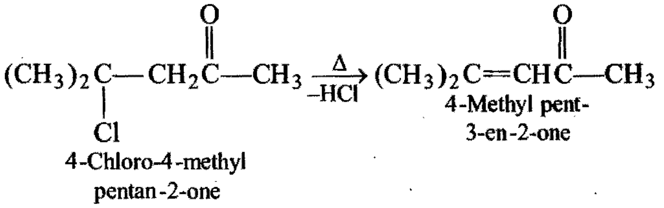
(xv) Action with urea : Acetyl chloride is acetylated to give acetyl urea.



$$CH_3—\overset{\overset{O}{\|}}{C}—Cl + \underset{\text{Urea}}{H_2N—\overset{\overset{O}{\|}}{C}—NH_2} \longrightarrow \underset{\text{Acetyl urea}}{CH_3—\overset{\overset{O}{\|}}{C}—NH—\overset{\overset{O}{\|}}{C}—NH_2} + HCl$$

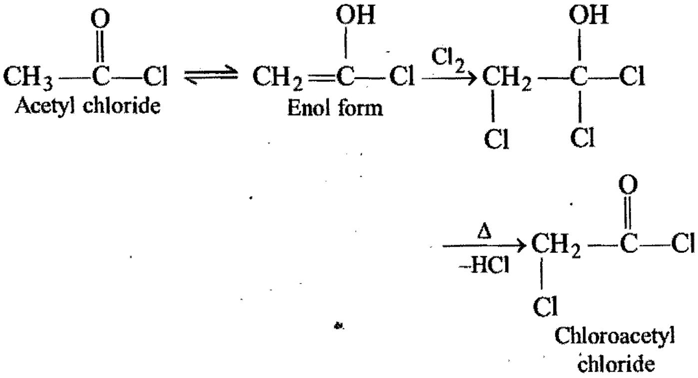
(xvi) Action with alkene : Acetyl chloride adds to an alkene in presence of catalyst ($ZnCl_2$ or $AlCl_3$) to form a chloroketone which, on heating eliminates HCl to give an unsaturated ketone.

$$\underset{\text{2-Methyl propene}}{(CH_3)_2C{=}CH_2} + CH_3COCl \xrightarrow{ZnCl_2}$$



$$\underset{\text{4-Chloro-4-methyl pentan-2-one}}{(CH_3)_2\underset{\underset{Cl}{|}}{C}—CH_2\overset{\overset{O}{\|}}{C}—CH_3} \xrightarrow[-HCl]{\Delta} \underset{\text{4-Methyl pent-3-en-2-one}}{(CH_3)_2C{=}CH\overset{\overset{O}{\|}}{C}—CH_3}$$

(xvii) α-Halogenation : Acid halides undergo tautomerization and so they proceeds for α-halogenation.



$$\underset{\text{Acetyl chloride}}{CH_3—\overset{\overset{O}{\|}}{C}—Cl} \rightleftharpoons \underset{\text{Enol form}}{CH_2{=}\overset{\overset{OH}{|}}{C}—Cl} \xrightarrow{Cl_2} \underset{\underset{Cl}{|}}{CH_2}—\overset{\overset{OH}{|}}{\underset{\underset{Cl}{|}}{C}}—Cl \xrightarrow[-HCl]{\Delta} \underset{\text{Chloroacetyl chloride}}{\underset{\underset{Cl}{|}}{CH_2}—\overset{\overset{O}{\|}}{C}—Cl}$$

(xviii) Reaction with HBr, HI and HF :

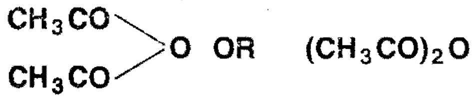
$$RCOCl + HBr \longrightarrow RCOBr + HCl$$
$$RCOCl + HI \longrightarrow RCOI + HCl$$
$$RCOCl + HF \longrightarrow RCOF + HCl$$

Uses : (i) As an acetylating agent.

(ii) In the estimation and determination of number of hydroxyl and amino groups.

(iii) In the preparation of acetaldehyde, acetic anhydride, acetamide, acetanilide, aspirin, acetophenone, etc.

13.4 ACETIC ANHYDRIDE OR ETHANOIC ANHYDRIDE,



Acetic anhydride is the most important and useful among anhydrides.

Methods of Preparation

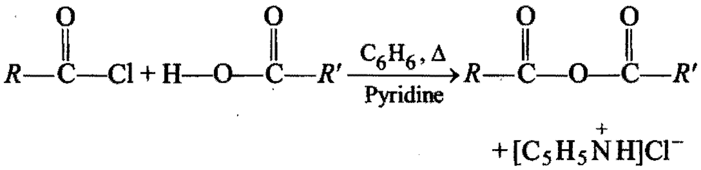
1. From carboxylic acids : Acetic anhydride is prepared by heating glacial acetic acid with a dehydrating agent like conc. H_2SO_4 or phosphorus pentoxide or anhydrous zinc chloride.

$$\underset{\text{(Glacial)}}{\underset{\text{Acetic acid}}{2CH_3COOH}} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + H_2O$$

2. From acid chlorides and carboxylic acids : Acetic anhydride is conveniently prepared by distilling a mixture of anhydrous sodium acetate and acetyl chloride.

$$\underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Acetyl chloride}}{ClCOCH_3} \xrightarrow[\text{Heat}]{\text{Pyridine}} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NaCl$$

Acetic anhydride is prepared in the **laboratory** by this reaction.



$$R-\overset{O}{\overset{\|}{C}}-Cl + H-O-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[\text{Pyridine}]{C_6H_6,\,\Delta} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R' + [C_5H_5\overset{+}{N}H]Cl^-$$

3. Manufacture : Acetic anhydride is prepared industrially by the following methods:

(i) By heating anhydrous sodium acetate with thionyl chloride, sulphuryl chloride or phosphorus oxychloride : One half of the sodium acetate is first converted into acetyl chloride which then reacts with remaining half of sodium acetate to give anhydride.

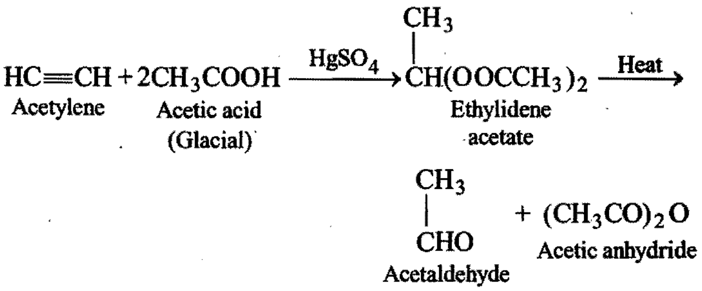
$$\underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow CH_3COCl + SO_2 + NaCl$$

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + CH_3COONa \longrightarrow \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NaCl$$

(ii) By passing chlorine in a mixture of sodium acetate and sulphur dichloride and distilling the mixture so obtained.

$$8CH_3COONa + \underset{\text{Sulphur dichloride}}{SCl_2} + 2Cl_2 \xrightarrow{\text{Distill}} \underset{\text{Acetic anhydride}}{4(CH_3CO)_2O} + 6NaCl + Na_2SO_4$$

(iii) From acetylene :



$$\underset{\text{Acetylene}}{HC\equiv CH} + \underset{\text{(Glacial)}}{\underset{\text{Acetic acid}}{2CH_3COOH}} \xrightarrow{HgSO_4} \underset{\text{acetate}}{\underset{\text{Ethylidene}}{\overset{CH_3}{\overset{|}{C}}H(OOCCH_3)_2}} \xrightarrow{\text{Heat}} \underset{\text{Acetaldehyde}}{\overset{CH_3}{\overset{|}{CHO}}} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

(iv) From acetone : Acetone is first converted into ketene by cracking (pyrolysis) at 700–750°C.

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{\text{Heat}} \underset{\text{Ketene}}{H_2C=C=O} + CH_4$$

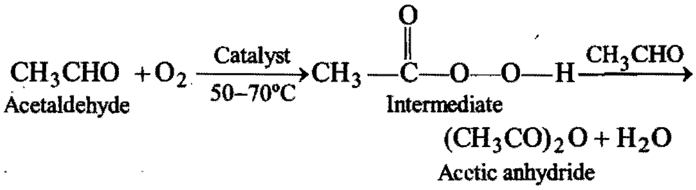
Ketene can also be obtained from acetic acid.

$$CH_3COOH \xrightarrow[800°C]{AlPO_4} H_2C=C=O + H_2O$$

The ketene is then passed through glacial acetic acid when formation of acetic anhydride takes place. This is the modern process for manufacture of acetic anhydride.

$$\underset{\text{Ketene}}{H_2C=C=O} + \underset{\text{(Glacial)}}{CH_3COOH} \longrightarrow \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

(v) From acetaldehyde : The air oxidation of acetaldehyde is done in presence of cobalt acetate-copper acetate catalyst at 50–70°C under pressure.



$$\underset{\text{Acetaldehyde}}{CH_3CHO} + O_2 \xrightarrow[50-70°C]{\text{Catalyst}} \underset{\text{Intermediate}}{CH_3-\overset{O}{\overset{\|}{C}}-O-O-H} \xrightarrow{CH_3CHO} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + H_2O$$

(vi) From acetic acid :

$$\underset{\text{Acetic acid}}{2CH_3COOH} \xrightarrow[\text{Porcelain chips, 800°C}]{\text{Quartz tube}} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + H_2O$$

Physical properties : It is a colourless, pungent smelling liquid. It boils at 139.5°C. It is sparingly soluble in water but soluble in ether, alcohol and acetic acid.

Chemical properties : It resembles acetyl chloride in its action towards compounds having active hydrogen but it is less reactive than acetyl chloride. One half of the acetic anhydride is used for acetylation while the other half is converted into acetic acid. Acetylation is best carried out in presence of sodium acetate or conc. H_2SO_4.

The following are the important reactions of acetic anhydride:

(i) Hydrolysis : The hydrolysis of acetic anhydride occurs with water or alkalies.

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + H_2O \longrightarrow \underset{\text{Acetic acid}}{2CH_3COOH}$$

$$(CH_3CO)_2O + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Acetic acid}}{CH_3COOH}$$

(ii) Action with ammonia : Acetic anhydride forms acetamide with ammonia.

$$(CH_3CO)_2O + 2NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Amm. acetate}}{CH_3COONH_4}$$

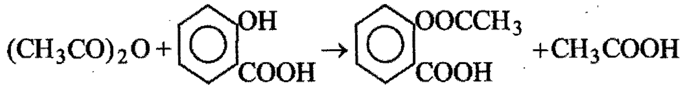
(iii) Acetylation : Acetic anhydride reacts with compounds having active hydrogen atom. The hydrogen atom is replaced by CH_3CO— group. The reaction is called **acetylation.** Acetylation with Ac_2O is usually best carried out in pyridine solution or in presence of a small amount of sodium acetate or conc. H_2SO_4 as catalyst.

$$(CH_3CO)_2O + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + CH_3COOH$$

$$(CH_3CO)_2O + \underset{\text{Ethylamine (1°)}}{H_2NC_2H_5} \rightarrow \underset{N\text{-Ethyl acetamide}}{CH_3CONHC_2H_5} + CH_3COOH$$

$$(CH_3CO)_2O + \underset{\text{Diethylamine (2°)}}{HN(C_2H_5)_2} \rightarrow \underset{N,N\text{-Diethyl acetamide}}{CH_3CON(C_2H_5)_2} + CH_3COOH$$

$$(CH_3CO)_2O + \underset{\text{Aniline}}{H_2NC_6H_5} \rightarrow \underset{\text{Acetanilide}}{CH_3CONHC_6H_5} + CH_3COOH$$



Salicylic acid   Acetyl salicyclic acid (Aspirin)

(iv) Action of dry HCl : Acetic anhydride reacts with dry HCl to form acetyl chloride.

$$(CH_3CO)_2O + HCl(\text{dry}) \longrightarrow CH_3COCl + CH_3COOH$$

(v) Action of chlorine : Acetic anhydride reacts with chlorine to form acetyl chloride and monochloroacetic acid.

$$(CH_3CO)_2O + Cl_2 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Monochloroacetic acid}}{CH_2ClCOOH}$$

(vi) Action of PCl_5 : When heated with PCl_5, acetic anhydride forms acetyl chloride.

$$(CH_3CO)_2O + PCl_5 \longrightarrow 2CH_3COCl + POCl_3$$

(vii) Friedel-Crafts reaction : In presence of anhydrous aluminium chloride, it reacts with benzene to form acetophenone.

$$(CH_3CO)_2O + \underset{\text{Benzene}}{C_6H_6} \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + CH_3COOH$$

(viii) Reaction with acetaldehyde : Acetic anhydride combines with one molecule of acetaldehyde to form ethylidene acetate.

$$(CH_3CO)_2O + \underset{\text{Acetaldehyde}}{CH_3CHO} \longrightarrow \underset{\text{Ethylidene acetate}}{CH_3CH(OOCCH_3)_2}$$

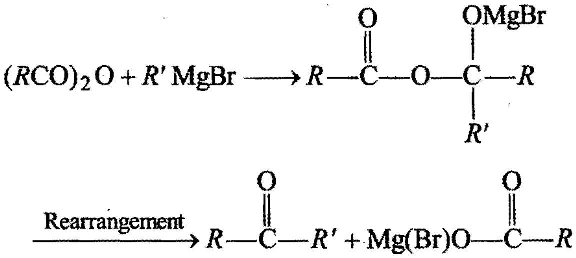
(ix) Reduction : It is reduced by $LiAlH_4$ in ether or Na/C_2H_5OH or $NaBH_4/AlCl_3$ or B_2H_4 in THF, etc., to ethyl alcohol.

$$(CH_3CO)_2O \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

(x) Action with ether : It forms ethyl acetate (an ester).

$$CH_3CO\boxed{OCOCH_3 + C_2H_5}O-\underset{\text{Diethyl ether}}{C_2H_5} \xrightarrow[\text{(Warm)}]{ZnCl_2} \underset{\text{Ethyl acetate}}{2CH_3COOC_2H_5}$$

(xi) Reaction with Grignard reagent :



$$(RCO)_2O + R'MgBr \longrightarrow R-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{R'}{|}}{\overset{\overset{OMgBr}{|}}{C}}-R$$

$$\xrightarrow{\text{Rearrangement}} R-\overset{\overset{O}{\|}}{C}-R' + Mg(Br)O-\overset{\overset{O}{\|}}{C}-R$$

(xii) Perkin reaction : When an aromatic aldehyde is heated with an aliphatic acid anhydride with atleast two α-H atoms in presence of Na or K salt of corresponding acid, a condensation reaction giving α, β-unsaturated acid is formed. This reaction is called Perkin reaction.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + (CH_3CO)_2O \xrightarrow[\text{Reflux}]{CH_3COONa} \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CHCOOH} + CH_3COOH$$

(xiii) Reaction with higher acids and their salts :

$$\underset{\text{Benzoic acid}}{2C_6H_5COOH} + (CH_3CO)_2O \rightarrow \underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} + 2CH_3COOH$$

$$\underset{\text{Sodium propionate}}{2C_2H_5COONa} + (CH_3CO)_2O \longrightarrow \underset{\text{Propionic anhydride}}{(C_2H_5CO)_2O} + 2CH_3COONa$$

(xiv) Reaction with N_2O_5 :

$$(CH_3CO)_2O + N_2O_5 \longrightarrow \underset{\text{Acetyl nitrate}}{2CH_3COONO_2}$$

$$CH_3COONO_2 + H_2O \xrightarrow{\text{Hydrolysis}} CH_3COOH + HNO_3$$

(xv) Reaction with barium peroxide :

$$(CH_3CO)_2O + BaO_2 \longrightarrow \underset{\text{Acetyl peroxide}}{CH_3CO-O-O-COCH_3} + BaO$$

Uses : Acetic anhydride is used :

(i) as an acetylating agent.

(ii) for the detection and estimation of hydroxyl and amino groups.

(iii) in the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, acetophenone, etc.

13.5 ACETAMIDE, CH_3CONH_2 OR ETHANAMIDE

Methods of Preparation

1. Laboratory preparation : Acetamide is formed by heating of ammonium acetate, at about 215°C.

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

Simple heating of ammonium acetate presents the following two difficulties :

(a) Some of the ammonium acetate dissociates into acetic acid.

$$CH_3COONH_4 \rightleftharpoons CH_3COOH + NH_3$$

(b) Some of the acetamide gets hydrolysed into acetic acid by the water formed in the reaction.

$$CH_3CONH_2 + H_2O \longrightarrow CH_3COOH + NH_3$$

To avoid the above two reactions, ammonium acetate is always heated in presence of glacial acetic acid.

2. Acetamide is obtained by the action of concentrated ammonia solution on acetyl chloride, acetic anhydride or ethyl acetate. These reactions are termed as **ammonolysis.**

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + 2NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + NH_4Cl$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + 2NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + CH_3COONH_4$$

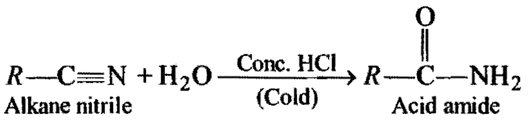
$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + C_2H_5OH$$

3. On heating glacial acetic acid with urea, acetamide is formed.

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Urea}}{H_2NCONH_2} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} + CO_2 + NH_3$$

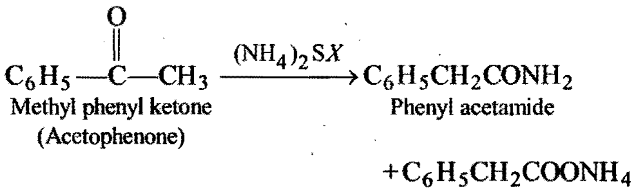
4. Acetamide is also obtained when partial hydrolysis of methyl cyanide is done either by alkaline H_2O_2 or by dilute sulphuric acid or conc. HCl.

$$\underset{\text{Methyl cyanide}}{CH_3CN} + H_2O \xrightarrow[\text{or conc. HCl}]{H_2O_2\text{(alk.)}} \underset{\text{Acetamide}}{CH_3CONH_2}$$



$$\underset{\text{Alkane nitrile}}{R{-}C{\equiv}N} + H_2O \xrightarrow[\text{(Cold)}]{\text{Conc. HCl}} \underset{\text{Acid amide}}{R{-}\overset{\overset{O}{\|}}{C}{-}NH_2}$$

5. By Wilgerodt reaction : This reaction was originally carried out by heating a carbonyl compound (aryl alkyl ketone) with an aqueous solution of yellow ammonium poly sulphide $(NH_4)_2SX$ to give an amide with the same number of carbon atoms.

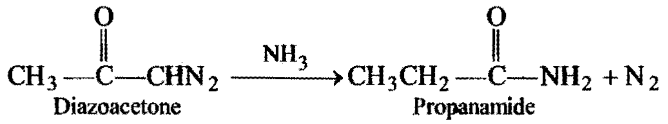


$$\underset{\substack{\text{Methyl phenyl ketone}\\ \text{(Acetophenone)}}}{C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}CH_3} \xrightarrow{(NH_4)_2SX} \underset{\text{Phenyl acetamide}}{C_6H_5CH_2CONH_2} + C_6H_5CH_2COONH_4$$

The amide group is always formed at the end of the chain whatever the size of R-group in C_6H_5COR.

$$\underset{\substack{\text{Phenyl propyl ketone}\\ \text{(Butyrophenone)}}}{C_6H_5COCH_2CH_2CH_3} \xrightarrow[\text{Heat}]{(NH_4)_2SX} \underset{\gamma\text{-Phenyl butyramide}}{C_6H_5\overset{\gamma}{C}H_2\overset{\beta}{C}H_2\overset{\alpha}{C}H_2CONH_2}$$

6. Amide is also obtained by heating diazoacetone with NH_3.



$$\underset{\text{Diazoacetone}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CHN_2} \xrightarrow{NH_3} \underset{\text{Propanamide}}{CH_3CH_2{-}\overset{\overset{O}{\|}}{C}{-}NH_2} + N_2$$

Physical properties : Acetamide is a colourless crystalline solid. It melts at 82°C and boils at 222°C. It is readily soluble in water and alcohol. It exists as a dimer due to hydrogen bonding. Impure acetamide has mousy odour.

Chemical properties : (i) Hydrolysis : Acetamide is hydrolysed slowly by boiling with water, rapidly by acids and far more rapidly by alkalies **(Laboratory test of amide group).**

$$CH_3CONH_2 + H_2O \xrightarrow{\text{Boil}} CH_3COOH + NH_3$$

$$CH_3CONH_2 + H_2O + HCl \xrightarrow{\Delta} CH_3COOH + NH_4Cl$$

Amides are decomposed by alkali solution liberating NH_3 gas which gives white fumes with HCl.

$$RCONH_2 + NaOH \xrightarrow{\Delta} RCOONa + NH_3\uparrow$$

$$(NH_3 + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl})$$

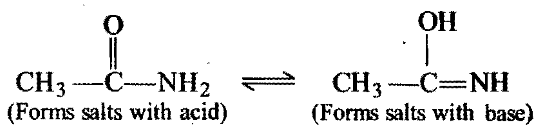
$$CH_3CONH_2 + NaOH \xrightarrow{\Delta} CH_3COONa + NH_3\uparrow$$

(ii) Amphoteric nature (Salt formation) : Acetamide behaves as an amphoteric compound, *i.e.*, shows feebly acidic as well as feebly basic nature. It forms salts with acids and bases both.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + HCl\text{(conc.)} \longrightarrow \underset{\substack{\text{Acetamide hydrochloride}\\ \text{(only stable in aqueous solution)}}}{CH_3CONH_2{\cdot}HCl}$$

$$\underset{\text{Acetamide}}{2CH_3CONH_2} + \underset{\substack{\text{Mercuric}\\ \text{oxide}}}{HgO} \longrightarrow \underset{\text{Mercuric acetamide}}{(CH_3CONH)_2Hg} + H_2O$$

This behaviour is due to the presence of tautomerism.



$$\underset{\text{(Forms salts with acid)}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}NH_2} \rightleftharpoons \underset{\text{(Forms salts with base)}}{CH_3{-}\overset{\overset{OH}{|}}{C}{=}NH}$$

$$CH_3CONH_2 + Na \xrightarrow{\text{Ether}} \underset{\text{Sodium acetamide}}{CH_3CONHNa} + \frac{1}{2}H_2$$

(iii) Reduction : Acetamide undergoes reduction with sodium and alcohol or ethereal solution of $LiAlH_4$ and is converted into ethylamine.

$$CH_3CONH_2 + 4[H] \xrightarrow{Na + C_2H_5OH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$

$$CH_3CONH_2 + 4[H] \xrightarrow[\text{Ether}]{\text{LiAlH}_4} CH_3CH_2NH_2 + H_2O$$

(iv) Dehydration : When heated with phosphorus pentoxide or $SOCl_2$ or $POCl_3$, it loses a molecule of water and forms methyl cyanide (nitrile).

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Methyl cyanide}}{CH_3CN} + H_2O$$

(v) Action of nitrous acid : The amino group is replaced by —OH group with evolution of nitrogen when treated with nitrous acid ($NaNO_2 + HCl$), *i.e.*, acetic acid is formed.

$$CH_3CONH_2 + HNO_2 \longrightarrow CH_3COOH + N_2 + H_2O$$

Reaction with HNO_2 is slow, a better method is to use butyl nitrite.

$$CH_3CONH_2 + C_4H_9ONO \longrightarrow CH_3COOH + N_2 + C_4H_9OH$$

(vi) Action of PCl_5 : When heated with PCl_5, acetamide forms methyl cyanide.

$$CH_3CONH_2 + PCl_5 \longrightarrow CH_3CCl_2NH_2 + POCl_3$$

$$CH_3CCl_2NH_2 \xrightarrow{\text{Heat}} \underset{\text{Methyl cyanide}}{CH_3CN} + 2HCl$$

(vii) Action with alcohol : Acetamide forms ester.

$$CH_3CONH_2 + CH_3OH \xrightarrow[70°C]{\text{HCl}} \underset{\text{Methyl acetate}}{CH_3COOCH_3} + NH_4Cl$$

(viii) Hofmann bromamide reaction or Hofmann degradation : Amides when heated with bromine and caustic soda or caustic potash solution, yield primary amines containing one carbon atom less than the amide. **This is an important reaction for reducing a carbon atom from a compound,** *i.e.*, —$CONH_2$ is changed to —NH_2 group.

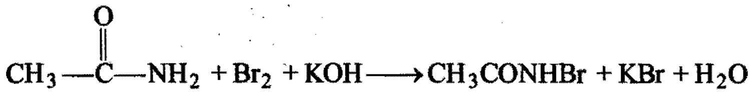
When acetamide is treated with bromine and caustic soda, methylamine is formed.

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{NaOH or KOH}]{Br_2} \underset{\text{Methylamine } (p\text{-})}{CH_3NH_2}$$

$$\underset{\text{Acid amide}}{RCONH_2} + Br_2 + 4KOH \xrightarrow{\text{Heat}} \underset{1° \text{ Amine}}{R\text{—}NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

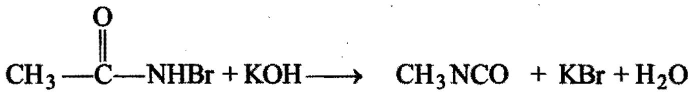
The reaction occurs in three stages :

(i)



$$CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}NH_2 + Br_2 + KOH \longrightarrow \underset{\text{Acetobromamide}}{CH_3CONHBr} + KBr + H_2O$$

(ii)



$$CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHBr + KOH \longrightarrow \underset{\text{Methyl isocyanate}}{CH_3NCO} + KBr + H_2O$$

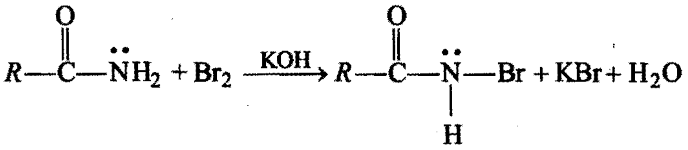
(iii)

$$CH_3NCO + 2KOH \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + K_2CO_3$$

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

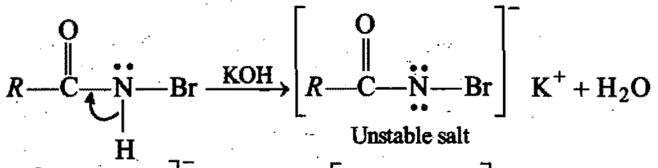
In this reaction, a number of intermediates have been isolated: *N*-bromamides, *R*CONHBr; salts of these bromamides, $[RCONBr^-]K^+$; and isocyanates, (*R*NCO). On this basis, a possible **mechanism** of the reaction is explained as follows:

(i)

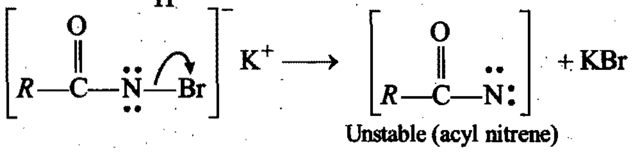


$$R\text{—}\overset{\overset{O}{\|}}{C}\text{—}\ddot{N}H_2 + Br_2 \xrightarrow{\text{KOH}} R\text{—}\overset{\overset{O}{\|}}{C}\text{—}\underset{\underset{H}{|}}{\ddot{N}}\text{—}Br + KBr + H_2O$$

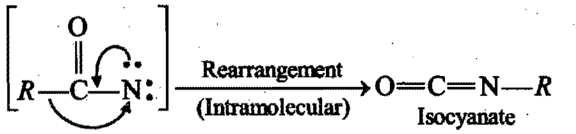
N-Bromamide

(ii) 

$$R-\overset{\overset{O}{\|}}{C}-\underset{H}{\ddot{N}}-Br \xrightarrow{KOH} \underset{\text{Unstable salt}}{\left[R-\overset{\overset{O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{N}}-Br\right]^-} K^+ + H_2O$$

(iii) 

$$\left[R-\overset{\overset{O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{N}}-Br\right]^- K^+ \longrightarrow \underset{\text{Unstable (acyl nitrene)}}{\left[R-\overset{\overset{O}{\|}}{C}-\ddot{N}:\right]} + KBr$$

(iv) 

$$\left[R-\overset{\overset{O}{\|}}{C}-\ddot{N}:\right] \xrightarrow[\text{(Intramolecular)}]{\text{Rearrangement}} \underset{\text{Isocyanate}}{O=C=N-R}$$

(v) $$R-N=C=O \xrightarrow{2KOH} RNH_2 + K_2CO_3$$

Amides containing upto 7 carbon atoms give 1° amine, but those containing more than that gives alkyl cyanide.

$$RCH_2CONH_2 \xrightarrow[KOH]{Br_2} RCN + H_2O$$

If the amide contains an electron withdrawing group (–*I* group), the product is a bromide.

$$C_3F_7CONH_2 \xrightarrow[NaOH,\ \Delta]{Br_2} C_3F_7Br$$

Instead of KOH, other alkali like NaOH can be used. Similarly, Cl_2 and I_2 may be used in place of Br_2.

Uses : Acetamide is used :

(i) in organic synthesis. The compounds like methyl cyanide, methylamine and ethylamine can be prepared.
(ii) in leather tanning and paper industry.
(iii) as a wetting agent and as soldering flux.
(iv) as a solvent for organic and inorganic compounds.

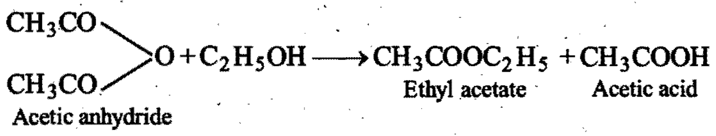
13.6 ETHYL ACETATE, $CH_3COOC_2H_5$ OR ETHYL ETHANOATE

It is the ethyl ester of acetic acid.

Methods of Preparation

1. **By the action of acetyl chloride or acetic anhydride on ethyl alcohol :**

$$\underset{\substack{\text{Acetyl}\\\text{chloride}}}{CH_3COCl} + \underset{\substack{\text{Ethyl}\\\text{alcohol}}}{C_2H_5OH} \xrightarrow[\text{Base}]{\text{Pyridine}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$



$$\underset{\text{Acetic anhydride}}{\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>\!O} + C_2H_5OH \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Acetic acid}}{CH_3COOH}$$

2. **By the action of ethyl halide on silver acetate :**

$$\underset{\text{Silver acetate}}{CH_3COOAg} + \underset{\text{Ethyl iodide}}{IC_2H_5} \xrightarrow[(C_2H_5OH)]{\text{Reflux}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + AgI$$

3. **By Tischenko reaction :** Acetaldehyde undergoes condensation in presence of aluminium ethoxide to form ethyl acetate.

$$\underset{\text{2 Molecules of acetaldehyde}}{CH_3CHO + OHCCH_3} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

4. **Laboratory method :** In laboratory as well as on **industrial scale,** ethyl acetate is prepared by refluxing a mixture of absolute alcohol and glacial acetic acid in presence of a few drops of conc. sulphuric acid (catalyst) or hydrogen chloride gas (Fisher-speir modification).

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \overset{H_2SO_4\text{(conc.)}}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Water}}{H_2O}$$

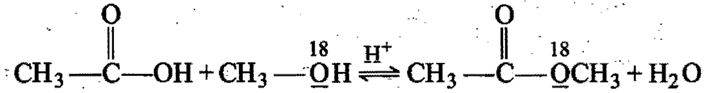
This reaction is termed **Fischer esterification.** It is a reversible reaction and the yield of the ethyl acetate can be increased by using excess of acid or alcohol and removing water as it is formed. Water may be removed by using conc. sulphuric acid or hydrogen chloride. Thus, sulphuric acid acts both as a catalyst and a dehydrating agent in the process of esterification.

The ease of esterification of alcohols is as follows:

$$1° > 2° > 3°$$

The ease of esterification with fatty acids is as follows:

$$HCOOH > CH_3COOH > CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + CH_3-\overset{18}{\underline{O}}H \overset{H^+}{\rightleftharpoons} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{18}{\underline{O}}CH_3 + H_2O$$

[For mechanism of esterification, see Section 12.11 problem 8.]

Direct esterification can also be done by passing the vapours of alcohols and acids over a heated catalyst like titanium dioxide, thoria and alumina at 300°C.

5. By the action of carbon monoxide on ether :

$$\underset{\text{Ether}}{R-O-R} + CO \xrightarrow[\text{500 atm.}]{BF_3,\ 150°C} \underset{\text{Ester}}{RCOOR}$$

6. By the action of diazomethane on carboxylic acids : Methyl esters are formed.

$$RCOOH + CH_2N_2 \xrightarrow{\text{Ether}} RCOOCH_3 + N_2$$

BF_3-CH_3OH is better than CH_2N_2 for the methylation of carboxylic acids.

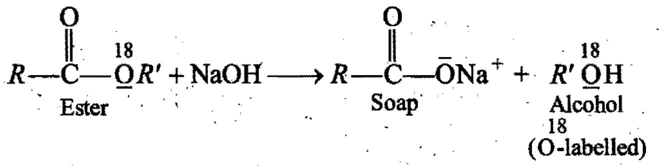
Physical properties : Ethyl acetate is a colourless, sweet smelling (fruity odour) liquid. It boils at 77.5°C. It is slightly soluble in water but more soluble in alcohol and ether. It is a neutral liquid.

Chemical properties : (i) Hydrolysis : Ethyl acetate undergoes slow hydrolysis with excess of boiling water but in presence of acids or alkalies, the hydrolysis is fast.

$$CH_3COOC_2H_5 + H_2O \overset{\text{Acid}}{\rightleftharpoons} CH_3COOH + C_2H_5OH$$

$$CH_3COOC_2H_5 + NaOH \xrightarrow{\text{Heat}} CH_3COONa + C_2H_5OH$$

The acid hydrolysis is reversible while alkaline hydrolysis is irreversible. The alkaline hydrolysis is termed as **saponification.** During saponification of esters, it is the **acyl-oxygen** rather than alkyl-oxygen bond which undergoes cleavage during hydrolysis.



$$\underset{\text{Ester}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{18}{\underline{O}}R'} + NaOH \longrightarrow \underset{\text{Soap}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{O}Na^+} + \underset{\substack{\text{Alcohol} \\ (\overset{18}{O}\text{-labelled})}}{R'\overset{18}{\underline{O}}H}$$

The carboxylate ion is very unreactive towards nucleophilic substitution because it is negatively charged. Base-promoted hydrolysis of an ester, as a result, is an essentially irreversible reaction.

(ii) Reaction with ammonia (Ammonolysis) : Ethyl acetate reacts with concentrated ammonia solution (aqueous or alcoholic) to form acetamide,

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\substack{\text{Ammonia} \\ \text{(conc.)}}}{NH_3} \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

and with amines, it forms alkyl acetamide.

$$\underset{\text{Ethyl acetate}}{CH_3CO\boxed{OC_2H_5 + H}} \underset{\text{Ethylamine}}{HNC_2H_5} \longrightarrow \underset{N\text{-Ethyl acetamide}}{CH_3CONHC_2H_5} + C_2H_5OH$$

$$\underset{\text{Ethyl acetate}}{CH_3CO\boxed{OC_2H_5 + H}} \underset{\text{Dimethylamine}}{N(CH_3)_2} \longrightarrow \underset{\substack{N, N\text{-Dimethyl} \\ \text{acetamide}}}{CH_3CON(CH_3)_2} + C_2H_5OH$$

(iii) **Reaction with phosphorus pentachloride or thionyl chloride :** Both react with ethyl acetate to form acetyl chloride.

$$CH_3COOC_2H_5 + PCl_5 \longrightarrow CH_3COCl + C_2H_5Cl + POCl_3$$

$$\underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + SOCl_2 \longrightarrow \underset{\text{Ethanoyl chloride}}{CH_3COCl} + \underset{\text{Chloroethane}}{C_2H_5Cl} + SO_2$$

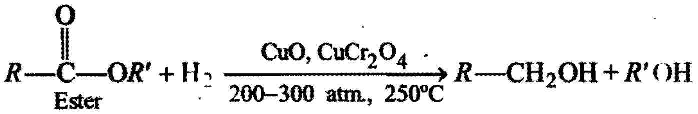
(iv) **Reduction :** (a) With sodium and alcohol, ethyl acetate is reduced to ethyl alcohol.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + 2H_2 \xrightarrow{Na + C_2H_5OH} \underset{\text{Ethyl alcohol}}{2CH_3CH_2OH}$$

This reduction is known as **Bouveault Blanc reduction.**

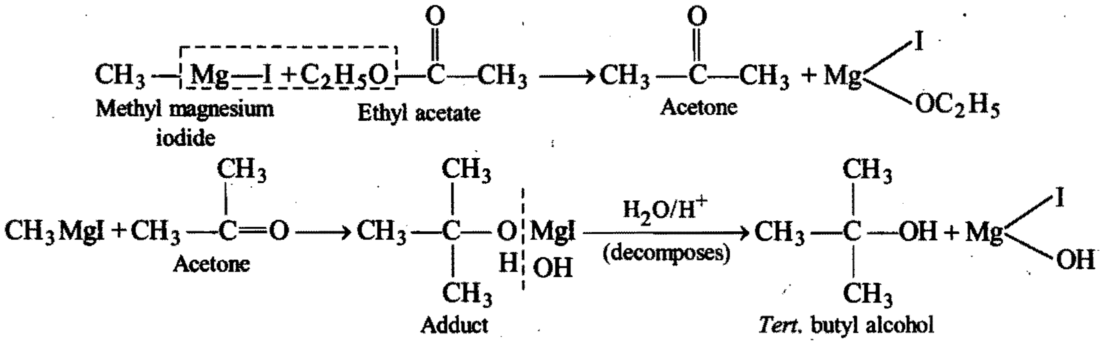
(b) $LiAlH_4$ in ether, $LiBH_4$ in THF or B_2H_6 in THF, etc., also reduce ethyl acetate into ethyl alcohol.

$$CH_3COOC_2H_5 + 2H_2 \xrightarrow[\text{Ether}]{LiAlH_4} 2CH_3CH_2OH$$

(c) 

$$\underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + H_2 \xrightarrow[200\text{–}300 \text{ atm., } 250°C]{CuO, CuCr_2O_4} R-CH_2OH + R'OH$$

(v) **Reaction with Grignard reagent :** Grignard reagent reacts with ethyl acetate and forms a ketone which at once reacts with more of Grignard reagent to give *tert.*-butyl alcohol (3°).

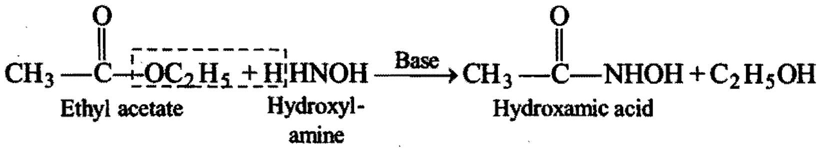


$$\underset{\text{Methyl magnesium iodide}}{CH_3-Mg-I} + \underset{\text{Ethyl acetate}}{C_2H_5O-\overset{O}{\overset{\|}{C}}-CH_3} \longrightarrow \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + Mg\begin{matrix} I \\ OC_2H_5 \end{matrix}$$

$$CH_3MgI + \underset{\text{Acetone}}{CH_3-\overset{CH_3}{\overset{|}{C}}=O} \longrightarrow \underset{\text{Adduct}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-O\,MgI} \xrightarrow[\text{(decomposes)}]{H_2O/H^+ \; (H\;OH)} \underset{\text{Tert. butyl alcohol}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH} + Mg\begin{matrix} I \\ OH \end{matrix}$$

Formic acid esters give 2° alcohols.

(vi) **Reaction with hydroxylamine :** Ethyl acetate reacts with hydroxylamine in presence of ethanolic KOH to form hydroxamic acid (a test of ester group).



$$\underset{\text{Ethyl acetate}}{CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5} + \underset{\text{Hydroxylamine}}{H\,HNOH} \xrightarrow{\text{Base}} \underset{\text{Hydroxamic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-NHOH} + C_2H_5OH$$

(vii) **Reaction with hydrazine :** Ethyl acetate reacts with hydrazine to form acid hydrazide.

$$CH_3COOC_2H_5 + \underset{\text{Hydrazine}}{H_2NNH_2} \longrightarrow \underset{\text{Acid hydrazide}}{CH_3CONHNH_2} + C_2H_5OH$$

(viii) **Halogenation :** Ethyl acetate reacts with chlorine or bromine in presence of red phosphorus to form α-halogenated ethyl acetate.

$$CH_3COOC_2H_5 + Br_2 \xrightarrow{\text{Red P}} \underset{\alpha\text{-Bromoethyl acetate}}{CH_2BrCOOC_2H_5} + HBr$$

(ix) **Claisen condensation :** Ethyl acetate (two molecules) undergoes Claisen condensation in presence of sodium ethoxide involving α-hydrogen atom. Two molecules of ethyl acetate combine together to form ethyl acetoacetate or acetoacetic ester (a, β-keto ester).

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + CH_3COOC_2H_5 \xrightarrow[\text{or (Na)}]{C_2H_5ONa} \underset{\text{Ethyl acetoacetate (Acetoacetic ester)}}{CH_3COCH_2COOC_2H_5} + C_2H_5OH$$

In place of C_2H_5ONa, other bases like sodamide, triphenyl methyl sodium, etc., can also be used.

If two molecules of different esters (*e.g.*, ethyl acetate and ethyl propionate) are used then four different keto esters are formed.

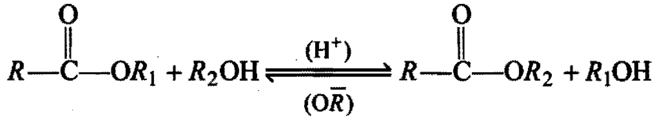
(x) Alcoholysis (Splitting by alcohol) : When an ester is refluxed with excess of alcohol (other than present in ester) in presence of a little acid (HCl gas) or sodium alkoxide as catalyst, a partial exchange of alcohol takes place. This is termed ***trans*-esterification.**

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Methyl alcohol}}{CH_3OH} \xrightleftharpoons{C_2H_5ONa \text{ or } H^+} \underset{\text{Methyl acetate}}{CH_3COOCH_3} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(xi) Acidolysis (*Trans*-esterification by acid) : When an ester is heated with other acid, it is the acid residue present in ester is partially replaced by other acid residue.

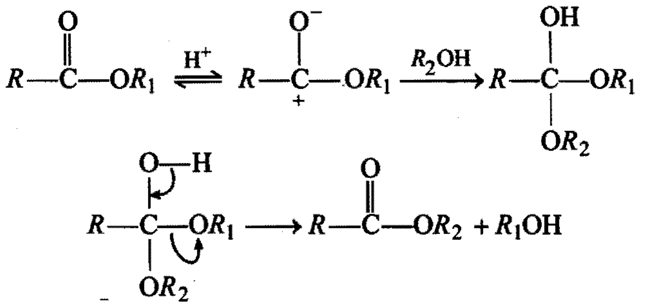
$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Propionic acid}}{C_2H_5COOH} \xrightarrow{\text{Heat}} \underset{\text{Ethyl propionate}}{C_2H_5COOC_2H_5} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Mechanism of *Trans*-esterification : *Trans*-esterification is catalysed by mineral acids like HCl, H_2SO_4 or dry HCl(g) or by strong base like alkoxide anion.

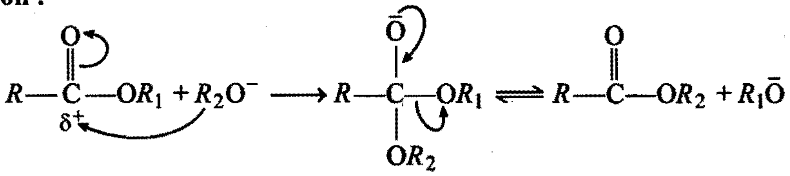


$$R-\overset{\overset{O}{\|}}{C}-OR_1 + R_2OH \underset{(\bar{O}R)}{\overset{(H^+)}{\rightleftharpoons}} R-\overset{\overset{O}{\|}}{C}-OR_2 + R_1OH$$

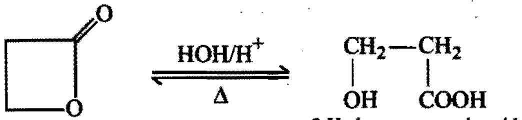
Acid Catalysed Reaction :



Base Catalysed Reaction :

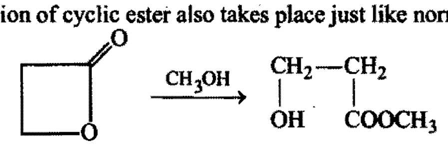


Note : (i) Cyclic esters on hydrolysis give hydroxy acid.



3-Hydroxy propanoic acid

(ii) *Trans*-esterification of cyclic ester also takes place just like normal esters.



(xii) Action of halogen acids:

$$CH_3COOC_2H_5 + HI \xrightarrow{\Delta} CH_3COOH + C_2H_5I$$

Uses : Ethyl acetate is used:

(i) as a solvent for oils, fats, cellulose, resins, etc.

(ii) in making artificial flavours and essences.

(iii) in the preparation of ethyl acetoacetate.

Tests : (i) Ethyl acetate has sweet smell.

(ii) Ethyl acetate is neutral towards the litmus.

(iii) A pink colour is developed when one or two drops of phenolphthalein are added to dilute sodium hydroxide solution. The pink colour is discharged when shaken or warmed with ethyl acetate.

(iv) Ethyl acetate on hydrolysis with caustic soda solution forms two compounds, sodium acetate and ethyl alcohol.

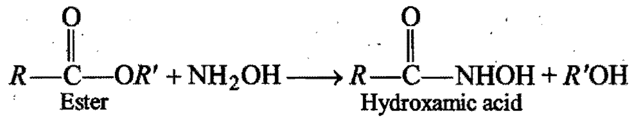
$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

The presence of these two compounds is confirmed by the following tests. The solution is divided into two parts:

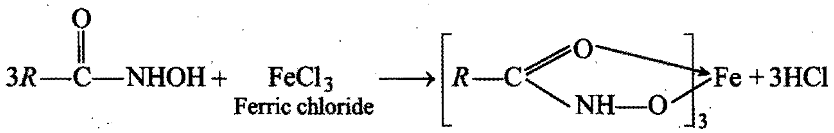
(a) First part $+ I_2 + NaOH \xrightarrow{\text{Heat}}$ yellow precipitate of iodoform.

(b) Second part + neutral ferric chloride solution $\longrightarrow$ red colouration.

(v) **Hydroxamic acid test:** Esters react with hydroxyl amine (NH_2OH) to give hydroxamic acid, which then complexes with Fe(III) to give a purple or deep red colour.



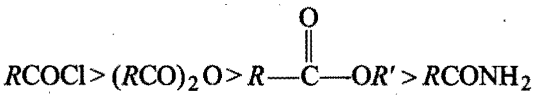
$$\underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'} + NH_2OH \longrightarrow \underset{\text{Hydroxamic acid}}{R-\overset{\overset{O}{\|}}{C}-NHOH} + R'OH$$



Purple or deep red colour

Relative Reactivity of Acyl Compounds

Nucleophilic substitution is most important characteristic of acid derivatives. Reactivity towards nucleophilic substitution lies in the following sequence:

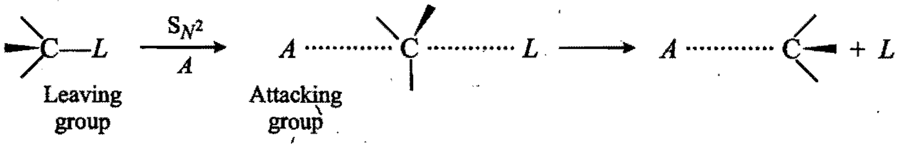


$$RCOCl > (RCO)_2O > R-\overset{\overset{O}{\|}}{C}-OR' > RCONH_2$$

Nucleophilic substitution takes place readily at an acyl carbon than at saturated carbon. Thus, for nucleophilic substitution acid chlorides ($RCOCl$) are more reactive than alkyl chloride (R—Cl); amides ($RCONH_2$) are more reactive than amines (R—NH_2) and esters ($RCOOR'$) are more reactive than ethers (R—OR').

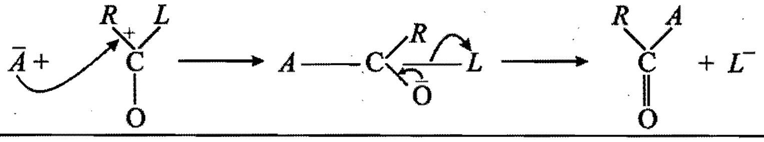
$$RCOCl > RCl;\ RCONH_2 > R-NH_2;\ R-COOR' > ROR'$$

Nucleophilic attack on tetrahedral alkyl carbon involves crowded transition state containing pentavalent carbon.



Due to formation of crowded transition state, alkyl compounds are less reactive towards nucleophilic substitution.

Nucleophilic attack on planar acyl compound involves less crowded transition state leading to a tetrahedral intermediate.



Note : Greater is the Lewis basic character more is the nucleophilic character of the group.

$NH_3 < R'OH < H_2O < RCOOH < HCl$ (Acidic character)

$Cl^- < RCOO^- < OH^- < RO^- < NH_2^-$ (Basic character)

Leaving tendency of nucleophiles lie in following sequence:

$NH_2^- < RO^- < OH^- < RCOO^- < Cl^-$

i.e., NH_2^- can substitute all other groups, *e.g.*, $RCOO^-$, OH^-, RO^-, Cl^-

RO^- can substitute all other groups, *e.g.*, OH^-, $RCOO^-$, Cl^-

OH^- can substitute all other groups, *e.g.*, $RCOO^-$, Cl^-

Cl^- cannot substitute any of these groups.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. In the following reaction, (X) and (Y) are respectively:

$$CH_3COOH + NH_3 \longrightarrow (X) \xrightarrow{\Delta} (Y) + H_2O$$

[EAMCET (Engg.) 2002]

(a) CH_3CONH_2, CH_4 ☐
(b) CH_3COONH_4, CH_3CONH_2 ☐
(c) CH_3CONH_2, CH_3COOH ☐
(d) CH_3NH_2, CH_3CONH_2 ☐
[Ans. (b)]

2. In the following reaction, (X) and (Y) are respectively:

$$C_2H_5OH \xrightarrow{KMnO_4/H^+} (X) \xrightarrow[H_2SO_4/\Delta]{(Y)} CH_3COOC_2H_5$$

(a) CH_3OH, C_2H_5OH ☐
(b) CH_3CHO, CH_3OH ☐
(c) $H_2C{=}CH_2, CH_3COOH$ ☐
(d) CH_3COOH, C_2H_5OH ☐
[Ans. (d)]

3. In the following reaction, (X) and (Y) are respectively:

$$(X) \xrightarrow[\text{Solution}]{\text{Aq. NaOH}} CH_3COOH \xrightarrow{(Y)} (CH_3CO)_2O$$

[EAMCET (Med.) 2002]

(a) CH_3CHO, PCl_5 ☐
(b) CH_3CN, P_2O_5 ☐
(c) CH_3CH_2OH, NaOAc ☐
(d) CH_3COCH_3, H_2SO_4 ☐
[Ans. (b)]

4. Pineapple flavours is obtained from which of the following esters? **[MGIMS (Wardha) 2003]**

(a) Iso-butyl ester ☐ (b) Iso-amyl ester ☐
(c) Iso-octanoyl ester ☐ (d) Ethyl methanoate ☐
[Ans. (a)]

5. When propanamide is reacted with Br_2 and NaOH, the product formed is: **[CMC (Vellore) PMT 2003]**

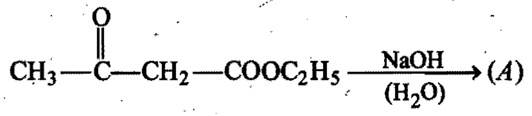
(a) propanamine ☐ (b) ethanamine ☐
(c) propanaldehyde ☐ (d) propionic acid ☐
[Ans. (b)]

6. At higher temperature, iodoform reaction is given by: **[AIIMS 2003]**

(a) $CH_3CO_2CH_3$ ☐ (b) $C_6H_5COOCH_3$ ☐
(c) $CH_3CO_2C_2H_5$ ☐ (d) $CH_3COOC_6H_5$ ☐
[Ans. (c)]

7. The ester among the following is: **[PMT (Kerala) 2003]**

(a) calcium lactate ☐ (b) ammonium acetate ☐
(c) sodium acetate ☐ (d) methyl butyrate ☐
[Ans. (d)]

8. 

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOC_2H_5 \xrightarrow[(H_2O)]{NaOH} (A)$$

The product (A) in above reaction is: **[PET (Raj.) 2003]**

(a) CH_3COOH ☐ (b) C_2H_5OH ☐
(c) CH_3COCH_3 ☐ (d) C_2H_5CHO ☐
[Ans. (c)]

9. The order of hydrolysis for the following is: **[PET (Raj.) 2003; DPMT 2005]**

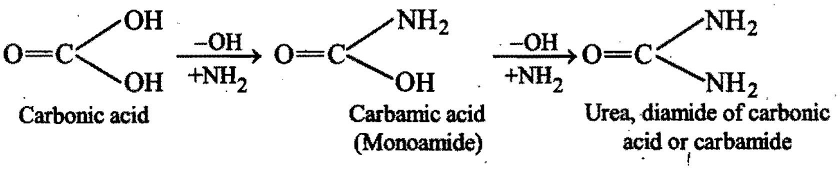
(a) $RCOX > RCONH_2 > RCOOCOR > RCOOR$ ☐
(b) $RCOX > RCOOCOR > RCOOR > RCONH_2$ ☐
(c) $RCOOR > RCONH_2 > RCOX > RCOOCOR$ ☐
(d) $RCOOCOR > RCOOR > RCOX > RCONH_2$ ☐
[Ans. (b)]

10. Which one of the following can produce hydrogen when treated with metallic sodium? **[CPMT 2003; PMT (Raj.) 2005]**

(a) $(CH_3)_2NH$ ☐ (b) CH_3NH_2 ☐
(c) $C_6H_5NH_2$ ☐ (d) CH_3CONH_2 ☐
[Ans. (d)]

13.7 UREA OR CARBAMIDE, NH_2CONH_2

Urea may be considered as diamide of an unstable and dibasic carbonic acid from which both the hydroxyl groups have been replaced by $—NH_2$ groups.



Urea is a historical compound. It was the first organic compound synthesized in the laboratory from inorganic materials (by heating a mixture of ammonium sulphate and potassium cyanate) by Wöhler in 1828. This preparation gave a death blow to *Vital force theory*. Urea is also important physiologically as it is the final decomposition product of protein's metabolism in man and mammals and is excreted alongwith urine. Adults excrete about 30 g of urea per day in the urine. It was first isolated from urine in 1773 by Roulle and hence the name urea was given.

Methods of Preparation

1. From urine : Urine is concentrated and treated with concentrated nitric acid where crystals of urea nitrate, $CO(NH_2)_2 \cdot HNO_3$, are obtained. The crystals are separated and dissolved in water. The solution is treated with barium carbonate. Free urea comes into the solution.

$$\underset{\text{Urea nitrate}}{2CO(NH_2)_2{\cdot}HNO_3} + BaCO_3 \longrightarrow \underset{\text{Urea}}{2CO(NH_2)_2} + Ba(NO_3)_2 + H_2O + CO_2$$

Urea is extracted with alcohol and the extract on evaporation yields crystals of urea.

2. Laboratory preparation : **(i) Wöhler synthesis :** 16 g potassium cyanate is dissolved in water. 13 g ammonium sulphate is added to the solution. The solution is then evaporated to dryness on water bath. When ammonium cyanate formed by double decomposition undergoes intramolecular change and forms urea.

$$\underset{\substack{\text{Potassium}\\\text{cyanate}}}{2KCNO} + \underset{\substack{\text{Ammonium}\\\text{sulphate}}}{(NH_4)_2SO_4} \xrightarrow{\Delta} \underset{\substack{\text{Ammonium}\\\text{cyanate}}}{2NH_4CNO} + K_2SO_4$$

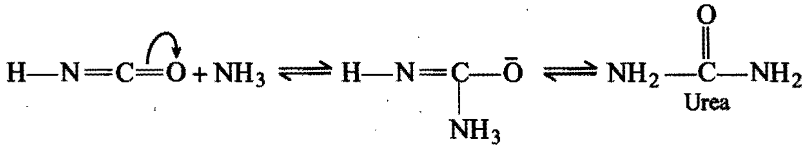
$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow[\text{on heating}]{\text{Isomeric change}} \underset{\text{Urea}}{NH_2CONH_2}$$

[NH_4CNO and urea are thus isomers.]

The solid residue is extracted with alcohol and the extract evaporated when the crystals of urea are obtained. It can be recrystallized from water.

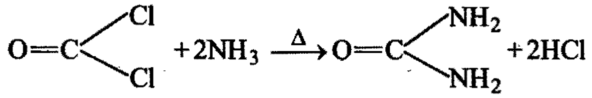
Mechanism of this reaction can be given as,

$$NH_4NCO \rightleftharpoons NH_3 + H{-}N{=}C{=}O \rightleftharpoons \underset{\text{Cyanic acid}}{HO{-}C{\equiv}N}$$

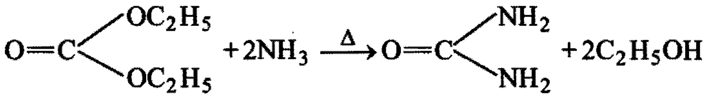


$$H{-}N{=}C{=}O + NH_3 \rightleftharpoons H{-}N{=}\underset{\displaystyle NH_3}{\underset{|}{C}}{-}\bar{O} \rightleftharpoons \underset{\text{Urea}}{NH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH_2}$$

(ii) From phosgene or alkyl carbonate : Urea can also be prepared in the laboratory by heating ammonia on carbonyl chloride or ethyl carbonate.

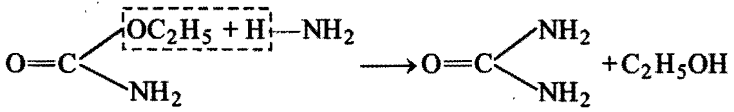


$$\underset{\substack{\text{Carbonyl chloride}\\\text{(Phosgene)}}}{O{=}C\begin{matrix}Cl\\Cl\end{matrix}} + 2NH_3 \xrightarrow{\Delta} \underset{\text{Urea}}{O{=}C\begin{matrix}NH_2\\NH_2\end{matrix}} + 2HCl$$



$$\underset{\text{Ethyl carbonate}}{O{=}C\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}} + 2NH_3 \xrightarrow{\Delta} \underset{\text{Urea}}{O{=}C\begin{matrix}NH_2\\NH_2\end{matrix}} + 2C_2H_5OH$$

Similarly ethyl carbamate (urethane) can be converted to urea.



$$O{=}C\begin{matrix}\boxed{OC_2H_5 + H}{-}NH_2\\NH_2\end{matrix} \longrightarrow \underset{\text{Urea}}{O{=}C\begin{matrix}NH_2\\NH_2\end{matrix}} + C_2H_5OH$$

3. Manufacture : **(i) By partial hydrolysis of calcium cyanamide :** Calcium cyanamide is obtained by passing nitrogen over calcium carbide at 800°C.

$$\underset{\substack{\text{Calcium}\\\text{carbide}}}{CaC_2} + N_2 \xrightarrow{\text{Heat}} \underset{\substack{\text{Calcium}\\\text{cyanamide}}}{CaCN_2} + C$$

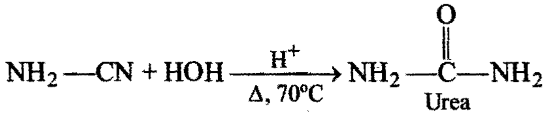
The cyanamide is treated with dilute sulphuric acid at 40°C where partial hydrolysis occurs with the formation of urea.

$$CaCN_2 \xrightarrow[-CaSO_4]{H_2SO_4} \underset{\text{Cyanamide}}{H_2NCN} \xrightarrow[(H_2O_2)]{H_2O} \underset{\text{Urea}}{H_2NCONH_2}$$

or

$$CaCN_2 + H_2O + H_2SO_4 \xrightarrow{40°C} NH_2CONH_2 + CaSO_4$$

Cyanamide on hydrolysis in acidic medium gives urea.

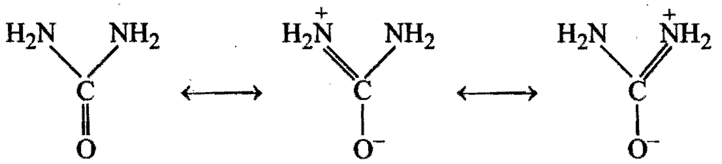


$$NH_2—CN + HOH \xrightarrow[\Delta,\ 70°C]{H^+} \underset{\text{Urea}}{NH_2—\overset{\overset{\Large O}{\|}}{C}—NH_2}$$

(ii) From carbondioxide and ammonia : Urea is made commercially by the reaction of liquid carbondioxide and liquid ammonia at 150–200°C under high pressure. Ammonium carbamate is first formed which decomposes at 140°C to form urea.

$$CO_2 + 2NH_3 \xrightarrow{\Delta} \underset{\text{Ammonium carbamate}}{NH_2COONH_4} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

Physical properties : Urea is a colourless, odourless crystalline solid. It melts at 132°C. It is very soluble in water, less soluble in alcohol but insoluble in ether, chloroform and benzene. Crystal structure studies have shown that in solid urea, both nitrogen atoms are identical. Bond length measurements in urea give the C—N distance as 1.37 Å. This is shorter than the C—N single bond distance in aliphatic amines (1.48 Å) but longer than the normal C—N double bond (1.28 Å). This indicates that the C—N bond in urea has some double bond character and can be explained by resonance.

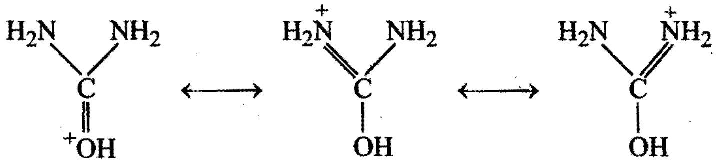


Chemical properties : (i) Basic nature (Salt formation) : The aqueous solution of urea is neutral in nature but urea behaves as a weak monoacidic base ($K_b = 1.5 \times 10^{-14}$ at 25°C). It forms salts with strong acids.

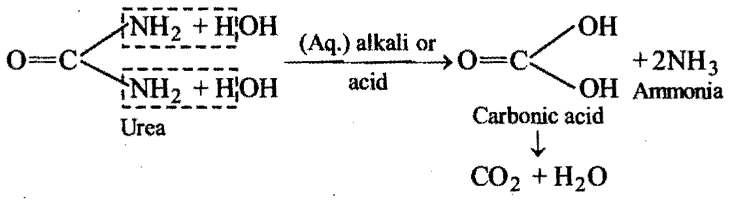
$$NH_2CONH_2 + HNO_3\,(\text{conc.}) \longrightarrow \underset{\text{Urea nitrate}}{NH_2CONH_2{\cdot}HNO_3}$$

$$2NH_2CONH_2 + \underset{\text{Oxalic acid}}{H_2C_2O_4} \longrightarrow \underset{\text{Urea oxalate}}{(NH_2CONH_2)_2\,H_2C_2O_4}$$

Urea is a stronger base than ordinary amides. It is due to resonance stabilization of cation. The negatively charged oxygen atom is capable of coordination with one proton (therefore, urea will be a monoacidic base) and thus the salt may be formulated as a resonance hybrid.



(ii) Hydrolysis : Like other amides, urea is hydrolysed when boiled with either acids or alkalies giving ammonia and carbon dioxide.



[Acid will combine with NH_3 to form ammonium compound while alkali will combine with CO_2 to form carbonate.]

$$NH_2CONH_2 + 2NaOH \longrightarrow 2NH_3 + Na_2CO_3$$

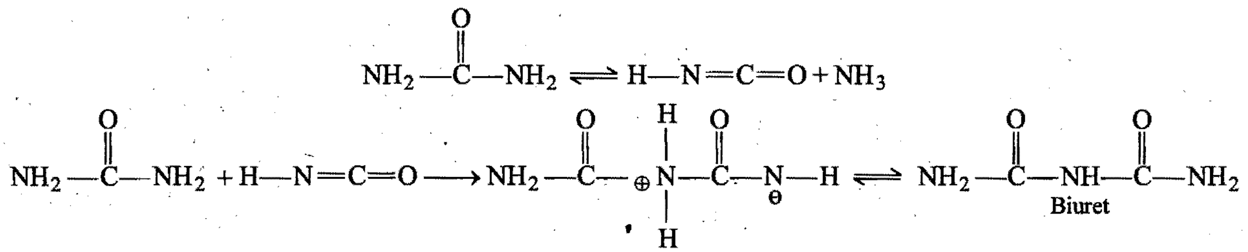
An enzyme, **urease**, present in soyabean and soil, also brings hydrolysis. It converts urea into ammonium carbonate. This reaction is rapid and quantitative and can be used for the estimation of urea.

$$NH_2CONH_2 + 2H_2O \longrightarrow \underset{\substack{\text{Ammonium}\\ \text{carbonate}}}{(NH_4)_2CO_3} \longrightarrow 2NH_3 + CO_2 + H_2O$$

(iii) Action of heat : (a) On heating at 132°C, urea melts. The liquid on gentle heating at a slightly higher temperature at 150°C, evolves ammonia and leaves a solid white residue known as **biuret.**

$$\underset{\text{(Two molecules of urea)}}{NH_2CO\boxed{NH_2 + H}HNCONH_2} \xrightarrow{\text{Heat}} \underset{\text{Biuret}}{NH_2CONHCONH_2} + NH_3$$

Mechanism of biuret test can be given as:



$$NH_2-\overset{\overset{O}{\|}}{C}-NH_2 \rightleftharpoons H-N=C=O+NH_3$$

$$NH_2-\overset{\overset{O}{\|}}{C}-NH_2 + H-N=C=O \longrightarrow NH_2-\overset{\overset{O}{\|}}{C}-\overset{\oplus}{N}H_2-\overset{\overset{O}{\|}}{C}-\underset{\ominus}{N}-H \rightleftharpoons \underset{\text{Biuret}}{NH_2-\overset{\overset{O}{\|}}{C}-NH-\overset{\overset{O}{\|}}{C}-NH_2}$$

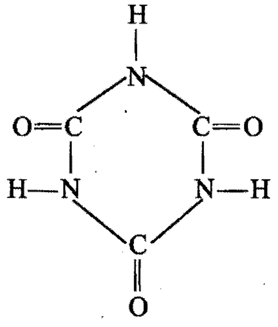
Urea is identified by the test known as biuret test. The biuret residue is dissolved in water and made alkaline with a few drops of NaOH. When a drop of copper sulphate solution is added to the alkaline solution of biuret, a violet colouration is produced.

This reaction is called **Biuret test** and is a characteristic of proteins, peptides and all other compounds containing —CONH— group.

(b) When heated rapidly above 170°C, urea decomposes into ammonia and cyanic acid. Cyanic acid undergoes polymerization forming cyanuric acid (a cyclic compound).

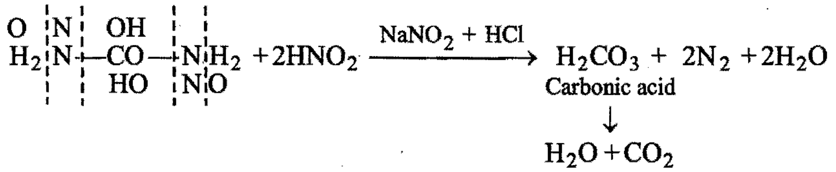
$$\underset{\text{Urea}}{NH_2CONH_2} \xrightarrow{\text{Heat}} NH_3 + \underset{\text{Cyanic acid}}{HOCN\ (H-N=C=O)}$$

$$3HOCN \xrightarrow{\text{Polymerization}} (HOCN)_3 \quad \text{or} \quad (H_3N_3C_3O_3) \quad \text{or}$$



Cyanuric acid

(iv) Reaction with nitrous acid : Urea is decomposed by nitrous acid into nitrogen, carbondioxide and water.



$$\begin{array}{l} O\ \vdots N \vdots\ OH\ \vdots\ \vdots \\ H_2\vdots N \vdots-CO-\vdots N \vdots H_2 + 2HNO_2 \xrightarrow{NaNO_2 + HCl} \underset{\text{Carbonic acid}}{H_2CO_3} + 2N_2 + 2H_2O \\ \ \ \vdots\ \ \vdots\ HO\ \vdots N \vdots O \end{array}$$

$$H_2CO_3 \downarrow H_2O + CO_2$$

(v) Reaction with alkaline hypohalides : Urea is oxidised to nitrogen when heated with excess of alkaline hypochlorite or hypobromite ($NaOH + Br_2 = NaOBr + HBr$).

$$NH_2CONH_2 + 3NaBrO \longrightarrow N_2 + 2H_2O + CO_2 + 3NaBr$$

$$NH_2CONH_2 + 3NaOCl \longrightarrow N_2 + 2H_2O + CO_2 + 3NaCl$$

This reaction forms the basis of **Hufner's method** for the quantitative estimation of urea.

(vi) Reaction with acetyl chloride or acetic anhydride : Urea reacts with acetylating agents to form *N*-acetyl ureas which are known as **Ureides.**

$$NH_2CONH_2 + \underset{\text{Acetyl chloride}}{CH_3COCl} \longrightarrow \underset{\text{Acetyl urea (Ureide)}}{NH_2CONHCOCH_3} + HCl$$

$$NH_2CONH_2 + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \longrightarrow \underset{\text{Acetyl urea}}{NH_2CONHCOCH_3} + \underset{\text{Acetic acid}}{CH_3COOH}$$

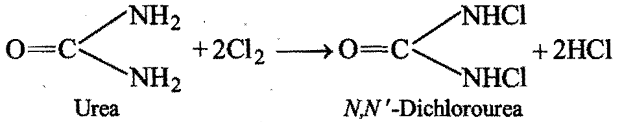
(vii) Reaction with hydrazine : Urea reacts with hydrazine at 100°C to form semicarbazide with evolution of an ammonia molecule.

$$\underset{\text{Urea}}{NH_2CONH_2} + \underset{\text{Hydrazine}}{H_2NNH_2} \xrightarrow{100^\circ C} \underset{\text{Semicarbazide}}{NH_2CONHNH_2} + NH_3$$

(viii) Reaction with ethanol : When urea is heated with ethanol, urethane (ethylcarbamate) is produced.

$$H_2NCO\boxed{NH_2 + H}\underset{\text{Ethanol}}{OC_2H_5} \xrightarrow{\text{Heat}} \underset{\text{Urethane}}{H_2NCOOC_2H_5} + NH_3$$

(ix) Reaction with chlorine water : Urea reacts with aqueous solution of chlorine to form *N, N'*-dichlorourea.



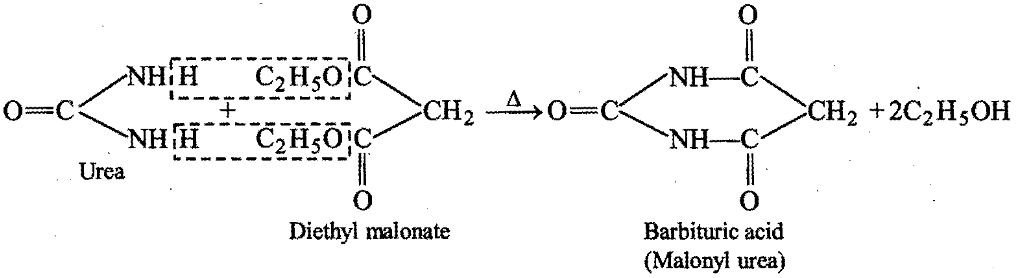
(x) Dehydration : On dehydration with $SOCl_2$, urea gives cyanamide.

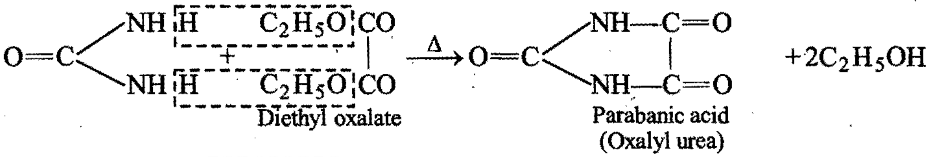
$$NH_2CONH_2 + SOCl_2 \longrightarrow H_2N-C{\equiv}N + SO_2 + 2HCl + H_2O$$

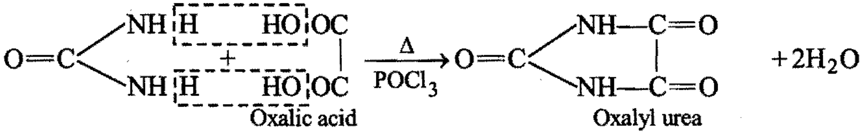
(xi) Reaction with fuming sulphuric acid : Urea reacts with fuming sulphuric acid (oleum) to yield sulphamic acid.

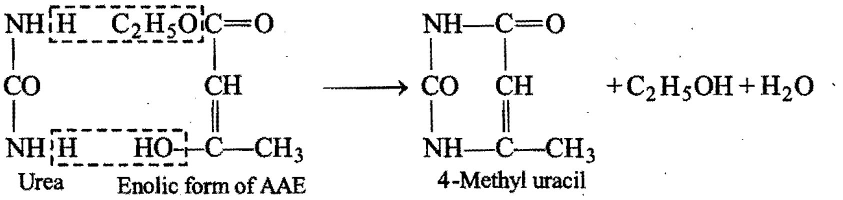
$$NH_2CONH_2 + \underbrace{H_2SO_4 + SO_3}_{\text{Oleum}} \longrightarrow \underset{\text{Sulphamic acid}}{2NH_2SO_3H} + CO_2$$

(xii) Formation of cyclic ureides : Urea reacts with malonic and oxalic esters in presence of sodium ethoxide (C_2H_5ONa) or phosphorus trichloride to form cyclic ureides.





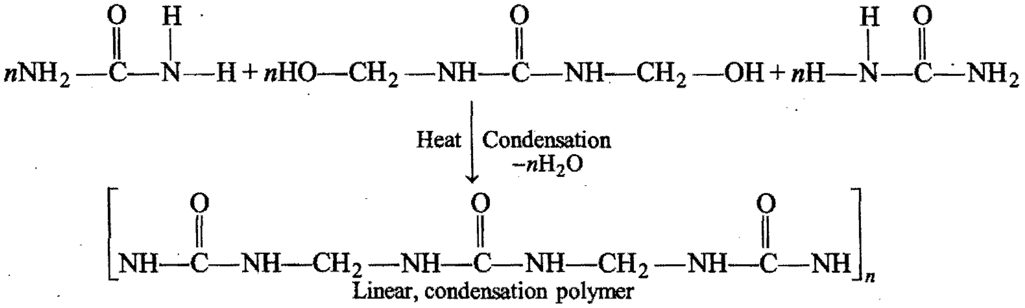




(xiii) Reaction with formaldehyde : Urea and formaldehyde react to form urea-formaldehyde resin which is used in the form of plastic.

$$\underset{\text{Formaldehyde}}{H_2C{=}O} + NH_2CONH_2 \xrightarrow{HCl} \underset{\text{Monomethylol urea}}{CH_2(OH)NHCONH_2} \xrightarrow{CH_2=O} \underset{\text{Dimethylol urea}}{CH_2(OH)NHCONH(OH)CH_2} \xrightarrow{\text{Urea}} \underset{\text{(Urea-Formaldehyde)}}{\text{Resin}}$$

Formation of resin can be represented as:



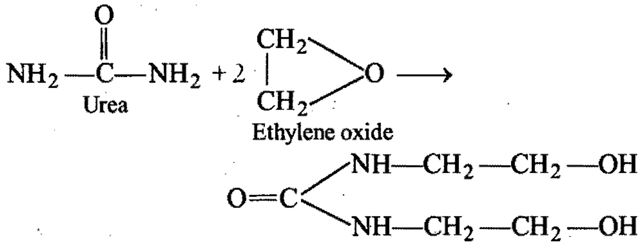
$$nNH_2-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-H + nHO-CH_2-NH-\overset{O}{\overset{\|}{C}}-NH-CH_2-OH + nH-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-NH_2$$

$$\Big\downarrow \text{Heat} \mid \text{Condensation } -nH_2O$$

$$\left[NH-\overset{O}{\overset{\|}{C}}-NH-CH_2-NH-\overset{O}{\overset{\|}{C}}-NH-CH_2-NH-\overset{O}{\overset{\|}{C}}-NH\right]_n$$

Linear, condensation polymer

(xiv) Reaction with ethylene oxide : In this reaction, epoxy bond is broken to form an intermediate in the production of non-ionic detergents.



Bis (Hydroxy methyl urea)

Uses : Urea is used:

(i) mainly as a nitrogen fertilizer. It has 46.6% nitrogen.
(ii) in the manufacture of formaldehyde-urea plastic and semicarbazide.
(iii) as animal feed.
(iv) for making barbiturates and other drugs.
(v) as a stabilizer for nitrocellulose explosives.

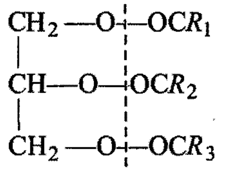
Tests :

(i) When heated with sodium hydroxide, ammonia is evolved.
(ii) When heated gently, it forms biuret which gives violet colouration with sodium hydroxide and a drop of copper sulphate solution.
(iii) Its aqueous solution with concentrated nitric acid gives a white precipitate.
(iv) On adding sodium nitrite solution and dil. HCl (*i.e.*, HNO_2) to urea solution, nitrogen gas is evolved and gives effervescence due to carbondioxide.

13.8 FATS, OILS AND WAXES

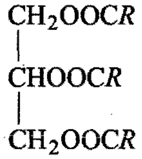
Oils, fats and waxes belong to naturally occurring groups of compounds called **Lipids.** When plant or animal tissues are extracted with a non-polar solvent, (*e.g.*, ether, chloroform or benzene) a portion of the material usually dissolves. The component of this soluble fraction are called lipids. **Lipids are thus constituents of plants and animals that are insoluble in water but soluble in organic solvents.** Lipids include compounds of many different kinds such as oils and fats, waxes, phospholipids, glycolipids, terpenes, steroids, etc. In the following discussion, we shall be studying only oils, fats and waxes.

Oils and fats are the triesters of glycerol (a trihydric alcohol) with a long chain monocarboxylic acids (usually 12 to 20 carbons). These esters are known as **Triglycerides** or **Triacyl glycerols** or **Glyceryl esters.** The following general structure represents an oil or a fat.



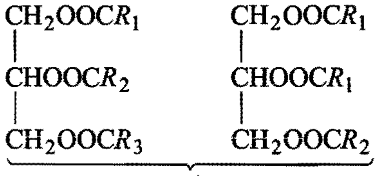
$$\begin{array}{l} CH_2{-}O{-}OCR_1 \\ | \\ CH{-}O{-}OCR_2 \\ | \\ CH_2{-}O{-}OCR_3 \end{array}$$

Three acyl groups present in the molecule may be same or different. When all the three are same, the triester is known as **simple glyceride,** (*i.e.*, three —OH groups of glycerol are esterified with the same acid) and if two or all the three are different, the triester is known as **mixed glyceride,** (*i.e.*, three —OH groups of glycerol are esterified with two or three different acids).



Simple glyceride

$$\begin{array}{l} CH_2OOCR \\ | \\ CHOOCR \\ | \\ CH_2OOCR \end{array}$$



Mixed glycerides

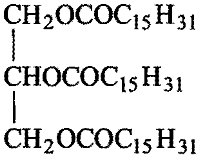
$$\underbrace{\begin{array}{l} CH_2OOCR_1 \\ | \\ CHOOCR_2 \\ | \\ CH_2OOCR_3 \end{array} \qquad \begin{array}{l} CH_2OOCR_1 \\ | \\ CHOOCR_1 \\ | \\ CH_2OOCR_2 \end{array}}$$

The monocarboxylic acids that form ester chains in natural oils and fats may be saturated or unsaturated. The most common monocarboxylic acids present in oils and fats are listed below:

Saturated	**Unsaturated**
$C_{11}H_{23}COOH$ (Lauric acid)	$C_{17}H_{33}COOH$ (Oleic acid)
$C_{13}H_{27}COOH$ (Myristic acid)	$C_{17}H_{31}COOH$ (Linoleic acid)
$C_{15}H_{31}COOH$ (Palmitic acid)	$C_{17}H_{29}COOH$ (Linolenic acid)
$C_{17}H_{35}COOH$ (Stearic acid)	

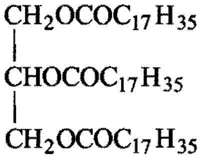
It has been observed that an ordinary oil or fat is a mixture of various glycerides; simple and mixed both, the latter predominating to a considerable extent.

The glycerides are named according to the acid residue present in them by replacing the terminal 'ic acid' by 'in'.



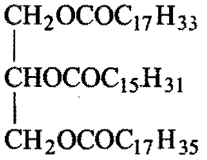
Tripalmitin
(Simple)

$$\begin{array}{l} CH_2OCOC_{15}H_{31} \\ | \\ CHOCOC_{15}H_{31} \\ | \\ CH_2OCOC_{15}H_{31} \end{array}$$



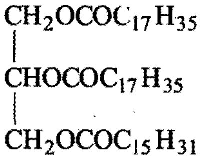
Tristearin
(Simple)

$$\begin{array}{l} CH_2OCOC_{17}H_{35} \\ | \\ CHOCOC_{17}H_{35} \\ | \\ CH_2OCOC_{17}H_{35} \end{array}$$



Oleopalmito-stearin
(Mixed)

$$\begin{array}{l} CH_2OCOC_{17}H_{33} \\ | \\ CHOCOC_{15}H_{31} \\ | \\ CH_2OCOC_{17}H_{35} \end{array}$$



Palmito-distearin
(Mixed)

$$\begin{array}{l} CH_2OCOC_{17}H_{35} \\ | \\ CHOCOC_{17}H_{35} \\ | \\ CH_2OCOC_{15}H_{31} \end{array}$$

At ordinary temperature, the glycerides of saturated carboxylic acids such as palmitin, stearin are solids while that of unsaturated acids such as olein are liquids.

Difference between oils and fats : Oils and fats belong to the same chemical group, yet they are different in their physical state.

1. Oils are liquids at ordinary temperature (below 20°C) while fats are semi solids or solids (their melting points are more than 20°C). A substance may be classed as fat in one season and oil in another season or the same glyceride may be solid at a hill station and liquid in plains. Thus, this distinction is not well founded as the physical state depends on climate and weather.

2. The difference in oils and fats is actually dependent on the nature of monocarboxylic acids present in the glyceride. Oils contain large proportion of the glycerides of lower carboxylic acids, (*e.g.*, butyric acid, caprylic acid and caproic acid) and unsaturated fatty acids, (*e.g.*, oleic, linoleic and linolenic acids) while fats contain a large proportion of glycerides of higher saturated carboxylic acids, (*e.g.*, palmitic, stearic acids).

Lard (fat of hogs) is a solid fat and its composition in terms of fatty acids produced on hydrolysis is approximately 32% palmitic acid, 18% stearic acid, 45% oleic acid and 5% linolenic acid. Olive oil on the other hand, contains 84% oleic acid, 4% linoleic acid, 9% palmitic acid and 3% stearic acid.

Occurrence : Oils and fats occur widely in animals and plants. In plants, oils and fats are found mainly in seeds, roots and fruits, while in animals, they are present under the skin in tissues and muscles. Few examples are given below:

Vegetable oils	**Vegetable fats**
Til oil	Coconut oil
Linseed oil	Vegetable ghee
Mustard oil	Margarine
Ground-nut oil	
Animal oils	**Animal fats**
Whale oil	Lard (fat of hogs)
Cod-liver oil	Tallow (fats of sheep or horses)
Sardine oil	Butter

Properties of Oils and Fats

Physical properties : (i) At room temperature, fats are solids, whereas oils are liquids.

(ii) They are insoluble in water but soluble in ether, chloroform and benzene.

(iii) They have less specific gravity than water and consequently float on the surface when mixed with it.

(iv) Pure fats and oils are colourless, odourless and tasteless but natural fats and oils possess a characteristic odour due to presence of other substances.

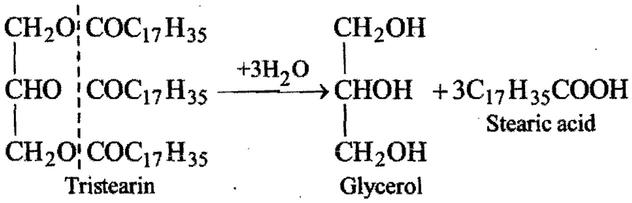
(v) They have specific melting points, specific gravity and refractive index hence they can be identified by these oil constants.

(vi) Animal fats contain cholesterol, an unsaturated alcohol, whereas vegetable fats contain phytosterol.

Chemical properties : Fats and oils are triesters of glycerol (triglycerides) with saturated and unsaturated fatty acids. Thus, they give reactions of carbon-carbon double bonds and ester groups.

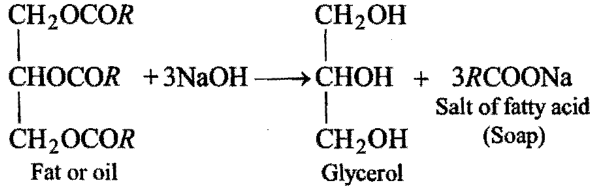
(i) Hydrolysis : They are hydrolysed by heating with superheated steam, acids or alkalies.

(a) By superheated steam : Under a pressure of about 8 atmospheres at 170°C in the presence of lime, zinc oxide or magnesia, oils and fats are hydrolysed. On cooling, free fatty acids separate with some calcium soap (or zinc or magnesium soap).



$$\begin{array}{l} CH_2O|COC_{17}H_{35} \\ CHO\,|COC_{17}H_{35} \\ CH_2O|COC_{17}H_{35} \end{array} \xrightarrow{+3H_2O} \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} + 3C_{17}H_{35}COOH$$

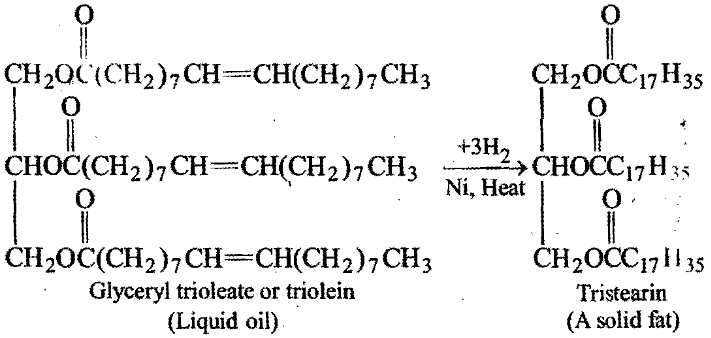
(b) Base hydrolysis : When fats and oils are heated with NaOH (or KOH) solution, the products are glycerol and sodium or potassium salts of higher fatty acids. The sodium or potassium salts of fatty acids are called soaps and the base hydrolysis of fats or oils is termed as saponification.



$$\begin{array}{l} CH_2OCOR \\ CHOCOR \\ CH_2OCOR \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} + 3RCOONa$$

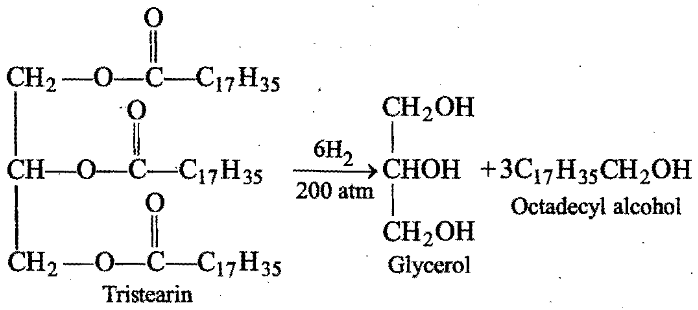
(c) Enzyme hydrolysis : Enzyme like lipase, when added to an emulsion of fat in water, hydrolysis it into acid and glycerol in about two or three days.

(ii) Hydrogenation : The vegetable oils containing glycerides of unsaturated fatty acids undergo catalytic hydrogenation with hydrogen at low pressure in presence of finely divided nickel. This results in the formation of saturated glycerides which are solid fats at room temperature. The hydrogenation process is called **Hardening of oils.**



Partial hydrogenation of oils is used for the manufacture of vegetable ghee. Complete hydrogenation would produce a hard brittle fat.

(iii) Hydrogenolysis (Reduction to alcohols) : If excess of hydrogen, under pressure, is passed through oil or fat in the presence of copper-chromium catalyst, it is converted into glycerol and higher aliphatic alcohols. This process of splitting up of the fat molecule by hydrogen is termed hydrogenolysis.



(iv) Drying : Certain oils, containing glycerides of unsaturated fatty acids having two or three double bonds have the tendency of slowly absorbing oxygen from atmosphere and undergoing polymerization to form a hard transparent coating. This process is known as drying and such oils are called drying oils. Unsaturated oils such as linseed oil are, therefore, used as medium of paints and varnishes.

(v) Rancidification : On long storage in contact with air and moisture, oils and fats develop unpleasant smell. The process is known as rancidification. It is believed that rancidification occurs due to hydrolysis-oxidation by following chemical changes:

(a) Enzymatic hydrolysis—producing bad smelling lower fatty acids.

(b) Oxidation of unsaturated acids—producing aldehydes and ketones.

Analysis of oils and fats : The composition and purity of a given oil or fat is determined by means of a number of physical and chemical tests. The various physical tests are the determination of its physical constants such as melting point, specific gravity and refractive index. The common chemical tests employed are the following:

1. Acid value : It indicates the amount of free acid present in the oil or fat. **It is defined as the number of milligrams of KOH required to neutralize the free acid present in one gram of the oil or fat.** It is determined by dissolving a weighed amount of oil or fat in alcohol and titrating it against a standard solution of KOH using phenolphthalein as an indicator.

2. Saponification value : It is a measure of fatty acids present as esters in oils and fats. **It is defined as the number of milligrams of KOH required to saponify one gram of the oil or fat or number of milligrams of KOH required to neutralize the free acids resulting from the hydrolysis of one gram of an oil or fat.** It is determined by refluxing a weighed amount of the oil or fat with known excess of standard alcoholic caustic potash solution and back titrating the excess of alkali with standard acid solution. Usually $N/2$ alkali solution is used.

Saponification value tells about the approximate molecular mass of a fat or oil. One mole of a fat or oil reacts with three moles of KOH. If M is the molecular mass of the fat or oil, M grams of it will require $3 \times 56 = 168$ grams or 168,000 milligrams of KOH for saponification. Therefore,

$$\text{saponification number of fat or oil} = \frac{168{,}000}{M}$$

Knowing the saponification number experimentally, the value of molecular mass, M, can be determined.

The saponification number is inversely proportional to the molecular mass. The smaller the saponification value, the higher the molecular mass. The saponification value is characteristic of a particular fat or oil and serves for its identification.

3. Iodine value : Iodine value of a fat or oil is a measure of its degree of unsaturation. **It is defined as the number of grams of iodine taken up by 100 grams of fat or oil for saturation.** For a saturated acid glyceride, the iodine value is zero. Thus, the iodine value for a fat is low whereas for oil, it is high. As iodine does not react readily, in actual practice, iodine monochloride is used. Iodine monochloride is known as Wij's reagent.

On the basis of iodine values, the oils have been subdivided into three groups:

(i) Drying oils : These oils have iodine values above 120. These are glycerides of highly unsaturated acids. Linseed oil is the typical example of drying oil. Tung oil (china-wood oil) is another example. These are used in the manufacture of paints, oil cloth and linoleum.

(ii) Semi-drying oils : These are oils with iodine value 90 to 120. They thicken very slowly on exposure. Cotton seed oil and sesame oil are examples of semi-drying oils.

(iii) Non-drying oils : These have iodine values less than 90. They do not thicken when exposed. Olive oil, coconut oil and castor oil are examples of non-drying oils.

4. Reichert-Meissl value (R/M value) : It indicates the amount of steam volatile fatty acids present in the oil or fat. **It is defined as the number of millilitres of 0.1 N KOH solution required to neutralize the distillate of 5 grams of hydrolysed fat.** It is determined by hydrolysing a known weighed amount (5 grams) of the fat with an alkali solution and the mixture is acidified with dilute sulphuric acid and steam distilled. The distillate is cooled, filtered and titrated against 0.1 N KOH.

Uses of oils and fats : (i) Many oils and fats are used as food material.

(ii) Oils and fats are used for the manufacture of glycerol, fatty acids, soaps, candles, vegetable ghee, margarine, hair oils, etc.

(iii) Oils like linseed oil, tung oil, etc., are used for the manufacture of paints, varnish, etc.

(iv) Castor oil is used as purgative and cod-liver oil as a source of vitamins A and D. Almond oil is used in pharmacy. Olive oil is also used as medicine.

(v) Oils are also used as lubricants and illuminants.

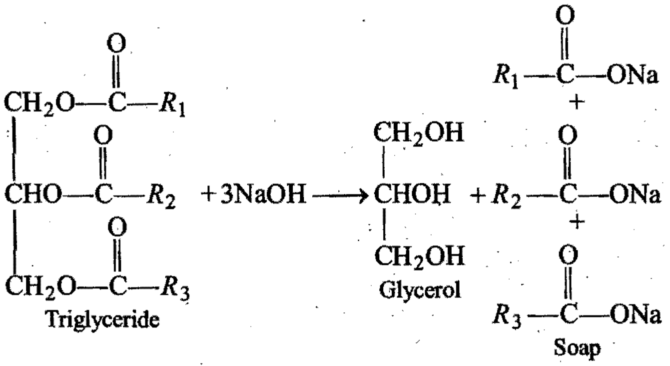
Difference between Vegetable oils and Mineral oils

Property	Vegetable oils	Mineral oils
1. Composition	These are triesters of glycerol with higher fatty acids.	These are hydrocarbons (saturated). Kerosene—Alkanes from C_{12} to C_{16}.
2. Source	Seeds, root and fruits of plants.	These occur inside earth's crust in the form of petroleum.
3. Hydrolysis	Undergo hydrolysis with alkali. Form soap and glycerol.	No hydrolysis occurs.
4. On adding NaOH and phenolphthalein	Decolourization of pink colour occurs.	No effect.
5. Burning	Burn slowly.	Burn very readily.
6. Hydrogenation	Hydrogenation occurs in presence of nickel catalyst. Solid glycerides (fats) are formed.	No hydrogenation occurs.

13.9 SOAP

Soaps are the metallic salts of higher fatty acids such as palmitic, stearic, oleic, etc. The sodium and potassium salts are the common soaps which are soluble in water and used for cleansing purposes. Soaps of other metals such as calcium, magnesium, zinc, chromium, lead, etc., are insoluble in water. These are not used for cleansing purposes but for other purposes (lubricants, driers, adhesives, etc.).

Ordinary soaps (sodium and potassium) are the products of hydrolysis of oils and fats with sodium hydroxide or potassium hydroxide. This process is called **saponification** of oils and fats. The oils and fats are mixed glycerides and thus **soaps are mixtures of salts of saturated and unsaturated long chain carboxylic acids containing 12 to 18 carbon atoms.** This process always yields glycerol as a byproduct.



Where, R is long chain alkyl group (*i.e.*, $C_{15}H_{31}$ or $C_{17}H_{35}$ or $C_{17}H_{33}$ or $C_{17}H_{31}$, etc.)

Some of the examples of soaps are:

Sodium palmitate,	$C_{15}H_{31}COO^-Na^+$
Sodium stearate,	$C_{17}H_{35}COO^-Na^+$
Potassium laurate,	$C_{11}H_{23}COO^-K^+$
Sodium oleate,	$C_{17}H_{33}COO^-Na^+$, etc.

Types of Soaps

1. Hard soaps : These are obtained from cheap oils and fats using sodium hydroxide. These contain free alkali and are used for washing purposes.

2. Soft soaps : These are obtained from good oils using potassium hydroxide. These do not contain free alkali and are used as toilet soaps, shaving creams, in shaving sticks (Pot. sod. stearate) and shampoo.

3. Transparent soaps : These are formed by dissolving toilet soaps in alcohol and evaporating the filtrate. They contain glycerol.

4. Medicated soaps : Toilet soaps containing some medicinal important substances are called medicated soaps.

5. Metallic soaps : These are soaps of metals other than sodium and potassium.

Manufacture of soap

The following raw materials are used for the manufacture of soap:

1. Oils or fats : Coconut oil, mustard oil, mahua oil, cotton seed oil, tallow, lard, etc., are generally used.

2. Caustic soda for hard soaps and potash for soft soaps is employed for saponification.

3. Filler : Certain substances, called fillers, are usually added to increase the weight and volume of the soap. These substances also help in solidification. Sodium silicate, soap stone, rosin, starch, sodium carbonate, etc., are generally added to washing soaps.

Perfumes are added to toilet soaps to make them pleasant smelling.

The following methods are employed for the manufacture of soap:

1. The cold process : The oil or fat is taken in a big vessel and heated to about 50°C. A calculated quantity of caustic soda is added with constant stirring. Some amount of filler like starch or sodium silicate is then mixed. The whole mass is left as such for 12 to 24 hours. It sets to a solid mass. It is cut into pieces of desired shape. The soap obtained by this process always consists glycerol, alkali and free oil or fat. It is used for washing purposes.

2. The hot process : The process is superior to the cold process. The oil or fat is taken in a big steel tank called kettle and heated with open steam. The alkali solution (10% caustic soda solution called lye) is slowly run in and the mass is kept boiling with steam. After several hours of continuous boiling, the saponification is completed to about 80%. Sodium chloride (brine) is then added. The soap gets precipitated and being lighter floats to the surface as curdy mass. This is called salting out of soap. The lower aqueous layer containing sodium chloride, glycerol and free alkali is drawn out. This is called spent lye and used for the recovery of glycerol. The soap left in the kettle still contains some unreacted fat. It is boiled with fresh supply of NaOH solution. More soap is formed. The lower layer is drawn off. The soap layer is boiled with water to wash away excess of NaOH. The soap, while still molten, is pumped into the crutcher. Here, the soap is mixed with colour, perfumes, germicides, etc., and stirred. In case of laundry soap, some fillers like rosin, sodium silicate, sodium carbonate, etc., are added. These have some detergent values and are cheaper than soap.

The crutched soap is poured into frames and on solidification cut into cakes.

3. Modern process : In this process, the oil or fat is hydrolysed with superheated steam under pressure in the presence of a catalyst like zinc oxide. The fatty acids produced as a result of hydrolysis float on water as these are lighter than water. These are separated and neutralized by calculated quantity of alkali solution when soap is obtained. This method is simple and cheap.

The aqueous solution is treated for the recovery of glycerol.

But hard water contains certain metal ions, such as calcium and magnesium. These ions (or their salts) react with soap to produce a curdy white precipitate of calcium and magnesium salts.

$$\underset{\text{(Soap)}}{2C_{17}H_{35}COONa} + \underset{\substack{\text{(Hardness of}\\ \text{water)}}}{MgCl_2} \longrightarrow \underset{\text{White precipitate}}{(C_{17}H_{35}COO)_2Mg\downarrow} + 2NaCl$$

$$\underset{\text{Soap}}{2C_{17}H_{35}COONa} + \underset{\substack{\text{(Hardness of}\\ \text{water)}}}{CaCl_2} \longrightarrow \underset{\substack{\text{White ppt.}\\ \text{(Insoluble)}}}{(C_{17}H_{35}COO)_2Ca\downarrow} + 2NaCl$$

Disadvantages of soaps

(i) The calcium and magnesium salts of fatty acids are insoluble in water and separate as white precipitate (which adheres to clothing and blocks the ability of soaps to remove oil and grease from fabrics). Thus, a lot of soap is wasted if water is hard.

(ii) Soaps cannot be used in acidic solutions since, the acids (present in the solution) precipitate free fatty acids which adhere to the fabrics and hence, prevent the process of dyeing.

13.10 NON-SOAPY DETERGENTS (SYNTHETIC DETERGENTS)

These are also called **synthetic detergents** or **syndets** or **soapless soaps** or just **detergents.** They have cleansing power as good or better than ordinary soaps and can be used for washing even with hard water and do not precipitate in presence of Ca^{2+}/Mg^{2+} or in acidic solution.

A synthetic detergent is the sodium salt of a long chain alkyl hydrogen sulphate or the sodium salt of a long chain benzene sulphonic acid. Like soap, they contain both hydrophilic (water soluble) and hydrophobic (oil soluble) parts in the molecule.

$$\underset{\substack{\text{Hydrophobic}\\ \text{part}}}{\boxed{C_{12}H_{25}}}\ \underset{\substack{\text{Hydrophilic}\\ \text{part}}}{\boxed{OSO_3Na}} \qquad \underset{\substack{\text{Hydrophobic}\\ \text{part}}}{\boxed{C_{15}H_{31}}}\ \underset{\substack{\text{Hydrophilic}\\ \text{part}}}{\boxed{COONa}}$$

Sodium lauryl sulphate (Detergent) Sodium palmitate (Soap)

Classification of detergents : Detergents are mainly classified into three categories, namely anionic, cationic and non-ionic.

(i) Anionic detergents : These are of two types:

(a) Alkyl hydrogen sulphates : They are obtained from long chain aliphatic alcohols ($C_{10} - C_{15}$) by treatment with conc. H_2SO_4 followed by neutralization with NaOH. The alcohols are obtained from oils or fats by hydrogenolysis.

$$\underset{n\text{-Lauryl alcohol}}{CH_3(CH_2)_{10}CH_2O}\boxed{H + HO}\underset{\text{Sulphuric acid}}{SO_3H} \longrightarrow \underset{n\text{-Lauryl hydrogen sulphate}}{CH_3(CH_2)_{10}CH_2OSO_3H}$$

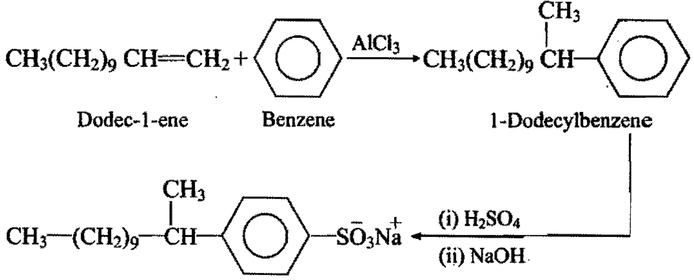
$$\Big\downarrow \text{NaOH}$$

$$\underset{\substack{\text{Sodium lauryl sulphate}\\ \text{(Anionic detergent)}}}{CH_3(CH_2)_{10}CH_2OSO_3^-Na^+}$$

The other examples are sodium cetyl sulphate, $C_{16}H_{33}OSO_3^-Na^+$, and sodium stearyl sulphate, $C_{17}H_{35}CH_2OSO_3^-Na^+$.

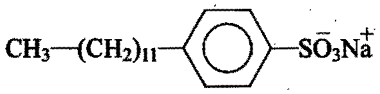
These alkyl hydrogen sulphates are 100% biodegradable. Unlike ordinary soaps, they do not produce OH^- ions on hydrolysis and thus, can be safely used for woolen garments. These detergents are called **anionic detergents** because a large part of the molecule is an anion. The single anionic detergent in largest household use today is alkyl benzene sulphonate.

(b) Sodium alkyl benzene sulphonates : These are obtained by Friedel-Crafts alkylation of benzene with a long chain alkyl halide (or an alkene or an alcohol) followed by sulphonation and neutralization with NaOH. Sodium *p*-dodecylbenzene sulphonate (SDS) is most widely used domestic detergent since, 1975.

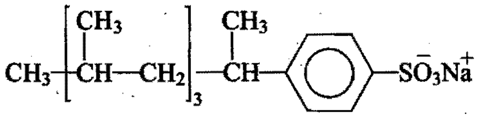


Sodium-2-dodecylbenzene sulphonate (SDS)

Another important example is sodium *p-n*-dodecylbenzene sulphonate.



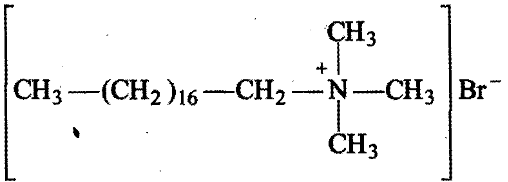
These alkyl benzene sulphonates are highly biodegradable and called soft detergents. These long chain alkyl benzene sulphonates, (Linear alkyl sulphonates) are called **LAS detergents,** while those having branched chains are called **ABS detergents** (Alkyl benzene sulphonates). An important example of ABS detergent is:



ABS detergent (hard or non-biodegradable)

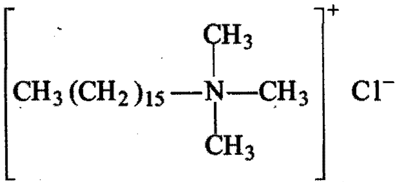
It is prepared by Friedel-Crafts reaction of tetramer of propylene with benzene followed by sulphonation and neutralization with alkali.

(ii) Cationic detergents : These are mostly acetates, chlorides or bromides of quaternary ammonium salts containing one or more long chain alkyl groups. Being more expensive than the anionic detergents, they find limited use. Such detergents however, possess germicidal properties and are used quite extensively as germicides (antiseptic). Examples are trimethyl stearyl ammonium bromide, cetyl trimethyl ammonium chloride or *N*-benzyl quaternary ammonium chlorides.



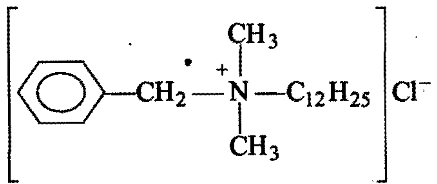
$$\left[CH_3-(CH_2)_{16}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{N}}}-CH_3\right]Br^-$$

Trimethyl stearyl ammonium bromide



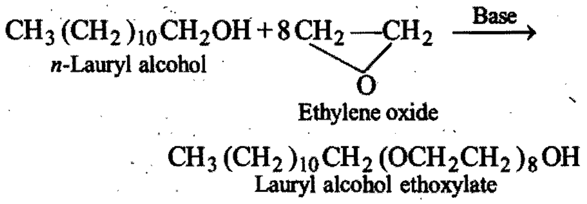
$$\left[CH_3(CH_2)_{15}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3\right]^+ Cl^-$$

Cetyl trimethyl ammonium chloride

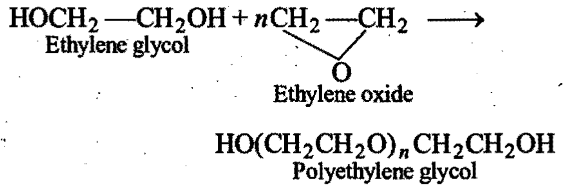


Benzalkonium chloride (antibacterial)

(iii) Non-ionic detergents : They are neutral surface active detergents (surfactants) and obtained from long chain alcohols by treatment with ethylene oxide in presence of a base. For example, lauryl alcohol ethoxylate.

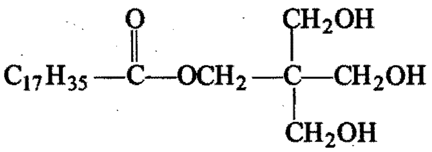


Other example is the ester of high molecular mass formed by the reaction between polyethylene glycol and stearic acid.

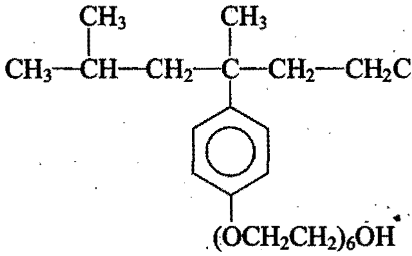


$$\underset{\text{Stearic acid}}{CH_3(CH_2)_{16}COOH} + \underset{\text{Polyethylene glycol}}{HO(CH_2CH_2O)_nCH_2CH_2OH} \xrightarrow{-H_2O} \underset{\text{Non-ionic detergent}}{CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH}$$

Another important examples are:



Pentaerythritol monostearate



Nonylphenol ethoxylate

Lauryl alcohol ethoxylate with 100% biodegradability is superior to nonphenol ethoxylate (30% biodegradable).

Synthetic Detergents (Syndets)

Synthetic detergents are widely used these days as cleansing agents. Washing powders available in the market contain about 15 to 30% detergents by weight and the remaining part is other chemicals which are added to it. These are:

(i) Sodium sulphate and sodium silicate—to keep the powder dry.
(ii) Sodium carbonate or sodium tripolyphosphate—to maintain its alkaline nature which helps in removing dirt and also, softens water.
(iii) Carboxy methyl cellulose (CMC)—to keep the dirt suspended in water.

(iv) Mild bleaching agent (Sodium perborate)—to give whiteness in clothes.

Surfactants (Surface Active Agents)

Substances like soaps and synthetic detergents concentrate at the surface of the solution or interfaces, form surface films, the non-polar hydrocarbon chains of the soap or detergent dissolves in oil or grease and the other part (Carboxylate group of the soap or sulphonate group of synthetic detergent) is held by surrounding water.

This lowers the surface tension between water and grease solution and helps in removing dirt and dust by emulsifying grease. Such substances are called surface active agents or surfactants. The molecule of a surfactant contains two characteristic groups:

(a) Hydrophilic—water soluble,
(b) Hydrophobic (Lyophilic)—oil soluble.

Advantages of Synthetic Detergents Over Soaps

Synthetic detergents are superior and most widely used cleansing agents due to the following properties:

(i) These can be used both in soft and hard waters whereas ordinary soaps cannot be used in hard water.
(ii) Synthetic detergents are prepared from the hydrocarbons obtained from petroleum while soaps are prepared from vegetable oils and fats.
(iii) The aqueous solution of detergents are neutral and hence, can be used for washing all types of fabrics without any damage. The solution of ordinary soap is alkaline and thus, cannot be used to wash delicate fabrics.
(iv) These can be used even in acidic medium as they are the salts of strong acids and are not decomposed in acidic medium whereas soaps are decomposed into carboxylic acids in acidic medium.

Disadvantages of Synthetic Detergents

Some of the synthetic detergents are not biodegradable. In the past, many detergents caused pollution in river and waterways. It has been found that if straight chain hydrocarbon is used in the detergent instead of branched chain hydrocarbons then the detergent is biodegradable because detergent molecules associated with branched chain hydrocarbon tail is a source of pollution.

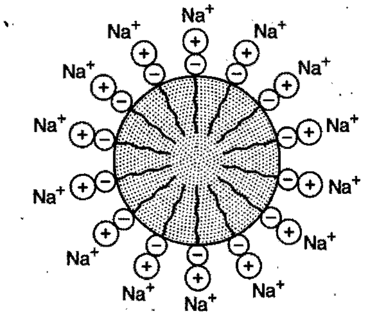
Cleansing action of soaps and detergents

The molecules of soaps and detergents are usually smaller than the colloidal particles. However, in concentrated solutions, these molecules associate and form aggregates of colloidal size. These aggregates of soaps or detergents molecules are called **micelles.** Soaps and detergents are strong electrolytes and when dissolved in water they furnish ions.

$$\underset{\text{Soap}}{C_{17}H_{35}COONa} \longrightarrow C_{17}H_{35}COO^{-} + Na^{+}$$

The negative ions aggregate to form a micelle of colloidal size. The negative ion has a long hydrocarbon chain and a polar group ($—COO^{-}$) at one end. In micelle formation, the long hydrocarbon chain (tail) which is insoluble in water is directed towards the centre while the soluble polar head is on the surface in contact with water (Fig.). The charge on the micelle is responsible for the stability of this system.

The initial concentration at which micellization begins is called critical micellization concentration **(*CMC*).** Every associated colloid has a definite CMC at a given temperature. Increase of temperature lowers CMC. The formation of micelles starts only above a certain temperature called Kraft temperature denoted by (T_k). For micelles of soap, CMC is $10^{-4} - 10^{-3}$ mol L^{-1}. The micellization is a reversible process, hence, by diluting an associated colloid, it is possible to revert to the original simple solution. **The cleansing action of soap is due to micelles.** The grease stain is absorbed into the interior of the micelle and gets detached from the fabric.



The dust particles sticking to the stain are also removed. This action is similar to emulsification of grease.

13.11 WAXES

Waxes are the esters of higher saturated and unsaturated fatty acids with higher monohydric alcohols. The acids and alcohols commonly found in waxes are palmitic, cerotic acid ($C_{25}H_{51}COOH$), melissic acid ($C_{30}H_{61}COOH$) and cetyl alcohol ($C_{16}H_{33}OH$), ceryl alcohol ($C_{26}H_{53}OH$), myricyl alcohol ($C_{30}H_{61}OH$), etc.

Waxes are insoluble in water but are readily soluble in benzene, petroleum, carbon disulphide, etc. Waxes on hydrolysis with water yield higher fatty acids and higher monohydric alcohols.

$$\underset{\text{Cetyl palmitate}}{C_{15}H_{31}COOC_{16}H_{33}} + H_2O \longrightarrow \underset{\text{Palmitic acid}}{C_{15}H_{31}COOH} + \underset{\text{Cetyl alcohol}}{C_{16}H_{33}OH}$$

When hydrolysis is carried with caustic alkalies, soap and higher monohydric alcohols are formed.

$$C_{15}H_{31}COOC_{16}H_{33} + NaOH \rightarrow C_{16}H_{33}OH + \underset{\substack{\text{Sodium palmitate}\\ \text{(Soap)}}}{C_{15}H_{31}COONa}$$

The common waxes are:

(i) **Bees wax,** myricyl palmitate, $C_{15}H_{31}COOC_{30}H_{61}$

(ii) **Spermaceti wax,** cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$

(iii) **Carnauba wax,** myricyl cerotate, $C_{25}H_{51}COOC_{30}H_{61}$

Waxes are used in the manufacture of candles, polishes, inks, water proof coating and cosmetic preparations.

Waxes obtained from plants and animals are different than **paraffin wax** which is a petroleum product and a mixture of higher hydrocarbons (20 to 30 carbon atoms). So paraffin wax is not an ester.

Candles are prepared by mixing paraffin wax (90%) with higher fatty acids like stearic and palmitic. The fatty acids are added to paraffin wax as to give strength to candles. The mixture is melted and poured into metal tubes containing streched threads. On cooling candles are obtained.

IMPORTANT POINTS TO REMEMBER (SUMMARY)

☐ The classes of compounds obtained from carboxylic acids by the replacement of —OH group of —COOH group with $—X\,(R—\overset{\overset{O}{\|}}{C}—X$, acid halide), $—NH_2\,(R—\overset{\overset{O}{\|}}{C}—NH_2$, acid amide), $—OR'\,(R—\overset{\overset{O}{\|}}{C}—OR'$, ester) or $—OCOR$ $(R—\overset{\overset{O}{\|}}{C}—O—\overset{\overset{O}{\|}}{C}—R$, acid anhydride) are termed as **acid derivatives.**

☐ All functional derivatives of carboxylic acids contain the common group, $R—\overset{\overset{O}{\|}}{C}—$ known as acyl group. These acid derivatives on hydrolysis produce carboxylic acids under appropriate conditions.

Acetyl Chloride (Ethanoyl Chloride), CH_3COCl or Acyl Halides

Methods of preparation

☐ By heating glacial acetic acid with PCl_5, PX_3 or $SOCl_2$.

☐ By distilling anhydrous sodium acetate or calcium acetate with PCl_3, $POCl_3$ or SO_2Cl_2.

☐ By adding HCl on ketene.

☐ **Properties :** Among the different acid derivatives, acyl chlorides are the most reactive. In acyl chlorides, the $(—\overset{\overset{O}{\|}}{C}—)$ group is attached to highly electronegative chlorine atom and at the same time, it has a weak electron releasing resonance effect (+*R* effect). Hence, acyl chlorides readily undergo a number of **nucleophilic substitution reactions.**

☐ **Hydrolysis :** Acyl chlorides are readily hydrolysed by water to give carboxylic acids.

☐ An acid chloride with a bulky alkyl group attached to a carbonyl carbon undergoes reaction more slowly than an acid chloride with a small alkyl group, *i.e.,*

$$CH_3CH_2CH_2COCl < CH_3CH_2COCl < CH_3COCl$$

☐ An acid chloride with a small alkyl group is more soluble and undergoes reaction faster.

☐ **Action with alcohols :** Formation of an ester.

☐ **Action with ammonia :** Formation of an acid amide.

☐ **Action with 1° amine and 2° amine :** Formation of *N*-alkyl amide (2°) and *N,N*-dialkyl amide (3°).

☐ **Action with hydroxylamine and hydrazine :** Formation of corresponding acetyl derivatives.

☐ **Action with thioalcohols :** Formation of thioesters.

☐ **Reduction :** On reduction with $LiAlH_4$ or $NaBH_4$ it gives ethyl alcohol.

☐ **Rosenmund's reduction :** On reduction with H_2 in presence of $Pd/BaSO_4$ and partially poisoned with a small amount of sulphur or quinoline as catalyst, it is reduced to acetaldehyde.

☐ **Action with salts of carboxylic acids :** Formation of acid anhydrides.

☐ **Friedel-Crafts reaction :** Acetyl chloride reacts with benzene in the presence of anhyd. $AlCl_3$ to form methyl phenyl ketone (acetophenone) is called Friedel-Crafts reaction.

☐ **Action with Grignard reagent :** With calculated amount of Grignard reagent, acetyl chloride forms ketones. But with excess of GR, tertiary alcohol (3°) is obtained.

☐ **Action with diethyl ether :** Formation of esters.

☐ **Action with KCN followed by hydrolysis :** Formation of acetyl cyanide followed by hydrolysis to yield α-keto acid (pyruvic acid).

☐ **Action with salicylic acid :** Acetyl salicylic acid (aspirin) is formed.

☐ **Action with sodium peroxide :** Formation of acetyl peroxide.

☐ **Action with diazomethane :** Acetyl chloride forms diazoketone. This diazoacetone gives chloromethyl ketone (with HCl), propanamide (with NH_3/Ag_2O catalyst) and hydroxy acetone (with $H_2O/HCOOH$). It is called **Arndt-Eistert synthesis.**

☐ Diazoacetone loses N_2 to form methyl ketene ($CH_3CH{=}C{=}O$) by **Wolff rearrangement** when warmed in presence of Ag_2O as catalyst.

☐ **Action with urea :** Formation of acetyl urea.

- **α-Halogenation :** Acid halides undergo tautomerization and so they proceeds for α-halogenation to form chloroacetyl chloride.
- Acetyl chloride is **used as an acetylating agent.** It is also used in the estimation and determination of number of —OH and —NH_2 groups.

Acetic Anhydride (Ethanoic Anhydride), $(CH_3CO)_2O$ or Acid Anhydride

Methods of preparation

- By heating glacial acetic acid with a dehydrating agent like P_2O_5 or anhydrous $ZnCl_2$.
- By distilling a mixture of anhydrous sodium acetate and acetyl chloride.
- By heating anhydrous sodium acetate with $SOCl_2$ or SO_2Cl_2 or $POCl_3$.
- By passing chlorine in a mixture of sodium acetate and sulphur dichloride and distilling the mixture so obtained **(Industrial method).**
- By heating acetylene with glacial acetic acid in presence of $HgSO_4$, acetic anhydride is obtained alongwith acetaldehyde **(Industrial method).**
- By heating acetone at high temperature to give ketene which is then passed through glacial acetic acid when formation of acetic anhydride takes place.
- **Properties :** It resembles acetyl chloride in its action towards compounds having active hydrogen but it is less reactive than acetyl chloride.
- **Hydrolysis :** Acetic anhydride is hydrolysed slowly with water, but rapidly by alkali to give carboxylic acid.
- **Action with ammonia :** Formation of acetamide.
- **Acetylation reactions :** One half of anhydride molecule is used in acetylation, but other half being converted into acetic acid. For example, Ac_2O and C_2H_5OH forms ethyl acetate and acetic acid; similarly, with ethylamine, it yields *N*-ethyl acetamide, with diethylamine yields *N,N*-diethyl acetamide, with aniline gives acetanilide and with salicylic acid, it is acetylated to aspirin.
- **Action of dry HCl :** Formation of acetyl chloride.
- **Action of thioalcohol :** Formation of ethyl thioacetate.
- **Action of chlorine :** Formation of acetyl chloride and monochloroacetic acid.
- **Action of PCl_5 :** Formation of acetyl chloride.
- **Friedel-Crafts reaction :** In presence of anhyd. $AlCl_3$ acetic anhydride reacts with benzene to form acetophenone.
- **Reaction with aldehyde :** Formation of ethylidene acetate.
- **Reaction with Grignard reagents :** Formation of ketones.
- **Reaction with ether :** Formation of an ester (ethyl acetate).
- **Reduction :** Acetic anhydride is reduced to ethyl alcohol by $LiAlH_4$ in ether or Na/alcohol or $NaBH_4/AlCl_3$, etc.
- **Perkin reaction :** Anhydrides having α-H atoms react with aromatic aldehydes in presence of sodium salt of the same acid to form α, β-unsaturated acid (cinnamic acid). This reaction is called Perkin reaction.
- **Reaction with N_2O_5 :** Formation of acetyl nitrate.
- **Reaction with barium peroxide :** Formation of acetyl peroxide.

Acetamide (Ethanamide), CH_3CONH_2 or Acid Amides

Methods of preparation

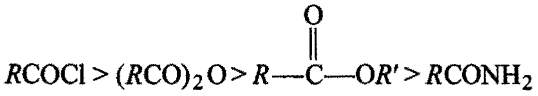
- **Laboratory preparation :** By heating ammonium acetate at 215°C acetamide is formed, while ammonium formate on heating gives formamide.
- By the action of concentrated ammonia solution on acetyl chloride, acetic anhydride or ethyl acetate **(ammonolysis of acid derivatives).**
- By heating glacial acetic acid with urea.
- By partial hydrolysis of alkane nitrile in cold conc. HCl or dil. H_2SO_4 or alkaline H_2O_2.
- **Properties :** Lower amides are soluble in water due to H-bond formation. The m.pt. and b.pt. are higher than expected from their molecular weights due to association through H-bonding.
- **Hydrolysis :** Acetamide is hydrolysed slowly by boiling with water, rapidly by acids and far more rapidly by alkalies to give acetic acid.
- **Amphoteric nature :** It forms salts with acids and bases both and this behaviour is due to the presence of tautomerism.
- **Reduction :** Acetamide undergoes reduction with Na/C_2H_5OH or ethereal solution of $LiAlH_4$ and is converted into ethylamine.
- **Dehydration :** When heated with P_2O_5 or $SOCl_2$ or $POCl_3$ or PCl_5, it loses a molecule of water and forms alkane nitrile.
- **Action of nitrous acid HNO_2 ($NaNO_2$ + HCl) :** Formation of carboxylic acid with the evolution of N_2.
- **Action with alcohol :** Formation of ester.
- **Action with Grignard reagent followed by hydrolysis :** Formation of ketone.
- **Hofmann bromamide reaction or Hofmann degradation :** Amides when heated with Br_2 and KOH solution, yield 1° amines containing one carbon atom less than the amide.
- A number of intermediates have been isolated : *N*-bromamides, *R*CONHBr; salts of these bromamides, $[RCONBr^-]K^+$ and *R*NCO.

Ethyl acetate (Ethyl Ethanoate), $CH_3COOC_2H_5$ or Organic Ester

Methods of preparation

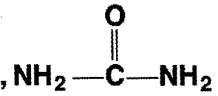
- By the action of acetyl chloride or acetic anhydride on ethyl alcohol.
- By the action of alkyl halides on silver salts of carboxylic acids.
- **Tischenko reaction :** Condensation between two moles of aldehyde in presence of aluminium ethoxide forms ethyl acetate.

- By heating a mixture of absolute alcohol and glacial acetic acid in presence of few drops of conc. H_2SO_4 (catalyst) or HCl gas.
- By the action of carbon monoxide on ether in presence of BF_3 at 150°C.
- By the action of diazomethane on carboxylic acids. Methyl esters are formed.
- **Properties :** The b.pt. of methyl and ethyl esters are lower than those of corresponding acid because of the fact that esters are not associated through intermolecular H-bonding.
- **Hydrolysis :** Ethyl acetate undergoes slow hydrolysis with excess of boiling water but in presence of acids or alkalies, the hydrolysis is fast. The alkaline hydrolysis is termed as **saponification.**
- **Reaction with ammonia :** Formation of an amide.
- **Reaction with 1° amine and 2° amine :** Formation of *N*-alkyl amide and *N,N′*-dialkyl amide.
- **Reaction with PCl_5 or $SOCl_2$:** Formation of acetyl chloride.
- **Reduction :** With Na/C_2H_5OH, ethyl acetate is reduced to ethyl alcohol **(Bouveault Blanc reduction).** $LiAlH_4$ in ether, $LiBH_4$ in THF, B_2H_6 in THF, etc., also reduce esters to alcohols. Copper-chromite at 250°C may also be used as catalyst (Adkin's method).
- **Reaction with Grignard reagent :** Formic acid esters give 2° alcohols while other esters give acetone and then finally 3° alcohols.
- **Reaction with hydroxylamine :** Formation of hydroxamic acid.
- **Reaction with hydrazine :** Formation of acid hydrazide.
- **Halogenation :** On treatment with Cl_2 or Br_2 in presence of red P yields α-halogenated ester.
- **Claisen condensation :** Two molecules of esters containing α-H atoms when heated with C_2H_5ONa (or $NaNH_2$) undergo Claisen condensation to give β-keto esters with the elimination of one molecule of alcohol.
- **Alcoholysis :** Splitting of ester by alcohol is called alcoholysis. When an ester is refluxed with excess of alcohol (other than present in ester) in presence of HCl gas or *R*ONa (catalyst), the alkyl part (alcoholic part) of the ester molecule is replaced by other alkyl group (usually a lower one). The process is also known as ***trans* esterification.**
- **Acidolysis :** When an ester is heated with other acid, it is the acid residue present in ester is replaced by another acid residue.
- **Action of halogen acids (H*X*) :** On heating ester with HI, it gives acid and *R*I.
- **Relative reactivity of acyl compounds :** Reactivity towards nucleophilic substitution lies in the following sequence :



$$RCOCl > (RCO)_2O > R—\overset{\overset{O}{\|}}{C}—OR' > RCONH_2$$

Urea or Carbamide, $NH_2—\overset{\overset{O}{\|}}{C}—NH_2$



- Urea may be considered as diamide of weak dibasic carbonic acid from which both the —OH groups have been replaced by $—NH_2$ groups. So, the diamide of carbonic acid or monoamide of carbamic acid is known as **urea** or **carbamide.**
- Urea was the first organic compound synthesized in the laboratory from inorganic compound, ammonium cyanate (obtained on heating a mixture of ammonium sulphate and potassium cyanate) by Wohler.
- **Isolation from urine :** The addition of conc. HNO_3 to urine gives crystals of urea nitrate. These crystals are separated and dissolved in water and treated with $BaCO_3$. Urea is then extracted with alcohol and the extract on evaporation yields crystals of urea.
- **Laboratory preparation :** When KCNO is heated with $(NH_4)_2SO_4$, an ammonium isocyanate is formed which undergoes molecular rearrangement to give urea.
- **From phosgene (carbonyl chloride) or ethyl carbonate :** By heating with NH_3.
- **Manufacture (Industrial method) :** By partial hydrolysis of calcium cyanamide. The calcium cyanamide is obtained by passing N_2 over calcium carbide at high temperature.
- **From NH_3 and CO_2 :** A mixture of liquid NH_3 and liquid CO_2 on heating gives ammonium carbamate (NH_2COONH_4). This decomposes at 140–150°C to form urea.

Properties

- **Basic nature :** The aqueous solution of urea is neutral in nature but it behaves as a weak mono acid base. It forms salts with strong acid like conc. HNO_3 and oxalic acid ($H_2C_2O_4$).
- The basic character of urea can be explained by the fact that its cation gets stabilized by **resonance.**
- **Hydrolysis :** Urea on hydrolysis gives CO_2 and HOH. The reaction is catalysed by acid, base and enzyme.
- **Action of heat :** When heated, urea melts at 132°C. On further heating, it loses NH_3 at 150°C and leaves a solid white residue known as **biuret.** An alkaline solution of biuret gives a violet colour on reaction with dilute copper sulphate solution. It is known as **biuret test.** It is given by all compounds having —NHCO— group.
- When urea is heated rapidly above 170°C, it loses a molecule of NH_3 and forms cyanic acid which trimerises to form cyanuric acid.
- **Reaction with nitrous acid :** Urea is decomposed by HNO_2 ($NaNO_2$ + HCl) into N_2, CO_2 and H_2O.
- **Reaction with alkaline hypohalides (Oxidation) :** Urea is oxidised to N_2 when heated with excess of alkaline hypochlorite or hypobromite (NaOCl or NaOBr).
- **Acetylation with acetyl chloride or acetic anhydride :** Urea reacts with acetylating agents to form N-acetyl ureas which are known as ureides.

☐ **Reaction with hydrazine :** Urea reacts with NH_2NH_2 at 100°C to form semicarbazide ($H_2NCONHNH_2$) with the evolution of NH_3 molecule.

☐ **Reaction with ethanol :** On heating with alcohol, urea gives ethyl carbamate (urethane).

☐ **Reaction with chlorine water :** Urea reacts with aqueous solution of chlorine to form *N,N′*-dichlorourea.

☐ **Reaction with thionyl chloride :** On dehydration with $SOCl_2$, urea gives cyanamide ($H_2N—C{\equiv}N$).

☐ **Reaction with fuming H_2SO_4 or oleum ($H_2SO_4 + SO_3 = H_2S_2O_7$) :** When urea is heated with fuming H_2SO_4 (oleum), the product is sulphamic acid.

☐ **Reaction with oxalic acid and its derivatives :** Urea, in presence of $POCl_3$ or C_2H_5ONa, reacts with oxalic acid, oxalyl chloride, ethyl oxalate, etc., to give five membered ring compounds. These are termed as cyclic ureides.

☐ **Reaction with diethyl malonate :** Formation of barbituric acid (malonyl urea).

☐ **Reaction with acetoacetic ester :** Formation of 4-methyl uracil.

☐ **Reaction with formaldehyde :** Urea and formaldehyde react to form urea-formaldehyde resin which is used in the form of plastic.

Uses : Urea is used:

(i) mainly as a nitrogen fertilizer (containing 46.6% nitrogen).
(ii) in the manufacture of formaldehyde-urea, plastic and semicarbazide.
(iii) for making barbiturates and other drugs.

QUESTIONS

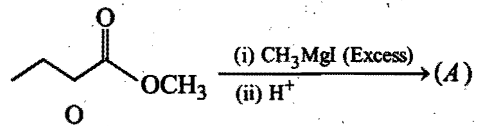
❖ Very Short Answer Type

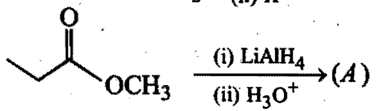
1. Fill in the blanks:
   - (a) Acetic anhydride is an acid derivative of ....
   - (b) Urea is an acid derivative of...........
   - (c) Acetyl chloride is...........reactive than acetamide.
   - (d) Urea nitrate is...........in water.
   - (e) Acetamide on heating with P_2O_5 forms...........
   - (f) Oils and fats are...........of higher fatty acids.
   - (g) Esters between long chain monohydric alcohols and long chain fatty acids are...........
   - (h) Acetyl chloride on heating with anhydrous sodium acetate forms...........
   - (i) Acid chlorides undergo nucleophilic.........reactions.
   - (j) The conversion of an amide into primary amine with the help of bromine and caustic potash is named as ....reaction.
   - (k) The isomer of ammonium cyanate is...........
   - (l) Biuret is formed when...........is heated. The biuret gives...........colouration when treated with NaOH and copper sulphate solution.
   - (m) The degree of unsaturation of a fat or oil is measured by its...........
   - (n) Vegetable ghee is manufactured by the...........of oils in presence of ....as a catalyst.
   - (o) Aspirin is formed by the action of acetyl chloride with ....
   - (p) Acetyl chloride is used in the laboratory in the determination of ....and...........groups in organic compounds.
   - (q) The final product in the following sequence is:

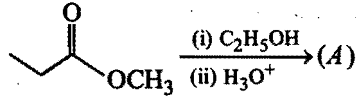
     $CH_3COCl + KCN \longrightarrow ...... \xrightarrow{H_2O} ......$
   - (r) The reaction between ketene and glacial acetic acid produces...........
   - (s) Acetic anhydride is...........reactive than acetyl chloride.
   - (t) Acetic anhydride undergoes reduction with $LiAlH_4$ to form...........
   - (u) Acetamide behaves as...........compound because it shows feebly acidic as well as feebly basic nature.
   - (v) Acyl halides and acid anhydrides are very good ....agents.
   - (w) Amides on reduction with $LiAlH_4$ yield...........
   - (x) The hybridization state of carbon atom changes from .... to .... in the conversion of a group $—CONH_2$ to $—CN$.
   - (y) Urea is also called as...........
   - (z) The reaction between an acyl halide and an alcohol gives ....
2. State whether the following statements are **True** or **False:**
   - (a) Hydrolysis of an ester in presence of a dilute acid is known as saponification.
   - (b) Oils and fats are the glycerides of higher fatty acids.
   - (c) Oils have higher percentage of saturated acids than fats.
   - (d) Soaps are the salts of higher fatty acids.
   - (e) Detergents can be used even in hard water.
   - (f) Potassium soaps are hard soaps.
   - (g) Acetamide forms acetic acid when treated with nitrous acid.
   - (h) Urea can be identified by the biuret test.
   - (i) The reactivity of acetic anhydride is more than acetyl chloride.
   - (j) Acetamide on reduction with $LiAlH_4$ forms ethylamine.
   - (k) Rosenmund's reduction of acetyl chloride forms ethyl alcohol.
   - (l) Waxes are esters of higher monocarboxylic acids and higher mono-saturated alcohols.
   - (m) Acetamide is amphoteric in nature.
   - (n) Acetamide can be hydrolysed more readily than acetyl chloride.
   - (o) Ethanol on treatment with ethanoyl chloride forms ethyl ethanoate.
   - (p) One mole of acetic anhydride on boiling with NaOH forms two moles of acetic acid.
   - (q) Acetylation is best carried out in presence of sodium acetate or conc. H_2SO_4.
   - (r) Esters are not neutral towards litmus.
   - (s) Two molecules of ethyl acetate condense in presence of sodium ethoxide to form acetoacetic ester. This condensation is named Perkin condensation.
   - (t) The pink colour of alkaline phenolphthalein is discharged when it is warmed with ester.
   - (u) Urea forms barbituric acid when reacts with malonic ester.
   - (v) Lipids are constituents of plants and animals which are insoluble in water but soluble in organic solvents.
   - (w) Stearic acid is an unsaturated acid while oleic acid is saturated one.
   - (x) Drying oils possess high iodine values.
   - (y) A soap contains only hydrophilic part while a detergent consists only hydrophobic part in the molecule.
   - (z) Rancidification is a process in which oils and fats develop unpleasant smell on long storage.
3. Match the following:

(A) Fats	(1) Sodium alkyl sulphonates
(B) Soap	(2) Esterification
(C) Acetylating agent	(3) Saponification
(D) Detergents	(4) Candles
(E) Hydrolysis of an ester with alkali	(5) Sodium salt of a higher fatty acid
(F) Conversion of amide to amine	(6) Glycerides
(G) Acid + alcohol	(7) Acetic anhydride
(H) Petroleum wax	(8) Hofmann bromamide reaction

4. What happens when?
   (i) Acetamide is heated with bromine and caustic potash.
   (ii) Acetyl chloride reacts with water.
   (iii) Acetyl chloride is distilled with sodium acetate.
   (iv) Acetamide reacts with nitrous acid.
   (v) Acetamide reacts with phosphorus pentoxide.
   (vi) Oils and fats are heated with NaOH.
   (vii) Acetyl chloride reacts with ethyl alcohol.
   (viii) Acetic acid is treated with P_2O_5. **[CPMT 2003]**
   (ix) Urea is heated.
   (x) Conc. HNO_3 is added to concentrated urea solution.
   (xi) Urea is heated with nitrous acid.
   (xii) Urea is heated with sodium hydroxide solution.
   (xiii) Urea is heated with acetyl chloride.
   (xiv) The solution containing potassium cyanate and ammonium sulphate is evaporated to dryness.
   (xv) Ammonia and carbon dioxide mixture is heated under pressure.

5. Complete the following reactions:
   (i) $CH_3COOC_2H_5 + NH_3 \longrightarrow .... + ...$
   (ii) $CH_3COCl + C_2H_5OH \longrightarrow .... + ...$
   (iii) $CH_3CONH_2 + Br_2 + 4NaOH \longrightarrow ....$
   (iv) $(CH_3CO)_2O + C_2H_5OH \longrightarrow ....$
   (v) $CH_3COOC_2H_5 + PCl_5 \longrightarrow ...... + C_2H_5Cl + ...$
   (vi)


   (vii)


   (viii)


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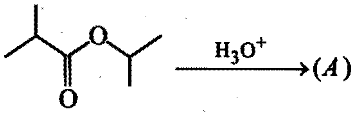
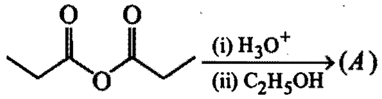
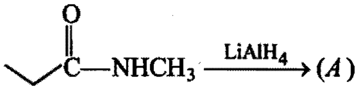
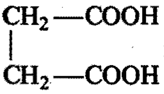
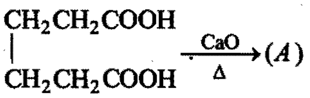
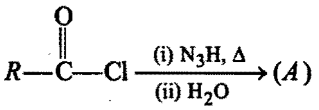
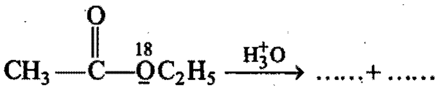
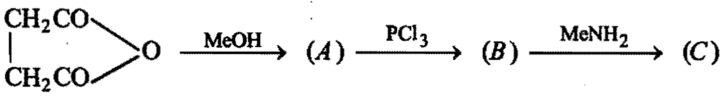


   (x)


   (xi)


   (xii) Succinic acid

$\begin{array}{l}CH_2-COOH\\ |\\ CH_2-COOH\end{array}$ is heated in presence of acetic anhydride to give (A). What is the structure of A?
   (xiii)

$\begin{array}{l}CH_2CH_2COOH\\ |\\ CH_2CH_2COOH\end{array} \xrightarrow[\Delta]{CaO} (A)$
   (xiv)

$R-\overset{\overset{\large O}{\|}}{C}-Cl \xrightarrow[\text{(ii) } H_2O]{\text{(i) } N_3H,\ \Delta} (A)$ **[Roorkee 2001]**
   (xv) $CH_3COOH + C_2H_5\overset{18}{O}H \overset{H^+}{\rightleftharpoons} ...... + ...$
   (xvi) $CH_3COOH + CH_2N_2 \xrightarrow{\text{Ether}} ...... + ...$
   (xvii) $HCOOCH_3 \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3CH_2MgBr} ......$
   (xviii)

$CH_3-\overset{\overset{\large O}{\|}}{C}-\overset{18}{O}C_2H_5 \xrightarrow{H_3^+O} ...... + ...$ **[IIT 2000]**

6. Identify (A), (B), (C), (D) and (E), ... in the following equations:
   (i) $HC\equiv CH \xrightarrow[HgSO_4]{H_2SO_4} (A) \xrightarrow{[O]} (B) \xrightarrow{SOCl_2} (C) \xrightarrow[AlCl_3]{\text{Benzene}} (D)$
   (ii) $(CH_3CO)_2O \xrightarrow{C_2H_5OH} (A) + CH_3COOH$
   (iii) $C_2H_5Cl \xrightarrow{KCN} (A) \xrightarrow[H^+]{H_2O} (B) \xrightarrow{NH_3} (C) \xrightarrow{\text{Heat}} (D) \xrightarrow{Br_2/NaOH} (E)$
   (iv) $C_2H_5Br \xrightarrow{KOH} (A) \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} (B) \xrightarrow{(C_2H_5O)_3Al} (C)$
   (v) $HCHO \xrightarrow{(A)} CH_3OH \xrightarrow{(B)} CH_3Cl \xrightarrow{(C)} CH_3CN \xrightarrow{(D)} CH_3COOH$
   (vi)


   (vii) $CH_3CH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} (A) \xrightarrow{PCl_5} (B) \xrightarrow{NH_3} (C) \xrightarrow{P_2O_5} (D)$

(viii) $CH_3CH_2COCl \xrightarrow{N_3H} (A) \xrightarrow{\text{Heat}} (B) \xrightarrow{H_2O} (C)$

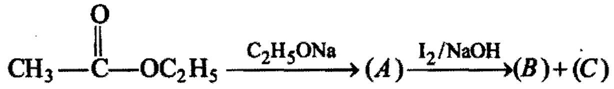
(ix) $CH_3CH_2COOCH_3 \xrightarrow{H_2NOH} (A) \xrightarrow{-H_2O} (B) \xrightarrow{H_2O} (C)$

(x) $(CH_3CO)_2O \xrightarrow{NH_3} (A) \xrightarrow{HNO_2} (B) \xrightarrow[\text{Heat}]{\text{Ca salt}} (C)$

(xi) $HC\equiv CH \xrightarrow[\text{Excess}]{CH_3COOH} (A) \xrightarrow{\text{Heat}} (B)+(C) \xrightarrow{HOH} CH_3COOH$

(xii)
$$\begin{tikzcd}
\text{Ester } (A) \arrow[r, "PCl_5"] & (B)+(C) \arrow[r, "\text{(Aq.) } KOH"] \arrow[d, "H_2/Pd"', "BaSO_4"] & (CH_3)_2CHCH_2OH \\
 & (D) \arrow[r, "LiAlH_4"] & (CH_3)_2CHCH_2OH
\end{tikzcd}$$

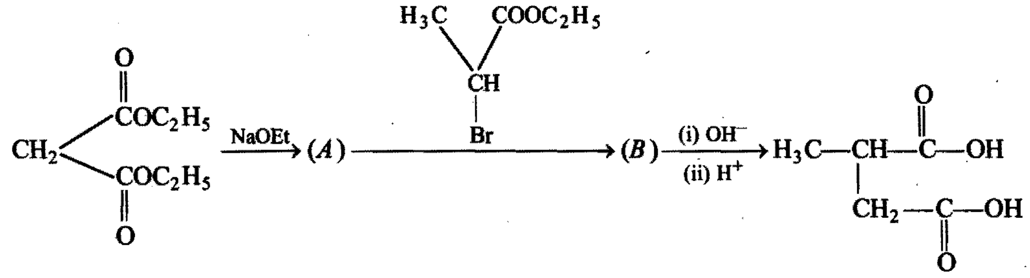
(xiii) $R\text{—}COOH \xrightarrow[\text{Heat}]{ND_3} (A) \xrightarrow[\text{Heat}]{Br_2,\ KOH} (B) \xrightarrow{NaNO_2\ +\ HCl} (C)$

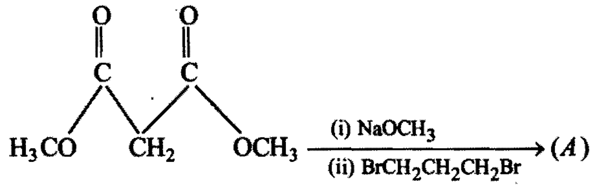
(xiv) 
$CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}OC_2H_5 \xrightarrow{C_2H_5ONa} (A) \xrightarrow{I_2/NaOH} (B)+(C)$

(xv) $[(CH_3)_2CHCO]_2O \xrightarrow{LiAlH_4} (A) \xrightarrow[H_2SO_4]{K_2Cr_2O_7} (B)$

(xvi) $\text{Ester } (A)\ C_3H_6O_2 \xrightarrow[\text{(2 mol)}]{CH_3MgBr} (B) \xrightarrow{H_3O^+} (CH_3)_2CHOH$

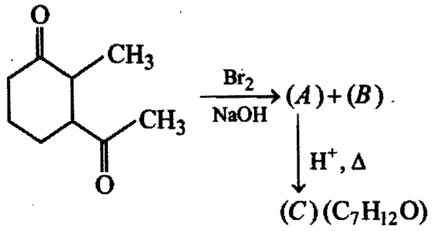
(xvii) $CaN_2 + HOH \xrightarrow{H_2SO_4} (A) \xrightarrow{CH_2(COOC_2H_5)_2} (B)$

(xviii) 

(xix) 

$(A) \xrightarrow{NaOCH_3} (B) \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) NaOH}} (C) \xrightarrow{-CO_2} (D)$ Cycloalkane Carboxylic acid

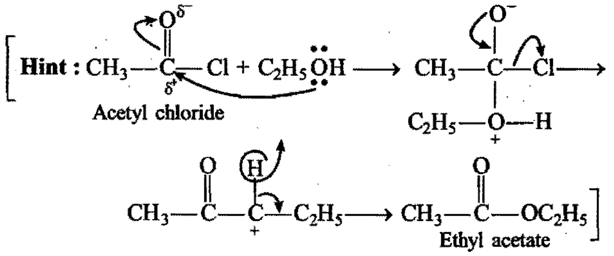
[Roorkee 2000]

(xx) 

[IIT 2000]

❖ Short Answer Type

7. What reagents are required for making the following changes in functional groups?
   (a) —CHO to —CH_2OH (b) —CN to —COOH
   (c) —COOH to H (d) —$CONH_2$ to —NH_2
8. How will you synthesize?
   (i) Acetyl chloride from methyl chloride.
   (ii) Acetamide from ethyl alcohol.
   (iii) Methylamine from acetyl chloride.
   (iv) Acetamide from acetone.
   (v) Acetic anhydride from acetic acid.
   (vi) Ethyl acetate from ethyl bromide.
   (vii) Ethyl acetate from acetic acid.
9. List three reagents for converting a carboxylic acid to its acyl chloride. Select the most convenient of the three reagents. Give a reason for the choice.
10. Give the industrial preparation of acetic anhydride. How many other anhydrides be prepared from acetic anhydride?
11. Prepare *n*-propyl acetate from:
    (i) acetic anhydride, (ii) acetyl chloride and (iii) acetic acid.
12. How will you obtain the following from acetyl chloride?
    (i) Acetamide, (ii) Ethyl acetate, (iii) Acetic anhydride,
    (iv) Acetic acid, (v) Ethyl alcohol, (vi) Acetaldehyde,
    (vii) Acetone.
13. Write the reactions of acetamide with the following compounds:
    (i) NaOH, (ii) P_2O_5, (iii) Br_2 + KOH, (iv) Na + C_2H_5OH,
    (v) HNO_2, (vi) $LiAlH_4$.
14. Give reactions of ethyl acetate with the following compounds:
    (i) NaOH, (ii) NH_3, (iii) PCl_5, (iv) Na + C_2H_5OH,
    (v) $LiAlH_4$.
15. Distinguish between the following pairs:
    (i) Urea and ammonium acetate
    (ii) Salt and ester
    (iii) Acetamide and urea
    (iv) Kerosene oil and vegetable oil
16. Write short notes on:
    (i) Esterification
    (ii) Saponification
    (iii) Hofmann bromamide reaction
    (iv) Soap
    (v) Oils and fats
    (vi) Waxes
    (vii) Detergents
    (viii) Types of soaps
    (ix) Hydrogenation of oils
    (x) Saponification value
    (xi) Iodine value
    (xii) Biuret test
17. Answer the following with reasoning:
    (i) Why all the acid derivatives (*R*CO*G*) [*G* may be —*X* (acid halides), —NH_2 (amides), O*R*′ (esters) or —OCO*R* (anhydrides)] are studied as a unit?
    (ii) Why the C—*G* bond in acid derivatives is expected to be shorter and stronger than in alkyl derivatives (*R*—*G*)?
    (iii) Why esters have lower boiling points than (a) ketones and (b) acids of comparable molecular masses?
    (iv) Amongst the following amides, $CH_3CONH_2, CH_3CONHCH_3$ and $CH_3CON(CH_3)_2$, why acetamide has the highest boiling point and $CH_3CON(CH_3)_2$ the minimum boiling point?
    (v) How the order of reactivity of the acid derivatives is related to the base strength of the leaving groups?
    (vi) Why cannot HCl convert *R*COOH to *R*COCl?
    (vii) Why does an acyl chloride undergo nucleophilic attack more rapidly than does an alkyl chloride?
    (viii) What is the essential difference between nucleophilic attack on the $>C{=}O$ of an aldehyde or ketone and on an acyl derivative?
    (ix) Why a ketone is not isolated from the reaction of an ester with one equivalent of *R*Mg*X*?
    (x) Amongst the following esters, $CH_3COOC_4H_9, CH_3COOC_3H_7, CH_3COOCH(CH_3)_2$ and CH_3COOCH_3; why CH_3COOCH_3 is most readily hydrolysed with NaOH?
    (xi) Why formic anhydride cannot be prepared by heating formic acid?
    (xii) Primary and secondary amides exist as dimers in the solid and pure liquid state.
    (xiii) Why urea is basic?
    (xiv) Why guanidine is a strong monoacid base?
    (xv) Why melting point of primary amide is higher than secondary and tertiary amides?
18. How does urea react with?
    (a) Nitrous acid, (b) Dilute NaOH, (c) Sodium hypobromite, (d) Malonic ester, (e) Hydrazine, (f) Acetyl chloride, (g) Succinic acid, (h) Acetoacetic ester.
19. (a) What are ureides? (b) What are barbiturates?
    (c) How urea is estimated?
20. (i) Give the mechanism for the reaction of acetyl chloride with ethyl alcohol.



    (ii) Give the mechanism for the Hofmann bromamide reaction.

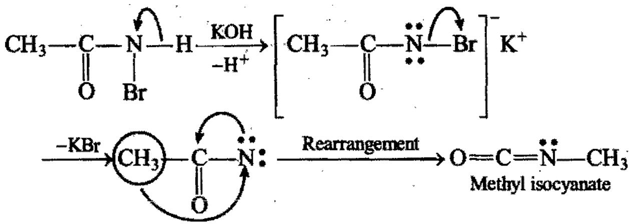
Hint : The reaction is:

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

Mechanism

$$CH_3CONH_2 + Br_2 \longrightarrow \underset{\text{Acetobromamide}}{CH_3CONHBr} + HBr \xrightarrow{KOH} KBr + H_2O$$

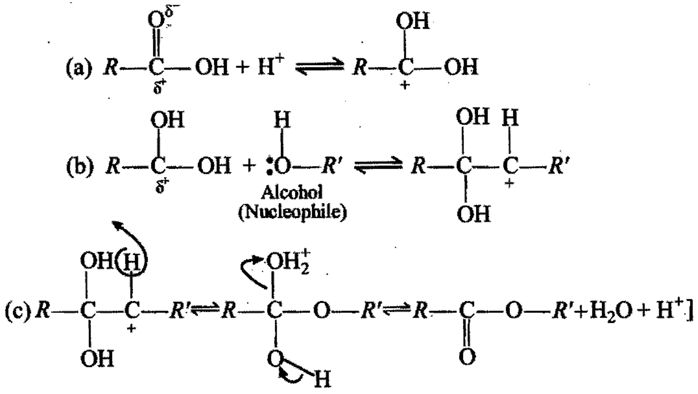
Acetobromamide is acidic in nature due to the presence of carbonyl group and bromine atom. It combines with alkali (KOH) and forms a salt which is unstable.



$$O{=}C{=}N{-}CH_3 + 2KOH \longrightarrow CH_3NH_2 + K_2CO_3]$$

(iii) Give the mechanism of esterification.

[**Hint :** The reaction is carried in presence of a strong acid like H_2SO_4 or HCl.



(iv) Give the mechanism of basic hydrolysis of an ester.

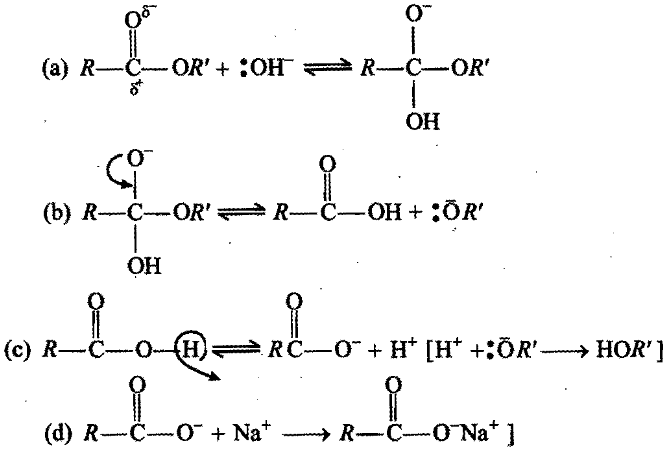
or

Give the mechanism of saponification.

[**Hint:** The overall reaction is:

$$RCOOR' + NaOH \longrightarrow RCOONa + R'OH$$

Mechanism

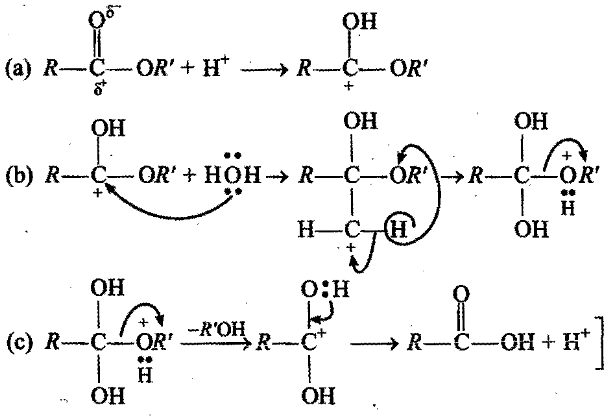


(v) Give the mechanism of acid hydrolysis of an ester.

[**Hint:** The overall reaction is:

$$\underset{\text{Ester}}{RCOOR'} + H_2O \xrightarrow{H^+} \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$$

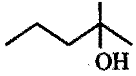
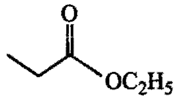
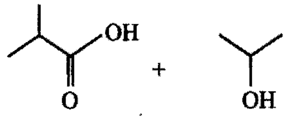
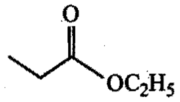
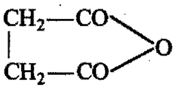
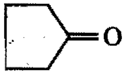
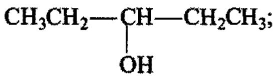
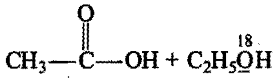
Mechanism

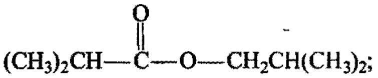
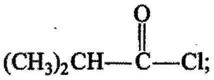
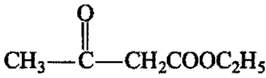
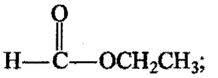
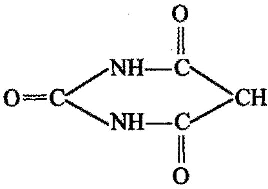
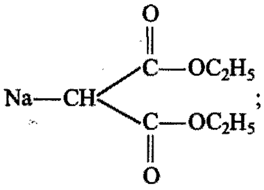
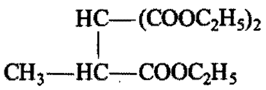
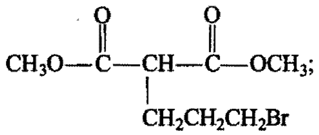
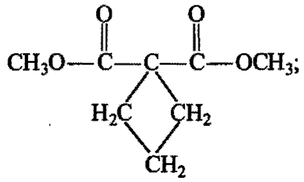
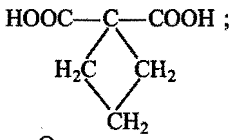
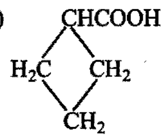
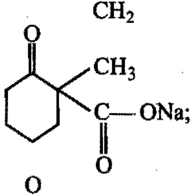
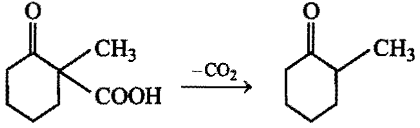


ANSWERS

1. (a) Acetic acid; (b) carbonic acid; (c) more; (d) insoluble; (e) ethane nitrile; (f) triglycerides; (g) waxes; (h) acetic anhydride; (i) substitution; (j) Hofmann bromamide; (k) urea; (l) urea, violet; (m) iodine value; (n) hydrogenation, nickel; (o) salicylic acid; (p) hydroxyl, amino; (q) $CH_3COCOOH$, pyruvic acid; (r) acetic anhydride; (s) less; (t) ethyl alcohol; (u) amphoteric; (v) acylating; (w) amines; (x) sp^2 to sp; (y) carbamide; (z) an ester.
2. (a) False—Hydrolysis of an ester in presence of alkali is known as saponification; (b) True; (c) False—Oils have low percentage of saturated acids than fats; (d) True; (e) True; (f) False—Potassium soaps are soft soaps; (g) True; (h) True; (i) False—The reactivity of acetic anhydride is less than acetyl chloride; (j) True; (k) False— Rosenmund's reduction of acetyl chloride forms acetaldehyde; (l) True; (m) True; (n) False—Acetamide is hydrolysed bit slowly than acetyl chloride; (o) True; (p) False—Forms one mole of acetic acid and one mole of sodium acetate; (q) True; (r) False—Esters are neutral toward litmus; (s) False—This condensation is called Claisen condensation; (t) True; (u) True; (v) True; (w) False— Stearic acid is saturated acid while oleic acid is unsaturated one; (x) True; (y) False—Both a soap and a detergent contain hydrophilic as well as hydrophobic parts in their molecules; (z) True.
3. (A—6); (B—5); (C—7); (D—1); (E—3); (F—8); (G—2); (H—4).
4. (i) $CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$
   - (ii) $CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$
   - (iii) $CH_3COCl + CH_3COONa \longrightarrow (CH_3CO)_2O + NaCl$
   - (iv) $CH_3CONH_2 + HNO_2 \longrightarrow CH_3COOH + N_2 + H_2O$
   - (v) $CH_3CONH_2 \xrightarrow[\text{Heat}]{P_2O_5} CH_3CN + H_2O$
   - (vi) Oils/Fats + NaOH ⟶ Soap + Glycerol
   - (vii) $CH_3COCl + CH_3CH_2OH \longrightarrow CH_3COOC_2H_5 + HCl$
   - (viii) $2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$
   - (ix) $2NH_2CONH_2 \xrightarrow{\text{Heat}} NH_2CONHCONH_2 + NH_3$
   - (x) $NH_2CONH_2 + HNO_3 \longrightarrow NH_2CONH_2 \cdot HNO_3$
   - (xi) $NH_2CONH_2 + 2HNO_2 \longrightarrow 2N_2 + 3H_2O + CO_2$
   - (xii) $NH_2CONH_2 + 2NaOH \longrightarrow 2NH_3 + Na_2CO_3$
   - (xiii) $NH_2CONH_2 + CH_3COCl \longrightarrow NH_2CONHCOCH_3 + HCl$
   - (xiv) $2KCNO + (NH_4)_2SO_4 \longrightarrow \underset{\displaystyle 2NH_2CONH_2}{\underset{\downarrow}{2NH_4CNO}} + K_2SO_4$

(xv) $2NH_3 + CO_2 \rightarrow NH_2COONH_4 \xrightarrow{\text{Heat}} NH_2CONH_2 + H_2O$

5. (i) $CH_3CONH_2 + C_2H_5OH$
   (ii) $CH_3COOC_2H_5 + HCl$
   (iii) $CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$
   (iv) $CH_3COOC_2H_5 + CH_3COOH$
   (v) $CH_3COCl, POCl_3$
   (vi) 
   (vii)  $+ CH_3OH$
   (viii) 
   (ix) 
   (x) 
   (xi) 
   (xii) 
   Succinic anhydride
   (xiii) 
   Cyclopentanone
   (xiv) RNH_2; (xv) $CH_3CO\overset{18}{O}C_2H_5 + H_2O$;
   (xvi) $CH_3COOCH_3 + N_2$; (xvii)  $CH_3CH_2—\underset{OH}{CH}—CH_2CH_3$;
   (xviii)  $CH_3—\overset{O}{\overset{\|}{C}}—OH + C_2H_5\overset{18}{O}H$

6. (i) (*A*) CH_3CHO; (*B*) CH_3COOH; (*C*) CH_3COCl; (*D*) $C_6H_5COCH_3$
   (ii) (*A*) $CH_3COOC_2H_5$
   (iii) (*A*) C_2H_5CN; (*B*) C_2H_5COOH; (*C*) $C_2H_5COONH_4$; (*D*) $C_2H_5CONH_2$; (*E*) $C_2H_5NH_2$
   (iv) (*A*) C_2H_5OH; (*B*) CH_3CHO; (*C*) $CH_3COOC_2H_5$
   (v) (*A*) $LiAlH_4$; (*B*) PCl_5; (*C*) KCN; (*D*) Dil. HCl
   (vi) (*A*) $HOOCCH_2CH_2COOMe$; (*B*) $ClCOCH_2CH_2COOMe$; (*C*) $MeNHCOCH_2CH_2COOMe$
   (vii) (*A*) CH_3COOH; (*B*) CH_3COCl; (*C*) CH_3CONH_2; (*D*) CH_3CN
   (viii) (*A*) $CH_3CH_2CON_3$; (*B*) CH_3CH_2NCO; (*C*) $CH_3CH_2NH_2$
   (ix) (*A*) $CH_3CH_2CONHOH$; (*B*) CH_3CH_2NCO; (*C*) $CH_3CH_2NH_2$
   (x) (*A*) CH_3CONH_2; (*B*) CH_3COOH; (*C*) CH_3COCH_3
   (xi) (*A*) $CH_3CH(OOCCH_3)_2$; (*B*) CH_3CHO; (*C*) $(CH_3CO)_2O$
   (xii) (*A*)  $(CH_3)_2CH—\overset{O}{\overset{\|}{C}}—O—CH_2CH(CH_3)_2$;
   (*B*)  $(CH_3)_2CH—\overset{O}{\overset{\|}{C}}—Cl$; (*C*) $(CH_3)_2CHCH_2Cl$;
   (*D*) $(CH_3)_2CHCHO$
   (xiii) (*A*) $RCOND_2$; (*B*) RNH_2; (*C*) $R—OH$
   (xiv) (*A*)  $CH_3—\overset{O}{\overset{\|}{C}}—CH_2COOC_2H_5$;
   (*B*) $CH_2(COONa)_2$; (*C*) CHI_3
   (xv) (*A*) $(CH_3)_2CH—CH_2OH$; (*B*) $(CH_3)_2CH—COOH$
   (xvi) (*A*)  $H—\overset{O}{\overset{\|}{C}}—OCH_2CH_3$; (*B*) $(CH_3)_2CH—OMgBr$
   (xvii) (*A*) NH_2CONH_2; (*B*) 
   (xviii) (*A*)  ; (*B*) 
   (xix) (*A*) 
   (*B*) 
   (*C*)  ; (*D*) 
   (xx)
   (*A*)  (*B*) $CHBr_3$;
   (*C*) 

7. (a) $LiAlH_4$, (b) Dil. HCl, (c) Soda lime, (d) Br_2 and KOH

8. (i) $CH_3Cl \xrightarrow{Mg} CH_3MgCl \xrightarrow[H_2O/H^+]{CO_2} CH_3COOH \xrightarrow{SOCl_2} CH_3COCl$
   (ii) $C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow{SOCl_2}$
   $CH_3COCl \xrightarrow{NH_3} CH_3CONH_2$

(iii) $CH_3COCl \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$

(iv) $CH_3COCH_3 \xrightarrow{I_2/NaOH} CH_3COONa \xrightarrow{H_2SO_4}$

$$CH_3COOH \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2$$

(v)
$$\begin{tikzcd}
CH_3COOH \arrow[r, "SOCl_2"] \arrow[rdd, "NaOH"'] & CH_3COCl \arrow[rd, "Heat"] & \\
 & & (CH_3CO)_2O + NaCl \\
 & CH_3COONa \arrow[ru] &
\end{tikzcd}$$

(vi) $CH_3CH_2Br \xrightarrow{\text{Aq. KOH}} CH_3CH_2OH \xrightarrow{K_2Cr_2O_7/H^+}$

$$CH_3COOH \xrightarrow[H^+]{CH_3CH_2OH} CH_3COOC_2H_5$$

(vii)
$$\begin{tikzcd}
CH_3COOH \arrow[r, "LiAlH_4"] & CH_3CH_2OH \arrow[rd, "CH_3COOH/H^+"] & \\
 & & CH_3COOC_2H_5
\end{tikzcd}$$

9. PCl_3, $SOCl_2$ and PCl_5, $SOCl_2$ is the best reagent because the products of the reaction besides acyl chloride are SO_2 and HCl which are gases and easily separated.

10. $CH_3COOH + \underset{\text{Ketene}}{H_2C{=}C{=}O} \longrightarrow (CH_3CO)_2O$

[Ketene is prepared by pyrolysis of acetone,

$$CH_3COCH_3 \xrightarrow{700°C} CH_4 + CH_2{=}C{=}O]$$

When the mixture of acetic anhydride and the carboxylic acid is distilled, anhydrides are formed.

$$2RCOOH + (CH_3CO)_2O \longrightarrow (RCO)_2O + 2CH_3COOH$$

11. (i) $(CH_3CO)_2O + CH_3CH_2CH_2OH \xrightarrow{\text{Base}}$

$$CH_3COOCH_2CH_2CH_3 + CH_3COOH$$

(ii) $CH_3COCl + CH_3CH_2CH_2OH \xrightarrow{\text{Base}}$

$$CH_3COOCH_2CH_2CH_3 + HCl$$

(iii) $CH_3COOH + CH_3CH_2CH_2OH \xrightarrow{H^+}$

$$CH_3COOCH_2CH_2CH_3 + H_2O$$

12.
$$\begin{tikzcd}
 & \underset{\text{Acetamide}}{CH_3CONH_2} & \\
 & \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} & \\
 & \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} & \\
\mathbf{CH_3COCl} \arrow[ruuu, "NH_3"] \arrow[ruu, "C_2H_5OH"] \arrow[ru, "CH_3COONa"] \arrow[r, "H_2O"] \arrow[rd, "LiAlH_4", "Ether"'] \arrow[rdd, "Pd\text{-}BaSO_4", "H_2"'] \arrow[rddd, "H_2O"] & \underset{\text{Acetic acid}}{CH_3COOH} & \\
 & \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} & \\
 & \underset{\text{Acetaldehyde}}{CH_3CHO} & \\
 & CH_3COOH \arrow[r, "Ca(OH)_2"] & (CH_3COO)_2Ca \arrow[d, "Heat"] \\
 & & \underset{\text{Acetone}}{CH_3COCH_3}
\end{tikzcd}$$

13. See the properties of acetamide.

14. See the properties of ethyl acetate.

15. (i) When urea is heated gently, it forms biuret which gives violet colouration with NaOH and a drop of copper sulphate. Ammonium acetate does not give this test.

(ii) See section 13.6

(iii) See section 13.7

(iv) See section 13.8

17. (i) Most of the acid derivatives are interconvertible and all can be prepared from the corresponding carboxylic acid.

(ii) In $RCOG$, C uses sp^2-hybrid orbital to form bond with G while in R—G, C uses sp^3-hybrid orbital to form bond with G. The increase in s-character makes the bond shorter and stronger. The presence of resonance in acid derivatives makes the molecule more stable.

(iii) The positive charge on the carbon of the carbonyl group in esters is comparatively less than ketones. Hence, weaker dipole-dipole attraction is present in esters than in ketones resulting in lower boiling points in esters.

Acids have strong intermolecular hydrogen bonds which are not present in esters. Hence, boiling points of esters are less than acid.

(iv) Dimethyl acetamide has no hydrogen on nitrogen atom for intermolecular hydrogen bonding, thus it has lowest boiling point. Acetamide has two hydrogen atoms and extensively hydrogen bonded compound resulting in the highest boiling point while methyl acetamide has only one hydrogen atom and less hydrogen bonding. Its boiling point is between the boiling points of acetamide and dimethyl acetamide.

(v) The order of reactivity decreases as the base strength of the leaving group increases, *i.e.*, $Cl^- < RCOO^- < RO^- < H_2N^-$.

(vi) If the reaction were to occur, the acyl chloride and water products would react rapidly with each other to form starting materials.

(vii) Nucleophilic attack on the tetrahedral carbon of RX involves a hindered transition state and to permit the attachment of the nucleophile, a sigma bond must be partly broken. In CH_3COCl, the nucleophilic attack on $>C{=}O$ group involves an unhindered transition state leading to a tetrahedral intermediate. Thus, nucleophilic attack on acid chloride occurs readily.

(viii) In each case, the addition step leads to a tetrahedral intermediate. The intermediate from the carbonyl compound would have to eliminate the very strong bases $H\colon^-$ or $R\colon^-$ from $RCHO$ and $RCOR'$ respectively to restore the $C{=}O$. The intermediate from the acyl derivative easily eliminates $G\colon^-$.

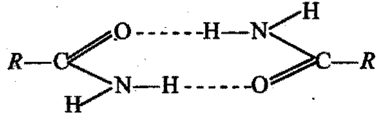
(ix) A ketone is formed initially. As it is more reactive than ester to $RMgX$, tertiary alcohol is formed.

(x) The size of the R determines the ease of hydrolysis. The larger the size of R group, the greater will be the steric effect. Hence, the CH_3COOCH_3 would be hydrolysed most readily.

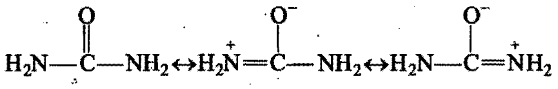
(xi) Formic acid on heating undergo intramolecular dehydration rather than intermolecularly.

$$HCOOH \longrightarrow H_2O + CO$$

(xii) Dimer formation is by H-bonding.

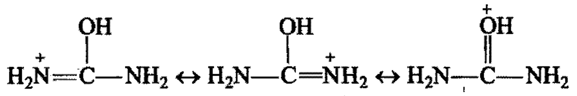


(xiii) Urea is a hybrid of the following resonance forms.



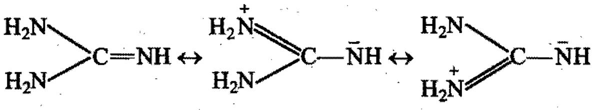
$$H_2N-\overset{\overset{O}{\|}}{C}-NH_2 \leftrightarrow H_2\overset{+}{N}=\overset{\overset{O^-}{|}}{C}-NH_2 \leftrightarrow H_2N-\overset{\overset{O^-}{|}}{C}=\overset{+}{N}H_2$$

Urea is basic because in resonance hybrid the oxygen atom carries a negative charge and can combine with a proton to form a new —OH bond. The positive ion thus formed is also stabilized by resonance.



$$H_2\overset{+}{N}=\overset{\overset{OH}{|}}{C}-NH_2 \leftrightarrow H_2N-\overset{\overset{OH}{|}}{C}=\overset{+}{N}H_2 \leftrightarrow H_2N-\overset{\overset{\overset{+}{O}H}{\|}}{C}-NH_2$$

(xiv) It can be explained by resonance stabilization of guanidinium ion.



(xv) The melting point in primary amides is highest due to the presence of hydrogen bonding. Therefore, melting point decreases in the order:

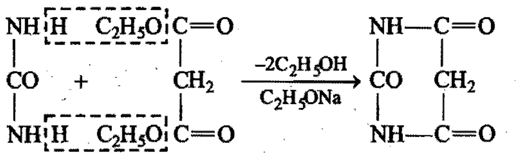
primary amide > secondary amide > tertiary amide > quaternary amide

18. (a) $(NH_2)_2CO + 2HNO_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$

(b) $(NH_2)_2CO + 2NaOH \xrightarrow{Heat} 2NH_3 + Na_2CO_3$

(c) $(NH_2)_2CO + 3NaOBr + 2NaOH \longrightarrow 3NaBr + Na_2CO_3 + N_2 + 3H_2O$

(d)



Barbituric acid

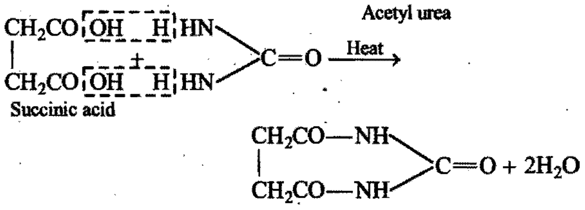
(e) $NH_2CONH_2 + H_2NNH_2 \xrightarrow{Heat} NH_2CONHNH_2 + NH_3$

Semicarbazide

(f) $NH_2CONH_2 + ClOCCH_3 \longrightarrow CH_3CONHCONH_2 + HCl$

Acetyl urea

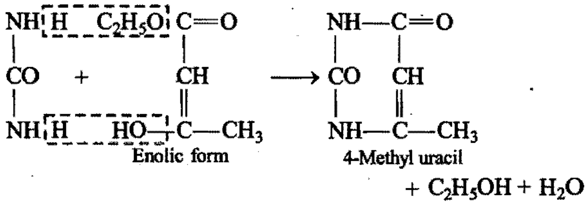
(g)



Succinic acid

Succinyl urea

(h)



Enolic form

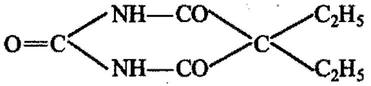
4-Methyl uracil

19. (a) Acyl derivatives of urea are called ureides. They are of two types:

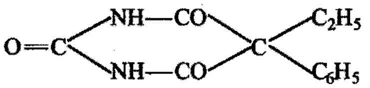
(i) **Simple ureides :** These are obtained by the reaction of acid halides and urea. Acetyl urea is the example of this class.

(ii) **Cyclic ureides :** These are obtained by the reaction of dicarboxylic acid or their derivatives and urea. Barbituric acid is the example of this class.

(b) Barbiturates are the derivatives of barbituric acid in which two hydrogen atoms of CH_2 group have been replaced by alkyl or aryl groups. Examples are:



Barbital



Phenobarbital

These are used as sedatives.

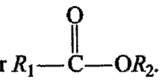
(c) Urea is estimated by hypobromite method. A known volume of urea solution is treated with sodium hypobromite solution containing NaOH. The evolved carbon dioxide is absorbed by NaOH and the volume of nitrogen evolved measured in the nitrometer. From the volume of nitrogen, the amount of urea in the sample can be determined.

PROBLEMS BASED ON STRUCTURE AND PROPERTIES

1. Show a sequence of reactions by which the ester propyl propionate, $CH_3CH_2COOCH_2CH_2CH_3$ could be prepared from 1-chloropropane without the use of other organic reagents.

Hint : $\underset{\text{Propyl chloride}}{CH_3CH_2CH_2Cl} \xrightarrow{NaOH(aq.)} \underset{\text{Propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow[Na_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow{NH_3} \underset{\text{Amm. propionate}}{CH_3CH_2COONH_4} \xrightarrow{AgNO_3} \underset{\text{Silver propionate}}{CH_3CH_2COOAg} \xrightarrow{CH_3CH_2CH_2Cl} \underset{\text{Propyl propionate}}{CH_3CH_2COOC_3H_7}$

2. A liquid (*X*), having a molecular formula, $C_6H_{12}O_2$, is hydrolysed with water in presence of an acid to give a carboxylic acid (*Y*) and an alcohol (*Z*). Oxidation of (*Z*) with chromic acid gives (*Y*). What are the structures of (*X*), (*Y*) and (*Z*)?



[**Hint :** (X) is an ester $R_1-\overset{\overset{\displaystyle O}{\|}}{C}-OR_2$. The alcohol is primary as on oxidation it gives an acid.

$$R_1COOH + R_2OH \longrightarrow R_1COOR_2 \qquad R_1 + R_2 = C_5H_{12}$$

$$R_2OH \xrightarrow{[O]} R_1COOH \qquad R_2 = R_1 + CH_2$$

(X) is $C_2H_5COOC_3H_7$, (Y) is C_2H_5COOH $\qquad 2R_1 = C_4H_{10}$ or $R_1 = C_2H_5$

and (Z) is C_3H_7OH. $\qquad R_2 = C_3H_7$]

3. An organic compound (A) on treatment with acetic acid in the presence of sulphuric acid produces an ester (B). (A) on mild oxidation gives (C). (C) with 50% KOH followed by acidification with dil. HCl generates (A) and (D). (D) with PCl_5 followed by reaction with ammonia gives (E). (E) on dehydration produces HCN. Identify the compounds (A), (B), (C), (D) and (E).

[**Hint :** $\underset{(A)}{CH_3OH} \xrightarrow{CH_3COOH} \underset{(B)}{CH_3COOCH_3}$

$$\xrightarrow{\text{Oxid.}} \underset{(C)}{HCHO} \xrightarrow[\text{Followed by acidification}]{\text{50\% KOH}} \underset{(A)}{CH_3OH} + \underset{(D)}{HCOOH} \xrightarrow[\text{(ii) } NH_3,\text{ Heat}]{\text{(i) } PCl_5} \underset{(E)}{HCONH_2} \xrightarrow[\text{Heat}]{P_2O_5} HCN]$$

4. The molecular formula of an organic compound is $C_3H_6O_2$. This compound on boiling with aqueous acidic solution produces (A) and (B) compounds. (A) gives positive test with Fehling's solution as well as with Tollens' reagent. (B) on boiling with iodine and aqueous potassium hydroxide produces potassium formate and compound (C). (C) on heating with silver produces acetylene. Identify all compounds.

[**Hint :** $\underset{(HCOOC_2H_5)}{C_3H_6O_2} \xrightarrow{H_2O} \underset{(HCOOH)}{(A)} + \underset{(C_2H_5OH)}{(B)} \xrightarrow[KOH]{I_2} \underset{(CHI_3)}{(C)} \xrightarrow{Ag} HC{\equiv}CH$]

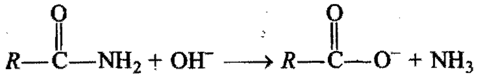
It reduces Fehling's solution and Tollen's reagent

5. An organic compound (A) on treatment with ethyl alcohol gives a carboxylic acid (B) and compound (C). Hydrolysis of (C) under acidic conditions gives (B) and (D). Oxidation of (D) with $KMnO_4$ also gives (B). (B) on heating with $Ca(OH)_2$ gives (E) (molecular formula C_3H_6O). (E) does not give Tollen's test and does not reduce Fehling's solution but forms a 2,4-dinitrophenylhydrazine. Identify (A), (B), (C), (D) and (E).

[**Hint :** (E) is acetone (CH_3COCH_3). The (B) is, therefore, acetic acid (CH_3COOH) and (D) ethyl alcohol (C_2H_5OH). Thus, (C) is ethyl acetate ($CH_3COOC_2H_5$). Since the compound (B) (acetic acid) and (C) (ethyl acetate) are obtained by treating (A) with ethyl alcohol; so the compound (A) is acetic anhydride ($(CH_3CO)_2O$).]

6. One mole of an organic amide (A) on alkaline hydrolysis gives one mole of NH_3 and one mole of a monobasic acid of equivalent mass 74. What is the molecular mass of (A)?

[**Hint:**



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + OH^- \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + NH_3$$

$R + 45 = 74$ or $R = 29$, *i.e.*, CH_3CH_2-,

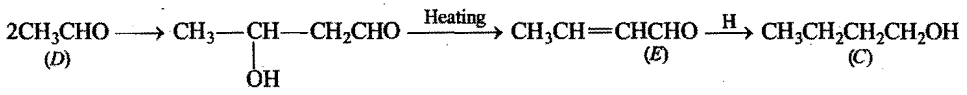
Monobasic acid = CH_3CH_2COOH, Mol. mass = $CH_3CH_2CONH_2$ = 73]

7. Compound (A) ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yielded two compounds (B) and (C). The compound (B) on oxidation gave (D) which on treatment with aqueous alkali and subsequent heating furnished (E). The latter on catalytic hydrogenation gave (C). The compound (D) was oxidized further to give (F) which was found to be monobasic acid (molecular mass = 60.0). Deduce the structures of (A), (B), (C), (D) and (E). **[BCECE 2007]**

[**Hint :** The compound (F) has molecular mass 60.

$$RCOOH = R + 45 = 60 \text{ or } R = 15, \textit{ i.e., } CH_3$$

Hence, the compound (F) is CH_3COOH. It is obtained by oxidation of (D). Thus, (D) is CH_3CHO. (D) is formed by oxidation of (B). Hence, (B) is CH_3CH_2OH. (D) undergoes aldol condensation which subsequently forms (E) on heating.



$$\underset{(D)}{2CH_3CHO} \longrightarrow CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2CHO \xrightarrow{\text{Heating}} \underset{(E)}{CH_3CH{=}CHCHO} \xrightarrow{H} \underset{(C)}{CH_3CH_2CH_2CH_2OH}$$

(A) is, thus an ester which forms two alcohols with $LiAlH_4$.

$$\underset{\substack{\text{or} \\ CH_3COOCH_2CH_2CH_2CH_3}}{CH_3CH_2CH_2COOCH_2CH_3} \xrightarrow{LiAlH_4} \underset{(C)}{CH_3CH_2CH_2CH_2OH} + \underset{(B)}{CH_3CH_2OH}]$$

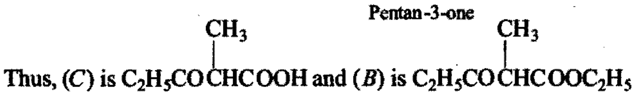
8. In the following reactions, identify the compounds (*A*), (*B*), (*C*) and (*D*).

$$PCl_5 + SO_2 \longrightarrow (A) + (B)$$
$$(A) + CH_3COOH \longrightarrow (C) + SO_2 + HCl$$
$$2(C) + (CH_3)_2Cd \longrightarrow 2(D) + CdCl_2$$

[**Hint :**
$$PCl_5 + SO_2 \longrightarrow \underset{(B)}{POCl_3} + \underset{(A)}{SOCl_2}$$
$$\underset{(A)}{SOCl_2} + CH_3COOH \longrightarrow \underset{(C)}{CH_3COCl} + SO_2 + HCl$$
$$\underset{(C)}{2CH_3COCl} + (CH_3)_2Cd \longrightarrow \underset{(D)}{2CH_3COCH_3} + CdCl_2\,]$$

9. Two moles of an ester (*A*) are condensed in the presence of sodium ethoxide to give a β-keto-ester (*B*) and ethanol. On heating in an acidic solution, (*B*) gives ethanol and β-keto acid (*C*). On decarboxylation, (*C*) gives 3-pentanone. Identify (*A*), (*B*) and (*C*) with proper reasoning. Name the reaction involved in the conversion of (*A*) to (*B*).

[**Hint :**
$$2(A) \xrightarrow{C_2H_5ONa} \underset{\beta\text{-keto-ester}}{(B)} + C_2H_5OH, \qquad \text{Claisen condensation}$$
$$(B) \xrightarrow[\text{Heat}]{H^+} (C) + C_2H_5OH$$
$$(C) \xrightarrow{\text{Decarboxylation}} \underset{\text{Pentan-3-one}}{C_2H_5COC_2H_5}$$


Thus, (*C*) is $C_2H_5CO\overset{\overset{\displaystyle CH_3}{|}}{C}HCOOH$ and (*B*) is $C_2H_5CO\overset{\overset{\displaystyle CH_3}{|}}{C}HCOOC_2H_5$

Hence, (*A*) should be $C_2H_5COOC_2H_5$ (ethyl propionate)]

10. An organic compound (*A*) $C_4H_7Cl_3$ yields (*B*) with KOH(aq) (*B*) on treating with NH_3 gives (*C*) which on heating gives (*D*). On heating (*D*) with P_2O_5, 2-methyl propane nitrile is formed. What are (*A*), (*B*), (*C*) and (*D*)?

[**Ans.** (*A*) $(CH_3)_2CHCCl_3$; (*B*) $(CH_3)_2CHCOOH$; (*C*) $(CH_3)_2CHCOONH_4$; (*D*) $(CH_3)_2CHCONH_2$]

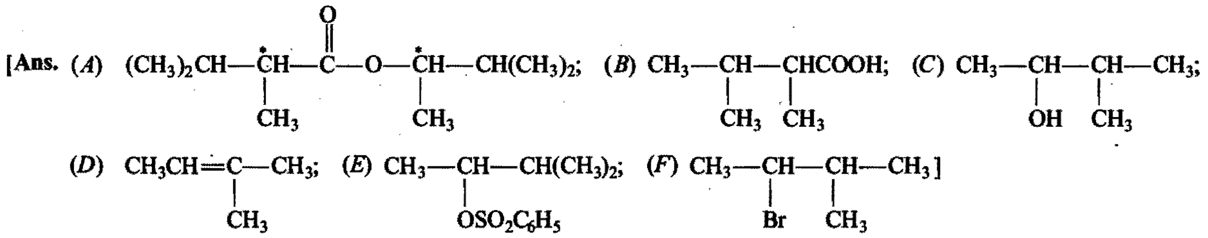
11. In the following reactions, identify the compounds (*A*), (*B*), (*C*) and *R*—MgBr.

$$(A)C_4H_8O_2\ (\text{Ester}) + 2RMgBr \xrightarrow{H_3O^+} (B)\ \text{Alcohol}$$
$$(A) \xrightarrow{H_3O^+} (C)\ \text{Acid} + (B)\ \text{Alcohol}$$

Acid (*C*) reduces Tollens' reagent and alcohol (*B*) gives haloform test.

[**Ans.** (*A*) $HCOOCH(CH_3)_2$; (*B*) $(CH_3)_2CHOH$; (*C*) HCOOH; *R*MgBr is CH_3MgBr]

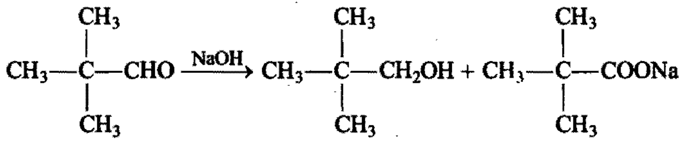
12. A pleasant smelling optically active ester (*A*) has M.W. = 186. It does not react with Br_2 in CCl_4. Hydrolysis of (*A*) gives two optically active compounds (*B*) soluble in NaOH and (*C*). Compound (*C*) gives a positive iodoform test and on warming with conc. H_2SO_4 gives (*D*) (Saytzeff-product) with no geometrical isomers. (*C*) on treatment with benzene sulphonyl chloride gives (*E*) which on treatment with NaBr gives optically active (*F*). When Ag^+ salt of (*B*) is treated with Br_2, racemic (*F*) is formed. Give the structures of (*A*) to (*F*).

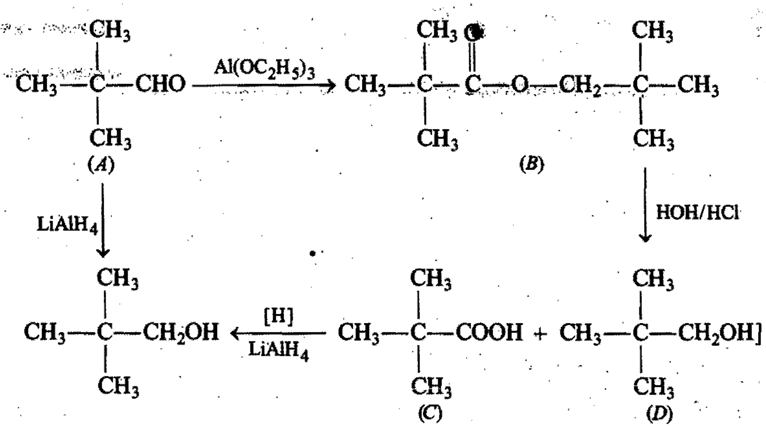

[**Ans.** (*A*) $(CH_3)_2CH-\underset{\underset{\displaystyle CH_3}{|}}{\overset{*}{C}H}-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{*}{C}H}-CH(CH_3)_2$; (*B*) $CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}COOH$; (*C*) $CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$;

(*D*) $CH_3CH=\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_3$; (*E*) $CH_3-\underset{\underset{\displaystyle OSO_2C_6H_5}{|}}{CH}-CH(CH_3)_2$; (*F*) $CH_3-\underset{\underset{\displaystyle Br}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$]

13. C_5H_{10} (*A*) can show Cannizzaro's reaction. (*A*) on treatment with $Al(OC_2H_5)_3$, forms $C_{10}H_{20}O_2$ (*B*) which on hydrolysis gives acid (*C*) and alcohol (*D*). Compounds (*A*), (*B*) and (*C*) each on reaction with $LiAlH_4$ is converted to alcohol (*D*). Identify (*A*), (*B*), (*C*) and (*D*). Give the reactions involved.

[**Hint :** Since, (*A*) gives Cannizzaro's reaction hence, it should not have any α-hydrogen.


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CHO \xrightarrow{NaOH} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2OH + CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-COONa$$



$$CH_3-C(CH_3)_2-CHO \xrightarrow{Al(OC_2H_5)_3} CH_3-C(CH_3)_2-CO-O-CH_2-C(CH_3)_2-CH_3$$

(A) (B)

$$(A) \xrightarrow{LiAlH_4} CH_3-C(CH_3)_2-CH_2OH$$

$$(B) \xrightarrow{HOH/HCl} CH_3-C(CH_3)_2-COOH + CH_3-C(CH_3)_2-CH_2OH]$$

(C) (D)

$$CH_3-C(CH_3)_2-CH_2OH \xleftarrow[LiAlH_4]{[H]} CH_3-C(CH_3)_2-COOH$$

14. An organic compound (*A*) reacts with ethanol to give (*B*) and (*C*). On acid hydrolysis, (*C*) yields (*B*) and (*D*). Oxidation of (*D*) gives (*B*). (*B*) is an acid and forms a salt with $Ca(OH)_2$ which on dry distillation gives (*E*), C_3H_6O. Give the structures of (*A*) to (*E*) with proper reasoning. **[Roorkee 2000]**

[**Ans.** $\underset{\substack{(A)\\ \text{Acetic anhydride}}}{(CH_3CO)_2O} + C_2H_5OH \longrightarrow \underset{\substack{(B)\\ \text{Acetic acid}}}{CH_3COOH} + \underset{\substack{(C)\\ \text{Ethyl acetate}}}{CH_3COOC_2H_5}$

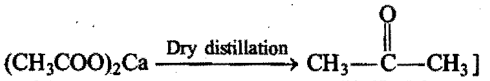
Acid hydrolysis of (*C*) gives (*B*) and (*D*)

$$\underset{(C)}{CH_3COOC_2H_5} + HOH \xrightarrow{H^+} \underset{(B)}{CH_3COOH} + \underset{(D)}{C_2H_5OH}$$

$$\underset{(D)}{C_2H_5OH} \xrightarrow{\text{Oxidation}} \underset{\substack{(B)\\ \text{Acetic acid}}}{CH_3COOH}$$

$$2CH_3COOH + Ca(OH)_2 \longrightarrow \underset{\text{Salt}}{(CH_3COO)_2Ca} + H_2O$$

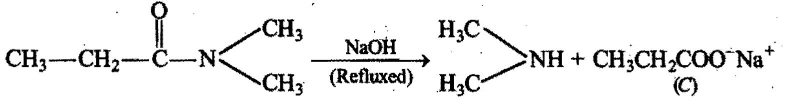
$$\underset{(B)}{}$$



$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\text{Dry distillation}} \underset{\substack{(E)\ (C_3H_6O)\\ \text{Acetone}}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}\,]$$

15. Compound (*A*), $C_5H_{11}NO$ is not soluble in cold dilute alkaline or acidic solutions. When (*A*) is refluxed in NaOH solution, a gas (*B*) is evolved and a salt (*C*) is formed. Acetyl chloride reacts with (*B*) to give (*D*) C_4H_9NO. (*B*) reacts with HNO_2 to give a yellow oil (*E*). Give the structures of (*A*) to (*E*) with reason. **[Roorkee 2000]**

[**Ans.** The given informations in the question clearly indicates that the compound (*A*) is substituted amide because it is not only insoluble in alkaline but also in acid solution. Reactions involved may be given as,



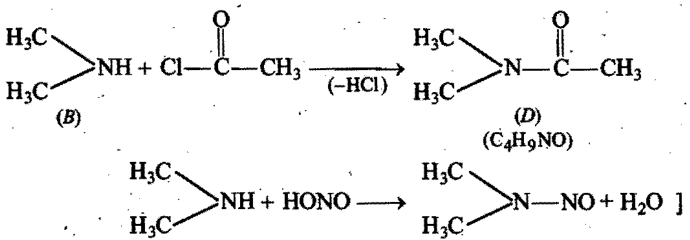
$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-N(CH_3)_2 \xrightarrow[\text{(Refluxed)}]{NaOH} (H_3C)_2NH + CH_3CH_2COO^-Na^+$$

(*A*) *N,N*-Dimethyl propanamide

(*B*) Dimethylamine

(*C*) Salt

Compound (*B*) gives yellow oily liquid with HNO_2 thus, it should be secondary amine.



$$\underset{(B)}{(H_3C)_2NH} + Cl-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[(-HCl)]{} \underset{\substack{(D)\\ (C_4H_9NO)}}{(H_3C)_2N-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

$$\underset{(B)}{(H_3C)_2NH} + HONO \longrightarrow \underset{(E)}{(H_3C)_2N-NO} + H_2O\ ]$$

N,N-Dimethyl-*N*-nitrosoamine (Yellow oily liquid)

OBJECTIVE QUESTIONS

SET I : This set contains questions with a single correct answer.

1. The formula $(RCO)_2O$ represents:

(a) esters ☐ (b) acid anhydrides ☐

(c) ketones ☐ (d) ethers ☐

2. The formula of ethyl ethanoate is:

(a) $CH_3COOC_2H_5$ ☐ (b) $C_2H_5COOC_2H_5$ ☐

(c) $C_2H_5COOCH_3$ ☐ (d) $C_2H_5OC_2H_5$ ☐

3. Acetic anhydride is prepared by:

(a) heating CH_3COCl with sodium acetate ☐

(b) combination of CH_3COOH and ketene ☐

(c) dehydration of acetic acid ☐

(d) all of the above ☐

4. Ammonium acetate on heating gives:

(a) N_2 gas ☐ (b) acetic acid ☐

(c) acetamide ☐ (d) NH_3 gas ☐

5. The reaction between acid and alcohol is known as: **[MHCET 2007]**

(a) esterification ☐ (b) saponification ☐

(c) hydrolysis ☐ (d) hydrogenation ☐

6. The reaction of acetamide with bromine and caustic potash gives: **[PET (Raj.) 2003; PMT (MP) 2005]**

(a) ethylamine ☐ (b) methylamine ☐

(c) acetic acid ☐ (d) bromoacetic acid ☐

7. When ammonium cyanate is heated, we get:

(a) nitrogen ☐ (b) carbondioxide ☐

(c) biuret ☐ (d) ammonium carbonate ☐

8. Hofmann bromamide or hypobromite reaction is given by:

(a) amines ☐ (b) esters ☐

(c) alcohols ☐ (d) amides ☐

9. Which will liberate ammonia when boiled with NaOH solution?

(a) Ethylamine ☐ (b) Acetamide ☐

(c) Aniline ☐ (d) All of these ☐

10. Alkaline hydrolysis of an ester is called:

(a) neutralisation ☐ (b) esterification ☐

(c) polymerisation ☐ (d) saponification ☐

11. The compound which is widely used as acetylating agent is:

(a) glacial acetic acid ☐

(b) ethyl acetate ☐

(c) acetic anhydride ☐

(d) anhydrous sodium acetate ☐

12. The reverse of esterification process is called:

(a) neutralisation ☐ (b) hydrolysis ☐

(c) acidolysis ☐ (d) alcoholysis ☐

13. In esterification, concentrated H_2SO_4 acts as:

(a) catalyst ☐

(b) dehydrating agent ☐

(c) hydrolysing agent ☐

(d) both as a catalyst and dehydrating agent ☐

14. When acetyl chloride reacts with any amine, the reaction is known as:

(a) saponification ☐ (b) esterification ☐

(c) acetylation ☐ (d) condensation ☐

15. Sodium acetate and acetyl chloride react to give:

(a) acetic anhydride ☐ (b) acetone ☐

(c) acetic acid ☐ (d) sodium formate ☐

16. Acetamide is treated separately with the following reagents which one of these would give methylamine?

(a) PCl_5 ☐ (b) $NaOH + Br_2$ ☐

(c) Soda lime ☐ (d) Hot conc. H_2SO_4 ☐

17. The end product in the following series of reactions is:

$$CH_3COOH \xrightarrow{NH_3} (A) \xrightarrow{\text{Heat}} (B) \xrightarrow{P_2O_5} (C)$$

(a) CH_4 ☐ (b) CH_3OH ☐

(c) acetonitrile ☐ (d) ammonium acetate ☐

18. Acetyl chloride is not obtained from acetic acid by the action of:

(a) $CHCl_3$ ☐ (b) $SOCl_2$ ☐

(c) PCl_3 ☐ (d) PCl_5 ☐

19. Acetamide is:

(a) neutral ☐ (b) acidic ☐

(c) basic ☐ (d) amphoteric ☐

20. The end product in the following sequence is:

$$\text{Acetamide} \xrightarrow{P_2O_5} (A) \xrightarrow{4H} (B)$$

(a) CH_3NH_2 ☐ (b) $C_2H_5NH_2$ ☐

(c) CH_3CN ☐ (d) CH_3COONH_4 ☐

21. Acetyl chloride is reduced to acetaldehyde by:

(a) $Na—C_2H_5OH$ ☐ (b) $LiAlH_4$ ☐

(c) $H_2/Pd—BaSO_4$ ☐ (d) H_2/Ni ☐

22. Acetoacetic ester is made by the process of:

(a) esterification ☐ (b) condensation ☐

(c) polymerisation ☐ (d) isomerisation ☐

23. Main product of the reaction, $CH_3CONH_2 + HNO_2 \longrightarrow$ is:

(a) CH_3NH_2 ☐ (b) $CH_3CH_2NH_2$ ☐

(c) CH_3COOH ☐ (d) CH_3OH ☐

24. The percentage of nitrogen in urea is:

(a) 46 ☐ (b) 23 ☐

(c) 48 ☐ (d) 52 ☐

25. The transformation of ammonium cyanate into urea on heating is:

(a) catalytic change ☐ (b) thermal decomposition ☐

(c) thermal dissociation ☐ (d) isomeric change ☐

26. The first organic compound synthesised in laboratory was:

(a) chloroform ☐ (b) glucose ☐

(c) ethanol ☐ (d) urea ☐

27. Urea is decomposed giving nitrogen and other substances when treated with:

(a) HNO_2 ☐ (b) HNO_3 ☐

(c) H_2SO_4(dil.) ☐ (d) NaOH ☐

28. A concentrated solution of urea gives a white precipitate with:

(a) HNO_3(conc.) ☐ (b) $AgNO_3$ ☐

(c) $BaCl_2$ ☐ (d) Na_2CO_3 ☐

29. Urea is converted into ammonia and carbondioxide by the enzyme:
(a) diastase ☐ (b) urease ☐
(c) lipase ☐ (d) amylase ☐

30. The addition of a drop of copper sulphate solution to an alkaline solution of biuret gives:
(a) red colour ☐ (b) violet colour ☐
(c) green colour ☐ (d) orange colour ☐

31. Urea is a:
(a) monobasic acid ☐ (b) dibasic acid ☐
(c) monoacid base ☐ (d) diacid base ☐

32. An aqueous solution of urea is:
(a) acidic ☐ (b) basic ☐
(c) neutral ☐ (d) amphoteric ☐

33. A detergent is a:
(a) cleansing agent ☐ (b) drug ☐
(c) catalyst ☐ (d) soap ☐

34. When a fat is heated with NaOH, the substances formed are:
(a) oil and Na_2CO_3 ☐
(b) soap and glycerol ☐
(c) soap and oil ☐
(d) soapless detergent and water ☐

35. A hydroxy acid on heating gives a 5-membered lactone. The acid is: **[DUMET 2010]**
(a) $CH_3CH_2CHOHCOOH$ ☐
(b) $CH_3CHOHCH_2COOH$ ☐
(c) $CH_2OHCH_2CH_2COOH$ ☐
(d) $CH_3CHOHCHOHCOOH$ ☐

36. During hydrogenation of oils, vegetable ghee is formed because:
(a) hydrogen is dissolved in the oil ☐
(b) hydrogen combines with O_2 of the oil ☐
(c) esters of unsaturated fatty acids are reduced to those of saturated fatty acids ☐
(d) hydrogen derives of the impurities from the oil ☐

37. Wax contains:
(a) ketone group ☐ (b) ester group ☐
(c) alcohol group ☐ (d) acid group ☐

38. In the hydrogenation of oil:
(a) Ni acts as a promoter ☐
(b) Cu acts as a catalyst ☐
(c) Tellurium acts as a promoter ☐
(d) Ni acts as a catalyst ☐

39. An alkali salt of palmitic acid is known as:
(a) alkaloid ☐ (b) an ester ☐
(c) a soap ☐ (d) an epoxide ☐

40. Oils and fats are mixtures of:
(a) higher alcohols ☐ (b) esters of higher acids ☐
(c) esters of lower acids ☐ (d) higher acids ☐

41. The process by which vegetable ghee is manufactured is known as:
(a) saponification ☐ (b) hydrogenation ☐
(c) esterification ☐ (d) hydrolysis ☐

42. Soft soaps are:
(a) sodium salt ☐ (b) calcium salt ☐
(c) magnesium salt ☐ (d) potassium salt ☐

43. Bees wax is:
(a) myricyl palmitate ☐
(b) myricyl stearate ☐
(c) myricyl oleate ☐
(d) mixture of higher hydrocarbons ☐

44. Candles contain a mixture of:
(a) bees wax and paraffin wax ☐
(b) bees wax and stearic acid ☐
(c) paraffin wax and stearic acid ☐
(d) higher fatty acids ☐

45. Fat is:
(a) a lipid ☐ (b) a protein ☐
(c) a carbohydrate ☐ (d) an amino acid ☐

46. Which one is not a glyceride?
(a) Fat ☐ (b) Oil ☐
(c) Phospholipid ☐ (d) Soap ☐

47. Paraffin wax is:
(a) an ester ☐
(b) a long chain acid ☐
(c) monohydric alcohol ☐
(d) a mixture of higher alkanes ☐

48. Which of the following is responsible for the rancidification of fats?
(a) Hydrogenation ☐
(b) Esterification and hydrolysis ☐
(c) Oxidation and hydrolysis ☐
(d) Dehydration ☐

49. Urea reacts with hydrazine to give:
(a) semicarbazide ☐ (b) phenylhydrazine ☐
(c) urethan ☐ (d) nitrogen ☐

50. Urea reacts with malonic ester to give:
(a) cyanuric acid ☐ (b) semicarbazide ☐
(c) urethan ☐ (d) barbituric acid ☐

51. ....is a measure of degree of unsaturation in oils and fats.
(a) Iodine value ☐ (b) Saponification value ☐
(c) Acid value ☐ (d) Acetyl value ☐

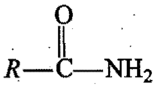
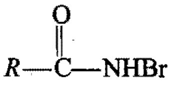
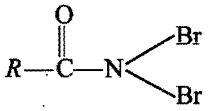
52. Which of the following enzymes hydrolysis triglycerides to fatty acids and glycerol?
(a) Lipase ☐ (b) Pepsin ☐
(c) Amylase ☐ (d) Maltase ☐

53. Detergent has a common group:
(a) $RONa$ ☐ (b) $RCOONa$ ☐
(c) $RC\equiv CNa$ ☐ (d) $RC_6H_4SO_3Na$ ☐

54. Acetyl chloride reacts with benzene in presence of anhydrous aluminium chloride to form acetophenone. This reaction is an example of:
(a) Perkin reaction ☐ (b) Aldol condensation ☐
(c) Claisen condensation ☐ (d) Friedel-Crafts reaction ☐

55. Urea can be distinguished from acetamide using:
(a) NaOH solution ☐ (b) Biuret test ☐
(c) Tollen's reagent ☐ (d) Fehling's solution ☐

56. The chemical formula of biuret is:
(a) $NH_2CONHNO_2$ ☐ (b) $NH_2CONHNH_2$ ☐
(c) $NH_2CONHCONH_2$ ☐ (d) $NH_2C(NH)_2 \cdot NH_2$ ☐

57. The reaction of  $R—\overset{O}{\overset{\|}{C}}—NH_2$ with a mixture of Br_2 and KOH gives $R—NH_2$ as a product. The intermediates involved in this reaction are: **[AFMC 2003]**
(a)  $R—\overset{O}{\overset{\|}{C}}—NHBr$ ☐ (b) $R—N=C=O$ ☐
(c) $R—NHBr$ ☐ (d)  ☐

58. The one which has least iodine value is? **[CET(Karnataka) 2009]**
(a) Ginger oil ☐ (b) Ghee ☐
(c) Groundnut oil ☐ (d) Sunflower oil ☐

59. Which of the following is not a mixture of hydrocarbons?
(a) Candle wax ☐ (b) Kerosene oil ☐
(c) Vegetable oil ☐ (d) Paraffin oil ☐

60. Benzalkonium chloride is a: **[AMU(Engg.) 2009]**
(a) cationic surfactant and antiseptic ☐
(b) anionic surfactant and soluble in most of organic solvents ☐
(c) cationic surfactant and insoluble in most of organic solvents ☐
(d) cationic surfactant and antimalarial ☐

61. The role of phosphate in detergent powder is due to: **[DPMT 2009]**
(a) control pH level of the detergent water mixture ☐
(b) remove Ca^{2+} and Mg^{2+} ions from the water that causes the hardness of water ☐
(c) provide whiteness to the fabrics ☐
(d) form solid detergent as, phosphate-less detergent are liquid in nature ☐

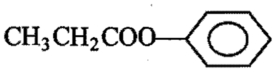
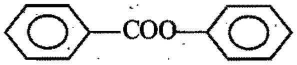
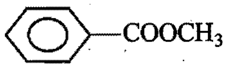
62. Urea on treatment with sodium hypobromite gives:
(a) sodium carbonate ☐ (b) nitrogen ☐
(c) CO_2 and H_2O ☐ (d) all of these ☐

63. Urea on hydrolysis gives: **[AIIMS 2010]**
(a) acetamide ☐ (b) NO_2 ☐
(c) carbonic acid ☐ (d) NH_4OH ☐

64. Urea is prepared in the laboratory by the action of NH_3 on:
(a) carbonyl chloride ☐ (b) ethyl carbonate ☐
(c) cyanamide ☐ (d) carbondioxide ☐

65. Why urea is known as carbamide?
(a) Because it is an amide of carbonic acid ☐
(b) Because it is a diamide of carbonic acid ☐
(c) Because it gives carbonic acid on hydrolysis ☐
(d) Because it resembles carbonic acid ☐

66. Mammals' fats are hydrolysed to release fatty acids by: **[AMU(Engg.) 2009]**
(a) amylase ☐ (b) lactase ☐
(c) lipase ☐ (d) insulin ☐

67. Claisen condensation is not given by: **[BCECE (Med.) 2008]**
(a)  ☐
(b)  ☐
(c)  ☐
(d)  ☐

68. Sodium acetamide smells like:
(a) garlic ☐ (b) rotten egg ☐
(c) pleasant ☐ (d) reminiscent of mice ☐

69. Among the following which one does not act as an intermediate in Hofmann rearrangement? **[AIIMS 2005]**
(a) $RNCO$ ☐ (b) RNC ☐
(c) $RCO\ddot{N}HBr$ ☐ (d) $RCO\ddot{N}$ ☐

70. Acetamide on reduction with Na/C_2H_5OH gives:
(a) ethylamine ☐ (b) methylamine ☐
(c) ethane ☐ (d) acetic acid ☐

71. Acid chlorides are prepared industrially by:
(a) $RCOONa + PCl_3$ ☐ (b) $RCOONa + POCl_3$ ☐
(c) $RCOONa + SO_2Cl_2$ ☐ (d) all of these ☐

72. When acetyl chloride reacts with ethyl magnesium iodide, it forms:
(a) ethyl methyl ketone ☐ (b) diethyl ketone ☐
(c) ethyl acetate ☐ (d) acetic anhydride ☐

73. Acetyl chloride reacts with ether in the presence of zinc chloride to form:
(a) $CH_3CO \cdot O \cdot COCH_3 + C_2H_5Cl$ ☐
(b) $CH_3COOC_2H_5 + CH_3Cl$ ☐
(c) $CH_3COOC_2H_5 + C_2H_5Cl$ ☐
(d) $CH_3COOH + C_2H_5Cl$ ☐

74. Acid hydrolysis of which of the following compounds yields two different organic compounds? **[AIIMS 2008]**
(a) CH_3COOH ☐ (b) $CH_3COOC_2H_5$ ☐
(c) $(CH_3CO)_2O$ ☐ (d) CH_3CONH_2 ☐

75. By the catalytic combination of ammonia and carbon monoxide under high pressure, it forms:
(a) CH_3CONH_2 ☐ (b) $CO_2 + NH_3$ ☐
(c) $HCONH_2$ ☐ (d) $CH_3COOH + NH_3$ ☐

76. Acetic anhydride is prepared industrially by:
(a) heating sodium acetate with thionyl chloride or sulphuryl chloride ☐
(b) heating acetylene into glacial acetic acid containing some mercuric sulphate ☐
(c) passing ketene through glacial acetic acid ☐
(d) all of the above ☐

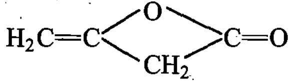
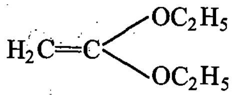
77. Acetic anhydride reacts with PCl_5 to give:
(a) $CH_3Cl + H_3PO_3$ ☐
(b) $CH_3COCl + POCl_3$ ☐
(c) $CH_3COOC_2H_5 + PCl_3$ ☐
(d) $CH_3COCH_3 + POCl_3$ ☐

78. Acetic anhydride reacts with dimethylamine to form:
(a) acetamide ☐
(b) *N*-methyl acetamide ☐
(c) *N,N*-dimethyl acetamide ☐
(d) dimethyl acetate ☐

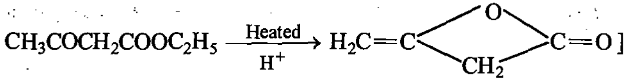
79. Acetic anhydride on reduction with $LiAlH_4$ in ether gives:
(a) acetaldehyde ☐ (b) ethyl alcohol ☐
(c) acetone ☐ (d) ethane ☐

80. Acetic anhydride is used:
(a) as an acetylating agent ☐
(b) for the detection and estimation of —OH and —NH_2 groups ☐
(c) in the manufacture of aspirin ☐
(d) all of the above ☐

81. Acetic anhydride on treatment with diethyl ether forms:
(a) $CH_3COCH_3 + C_2H_5OH$ ☐
(b) only ethyl acetate ☐
(c) $CH_3COOH + C_2H_5OH$ ☐
(d) only methyl acetate ☐

82. $CH_3CO_2C_2H_5$ on reaction with sodium ethoxide in ethanol gives (*A*), which on heating in the presence of acid gives (*B*). Compound (*B*) is: **[AIIMS 2005]**
(a) CH_3COCH_2COOH ☐
(b) CH_3COCH_3 ☐
(c)  ☐
(d)  $H_2C{=}C(OC_2H_5)_2$ ☐

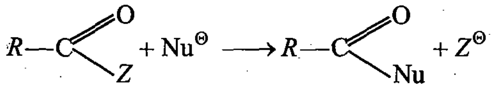
[**Hint :** $CH_3COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5ONa}$
$CH_3COCH_2COOC_2H_5$
Ethyl aceto acetate
(This reaction is an example of Claisen condensation.)



83. By treating acetic acid with an etheral solution of diazomethane, it forms:
(a) methyl acetate ☐ (b) ethyl acetate ☐
(c) acetamide ☐ (d) acetic anhydride ☐

84. $2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} CH_3COOCH_2CH_3$
This reaction is called:
(a) Cannizzaro's reaction ☐
(b) Aldol condensation ☐
(c) Claisen's reaction ☐
(d) Tischenko reaction ☐

85. Rate of the reaction,



is fastest when *Z* is: **[AIEEE 2005]**
(a) Cl ☐ (b) NH_2 ☐
(c) OC_2H_5 ☐ (d) $OCOCH_3$ ☐

86. *Ortho*-esters have the general formula:
(a) $RCOOR'$ ☐ (b) $(RCO)_3R'$ ☐
(c) $RC(OR')_3$ ☐ (d) $(RCOO)_3R'$ ☐

87. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is: **[CBSE (PMT) Prelims 2010]**
(a) CH_3COOCH_3 ☐ (b) CH_3CONH_2 ☐
(c) $CH_3COOCOCH_3$ ☐ (d) CH_3COCl ☐

88. Esterification is fastest in case of:
(a) CH_3COOH ☐ (b) HCOOH ☐
(c) CH_3CH_2COOH ☐ (d) $(CH_3)_2CHCOOH$ ☐

89. In a reaction, $(A) \xrightarrow{NH_3} (B) \xrightarrow{Heat} (C) \xrightarrow{P_2O_5} C_2H_5CN$
(*A*), (*B*) and (*C*) are:
(a) CH_3COOH, CH_3COONH_4 and CH_3CONH_2 ☐
(b) CH_3COCl, CH_3CONH_2 and CH_3COONH_4 ☐
(c) C_2H_5COOH, $C_2H_5COONH_4$ and $C_2H_5CONH_2$ ☐
(d) $C_2H_5COONH_4$, $C_2H_5CONH_2$ and C_2H_5COOH ☐

90. Explain the reactivity of acyl compounds in the order: **[CBSE (Med.) 2008]**
(a) acid chloride > amide > anhydride > ester ☐
(b) acid chloride > anhydride > ester > amide ☐
(c) ester > acid chloride > anhydride > amide ☐
(d) ester > anhydride > acid chloride > amide ☐

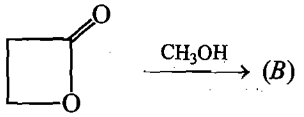
91. Which of the following esters cannot undergo Claisen self condensation?
(a) $CH_3CH_2CH_2CH_2COOC_2H_5$ ☐
(b) $C_6H_5COOC_2H_5$ ☐
(c) $C_6H_{11}CH_2COOC_2H_5$ ☐
(d) $C_6H_5CH_2COOC_2H_5$ ☐

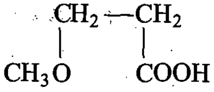
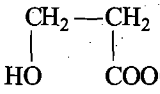
92. Ethyl acetate is obtained when methyl magnesium bromide reacts with: **[AMU (Med.) 2008]**
(a) ethyl formate ☐ (b) acetyl chloride ☐
(c) ethyl chloroformate ☐ (d) carbondioxide ☐

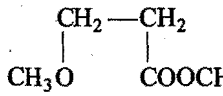
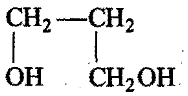
93. Acetamide is treated with the following reagents separately. Which one of these would yield methylamine ? **[CBSE (PMT) Prelims 2010]**
(a) Hot conc. H_2SO_4 ☐ (b) PCl_5 ☐
(c) NaOH-Br_2 ☐ (d) Sodalime ☐

94. Hydrolysis of an ester gives a carboxylic acid which on Kolbe's electrolysis yields ethane. The ester is: **[UGET (Med.) 2011]**
(a) ethyl methanoate ☐ (b) methyl ethanoate ☐
(c) methyl methanoate ☐ (d) methyl propanoate ☐

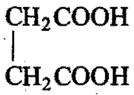
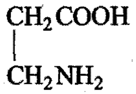
95. Cyclic ester (*A*) reacts with methyl alcohol to give (*B*)

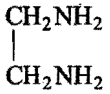
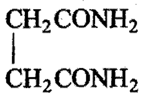


What is the compound (*B*)?
(a)  $CH_3O{-}CH_2{-}CH_2{-}COOH$ ☐ (b)  $HO{-}CH_2{-}CH_2{-}COOCH_3$ ☐

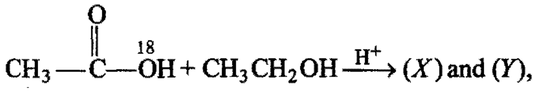
(c) 
$\underset{CH_3O}{CH_2}—\underset{COOCH_3}{CH_2}$ ☐ (d) 
$\underset{OH}{CH_2}—\underset{CH_2OH}{CH_2}$ ☐

96. Succinimide when subjected to Hofmann bromamide reaction gives a compound having one of the given structures. Select the correct structure:

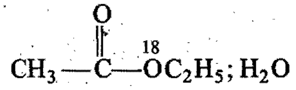
(a) 
$\begin{array}{l}CH_2COOH\\|\\CH_2COOH\end{array}$ ☐ (b) 
$\begin{array}{l}CH_2COOH\\|\\CH_2NH_2\end{array}$ ☐

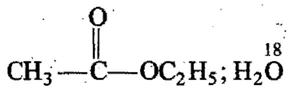
(c) 
$\begin{array}{l}CH_2NH_2\\|\\CH_2NH_2\end{array}$ ☐ (d) 
$\begin{array}{l}CH_2CONH_2\\|\\CH_2CONH_2\end{array}$ ☐

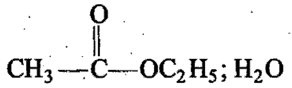
97. Let us consider an esterification of isotopically labelled carboxylic acid:


$CH_3—\overset{\overset{O}{\|}}{C}—\overset{18}{O}H + CH_3CH_2OH \xrightarrow{H^+} (X) \text{ and } (Y),$

(X) and (Y) respectively are:

(a) 
$CH_3—\overset{\overset{O}{\|}}{C}—\overset{18}{O}C_2H_5; H_2O$ ☐

(b) 
$CH_3—\overset{\overset{O}{\|}}{C}—OC_2H_5; H_2\overset{18}{O}$ ☐

(c) 
$CH_3—\overset{\overset{O}{\|}}{C}—OC_2H_5; H_2O$ ☐

(d) both (a) and (b) ☐

98. $\underset{\text{Ester }(X)}{C_4H_8O_2} \xrightarrow[\text{(ii) HOH/HCl}]{\text{(i) }CH_3MgBr} \underset{\text{Alcohol }(Y)}{C_4H_{10}O}$

Alcohol (Y) gives Lucas test within 5 minutes. Thus, (X) and (Y) respectively are:

(a) $CH_3COOC_2H_5; (CH_3)_3COH$ ☐
(b) $HCOOC_3H_7; (CH_3)_2CHOH$ ☐
(c) $C_2H_5COOCH_3; (C_2H_5)_3COH$ ☐
(d) $HCOOC_3H_7; (CH_3)_3COH$ ☐

99. Which one of the following pairs gives effervescence with aq. $NaHCO_3$? **[JEE (WB) 2008]**

$$\underset{\text{(I)}}{CH_3COCl}, \underset{\text{(II)}}{CH_3COCH_3}, \underset{\text{(III)}}{CH_3COOCH_3}, \underset{\text{(IV)}}{CH_3COOCOCH_3},$$

(a) I and IV ☐ (b) I and III ☐
(c) I and II ☐ (d) II and III ☐

100. Acetyl chloride and sodium propanoate will give: **[DPMT 2002]**

(a) acetic anhydride ☐
(b) propionic anhydride ☐
(c) acetic propionic anhydride ☐
(d) ethyl propanoate ☐

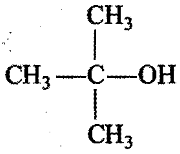
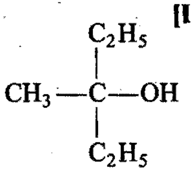
101. Ethyl benzoate reacts with PCl_5 to give: **[CET (Karnataka) 2003]**

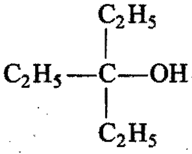
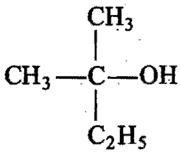
(a) $C_2H_5Cl + C_6H_5COCl + POCl_3 + HCl$ ☐
(b) $C_2H_5Cl + C_6H_5COCl + POCl_3$ ☐
(c) $CH_3COCl + C_6H_5COCl + POCl_3$ ☐
(d) $C_2H_5Cl + C_6H_5COOH + POCl_3$ ☐

102. Acetamide and ethylamine are distinguished by reacting with: **[UGET (Med.) 2003]**

(a) Br_2 water ☐
(b) acidic $KMnO_4$ ☐
(c) aqueous NaOH and heat ☐
(d) aqueous HCl and heat ☐

103. Methyl acetate on treating with excess of C_2H_5MgBr produces: **[IIT 2003]**

(a) 
$CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—OH$ ☐ (b) 
$CH_3—\overset{\overset{C_2H_5}{|}}{\underset{\underset{C_2H_5}{|}}{C}}—OH$ ☐

(c) 
$C_2H_5—\overset{\overset{C_2H_5}{|}}{\underset{\underset{C_2H_5}{|}}{C}}—OH$ ☐ (d) 
$CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}—OH$ ☐

104. In a set of reactions, propionic acid yielded a compound (D).

$$CH_3CH_2COOH \xrightarrow{SOCl_2} (B) \xrightarrow{NH_3} (C) \xrightarrow[Br_2]{KOH} (D)$$

The structure of (D) would be: **[CBSE (Med.) 2006]**

(a) $CH_3CH_2NHCH_3$ ☐ (b) $CH_3CH_2NH_2$ ☐
(c) $CH_3CH_2CH_2NH_2$ ☐ (d) $CH_3CH_2CONH_2$ ☐

105. Self condensation of two moles of ethyl acetate in presence of sodium ethoxide yields: **[CBSE (Med.) 2006]**

(a) methyl acetoacetate ☐ (b) ethyl propionate ☐
(c) ethyl butyrate ☐ (d) acetoacetic ester ☐

106. A distinctive and characteristic functional group of fat is: **[CET (Karnataka) 2006]**

(a) a peptide group ☐ (b) an ester group ☐
(c) an alcoholic group ☐ (d) a ketonic group ☐

107. Acrolein test is positive for: **[CET (Karnataka) 2006]**

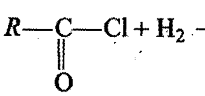
(a) polysaccharides ☐ (b) proteins ☐
(c) oils and fats ☐ (d) reducing sugars ☐

108. Amides may be converted to amines by the reaction named after: **[PMT (HP) 2006]**

(a) Perkin ☐ (b) Claisen ☐
(c) Hofmann ☐ (d) Clemmensen ☐

109. Which of the following compounds, when heated with CO at 150°C and 500 atm. pressure in presence of BF_3, forms ethyl propionate? **[EAMCET (Engg.) 2006]**

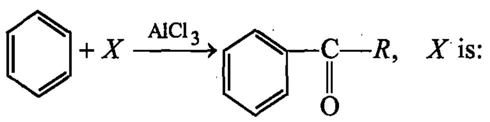
(a) C_2H_5OH ☐ (b) CH_3OCH_3 ☐
(c) $CH_3OC_2H_5$ ☐ (d) $C_2H_5OC_2H_5$ ☐

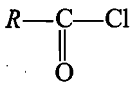
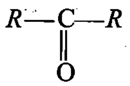
110. 
$R—\underset{\underset{O}{\|}}{C}—Cl + H_2 \xrightarrow[S]{Pd/BaSO_4} RCHO$, the name of reaction is: **[DPMT 2006]**

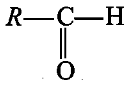
(a) Cannizzaro's reaction ☐
(b) Rosenmund reduction ☐
(c) Clemmensen reduction ☐

(d) Wolff-Kishner reduction ☐

111. Friedel-Crafts acylation can be given by: **[DCE 2006]**



(a) 
$R-\underset{\underset{O}{\|}}{C}-Cl$ ☐ (b) 
$R-\underset{\underset{O}{\|}}{C}-R$ ☐

(c) 
$R-\underset{\underset{O}{\|}}{C}-H$ ☐ (d) $R-O-R$ ☐

112. End of detergent have: **[AMU (Med.) 2006]**

(a) ester group ☐ (b) aldehyde ☐
(c) amine group ☐ (d) sodium sulphate ☐

113. Soaps can be classified as: **[PMT (Raj.) 2006]**

(a) carbohydrates ☐ (b) ethers ☐
(c) salts of fatty acids ☐ (d) none of these ☐

114. $CH_3CH_2CONH_2 \xrightarrow{X} CH_3CH_2CH_2NH_2$,
X is: **[DCE (Engg.) 2007]**

(a) Pt/H_2 ☐ (b) Ni/H_2 ☐
(c) $LiAlH_4$ ☐ (d) Zn ☐

115. Amides are formed by the reaction of acid chloride with: **[CET (J & K) 2007]**

(a) NH_2NH_2 ☐ (b) NH_3 ☐
(c) NH_2OH ☐ (d) $C_6H_5NHNH_2$ ☐

116. A pure dextrorotatory monocarboxylic acid is treated with racemic mixture of an alcohol containing one chiral carbon. The ester formed will be: **[PMT (Kerala) 2007]**

(a) pure dextrorotatory ☐
(b) racemic mixture ☐
(c) meso compound ☐
(d) optically active mixture containing excess dextrorotatory compound ☐
(e) optically active mixture containing excess laevorotatory compound ☐

117. The Claisen condensation reaction is given by: **[VMCC 2007]**

(a) $CH_3COOC_2H_5$ ☐ (b) CH_3CHO ☐
(c) C_6H_5Cl ☐ (d) HCHO ☐

118. Detergents are known to pollute rivers and water-ways. However detergents can be made biodegradable and pollution free by taking: **[PMT (Kerala) 2007]**

(a) cyclic hydrocarbon chain ☐
(b) shorter hydrocarbon chain ☐
(c) unbranched hydrocarbon chain ☐
(d) hydrocarbons with more branching ☐
(e) benzenoid hydrocarbons ☐

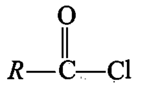
119. Which one of the following forms micelles in aqueous solution above certain concentration? **[JIPMER (Med.) 2007]**

(a) Urea ☐
(b) Dodecyl trimethyl ammonium chloride ☐
(c) Pyridinium chloride ☐
(d) Glucose ☐

120. Fruity smell is given by: **[AMU (Med.) 2007]**

(a) esters ☐ (b) alcohols ☐
(c) chloroform ☐ (d) acid anhydrides ☐

121. Which of the following would undergo Hofmann reaction to give a primary amine? **[CET (Engg.) Pb 2007]**

(a) 
$R-\overset{\overset{O}{\|}}{C}-Cl$ ☐ (b) $RCONHCH_3$ ☐
(c) $RCONH_2$ ☐ (d) $RCOOR$ ☐

122. An ester is boiled with KOH. The product is cooled and acidified with concentrated HCl. A white crystalline acid separates. The ester is: **[CMC (Med.) Vellore 2007]**

(a) methyl acetate ☐ (b) ethyl acetate ☐
(c) ethyl formate ☐ (d) ethyl benzoate ☐

123. Methyl acetate and ethyl acetate can be distinguished by: **[AIIMS 2007]**

(a) hot alkaline $KMnO_4$ ☐ (b) neutral $FeCl_3$ ☐
(c) iodoform test ☐ (d) none of these ☐

SET II : This set contains the questions with two or more correct answers.

124. Acetoacetic ester is used for the synthesis of:

(a) α, β-unsaturated acids ☐
(b) γ-keto acids ☐
(c) monocarboxylic acids ☐
(d) dicarboxylic acids ☐

125. Starting from diethyl malonate, what type of acids can be prepared from it?

(a) Succinic acid ☐ (b) Barbituric acid ☐
(c) Adipic acid ☐ (d) Monoalkyl acetic acid ☐

126. Acetic anhydride may be prepared by the reaction of acetic acid with:

(a) $H_2C{=}C{=}O$ ☐
(b) $LiAlH_4$ ☐
(c) P_2O_5 ☐
(d) $C_2H_5OH/HgSO_4$ on heating ☐

127. Acetic anhydride is prepared industrially by heating sodium acetate with:

(a) PCl_5 ☐ (b) $SOCl_2$ ☐
(c) CH_3COCl ☐ (d) Cl_2 and SCl_2 ☐

128. Acetyl chloride is prepared industrially by distilling sodium acetate with:

(a) HCl ☐ (b) SO_2Cl_2 ☐
(c) PCl_5 ☐ (d) $POCl_3$ ☐

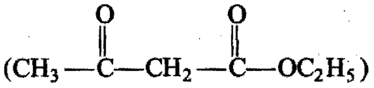
129. Urea on heating with ethyl alcohol gives:
(a) urethane ☐ (b) semicarbazide ☐
(c) malonyl urea ☐ (d) ethyl carbamate ☐

130. Urea may be identified by which of the following tests?
(a) With $CHCl_3/KOH$, it gives very offensive odour ☐
(b) With nitrous acid, it evolves N_2 and CO_2 ☐
(c) With NaOH and a drop of $CuSO_4$, it gives violet colour ☐
(d) With NaOH on heating, it gives a smell of NH_3 gas ☐

ASSERTION-REASON TYPE QUESTIONS

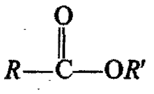
Following questions consists of **Assertion (A)** and **Reason (R)**. Select the correct answer using following keys:

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct but (R) is not correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) Acetoacetic ester  $(CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5)$ will give iodoform test.
(R) It contains methyl keto group.

2. (A) Ethanamide (CH_3CONH_2) undergoes dehydration by heating with P_2O_5.
(R) Ethanamide undergoes dehydration to give nitro compound.

3. (A) Ethyl acetate is more reactive than acetamide towards nucleophilic substitution.
(R) $—OC_2H_5$ is more electron attracting than $—NH_2$ group.

4. (A) $RCOCl$, $(RCO)_2O$ and  $R-\overset{O}{\overset{\|}{C}}-OR'$ all react with Grignard reagent to form tertiary alcohol.
(R) $RCOCl$ reacts with dialkyl cadmium R_2Cd to form ketone but $(RCO)_2O$ and $RCOOR'$ do not react with dialkyl cadmium.

5. (A) 1°-Amides react with Br_2 in presence of NaOH to form 1°-amine having one carbon atom less than amide.
(R) It is degradative reduction involving acylnitrene intermediate.

ANSWERS

OBJECTIVE QUESTIONS

1. (b)	2. (a)	3. (d)	4. (c)	5. (a)	6. (b)	7. (c)	8. (d)	9. (b)	10. (d)
11. (c)	12. (b)	13. (d)	14. (c)	15. (a)	16. (b)	17. (c)	18. (a)	19. (d)	20. (b)
21. (c)	22. (b)	23. (c)	24. (a)	25. (d)	26. (d)	27. (a)	28. (a)	29. (b)	30. (b)
31. (c)	32. (c)	33. (a)	34. (b)	35. (c)	36. (c)	37. (b)	38. (d)	39. (c)	40. (b)
41. (b)	42. (d)	43. (a)	44. (c)	45. (a)	46. (d)	47. (d)	48. (c)	49. (a)	50. (d)
51. (a)	52. (a)	53. (d)	54. (d)	55. (b)	56. (c)	57. (a) and (b)	58. (b)	59. (c)	60. (a)
61. (b)	62. (d)	63. (c)	64. (a) and (b)	65. (b)	66. (c)	67. (b)	68. (d)	69. (b)	70. (a)
71. (d)	72. (a)	73. (c)	74. (b)	75. (c)	76. (d)	77. (b)	78. (c)	79. (b)	80. (d)
81. (b)	82. (c)	83. (a)	84. (d)	85. (a)	86. (c)	87. (d)	88. (b)	89. (c)	90. (b)
91. (b)	92. (c)	93. (c)	94. (b)	95. (b)	96. (b)	97. (b)	98. (a)	99. (a)	100. (c)
101. (b)	102. (c)	103. (b)	104. (b)	105. (d)	106. (b)	107. (c)	108. (c)	109. (d)	110. (b)
111. (a)	112. (d)	113. (c)	114. (c)	115. (b)	116. (d)	117. (a)	118. (c)	119. (b)	120. (a)
121. (c)	122. (d)	123. (c)	124. (a,b,c,d)	125. (a,b,c,d)	126. (a,c,d)	127. (b,c,d)	128. (b,d)	129. (a,d)	130. (b,c,d)

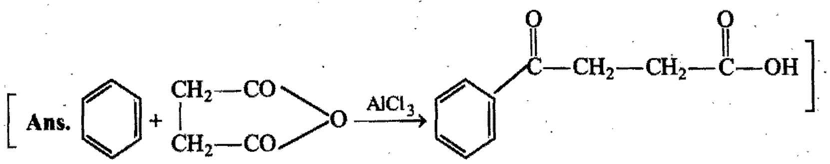
ASSERTION-REASON TYPE QUESTIONS

1. (d)	2. (c)	3. (a)	4. (b)	5. (a)

BRAIN STORMING PROBLEMS

1. What happens when benzene undergoes Friedel-Crafts acylation with succinic anhydride in presence of $AlCl_3$?

[**Ans.**

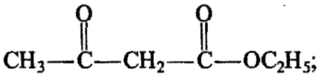


]

2. Complete the following Claisen condensation products. Indicate whether (*X*), (*Y*) and (*Z*) will show iodoform test or not.

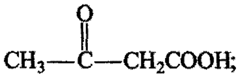
$$2CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa} (X) \xrightarrow{HOH/HCl} \underset{\text{(Ketoacid)}}{(Y)} + \underset{\text{(An alcohol)}}{(Z)}$$

[**Ans.** (*X*) :



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$; Acetoacetic ester

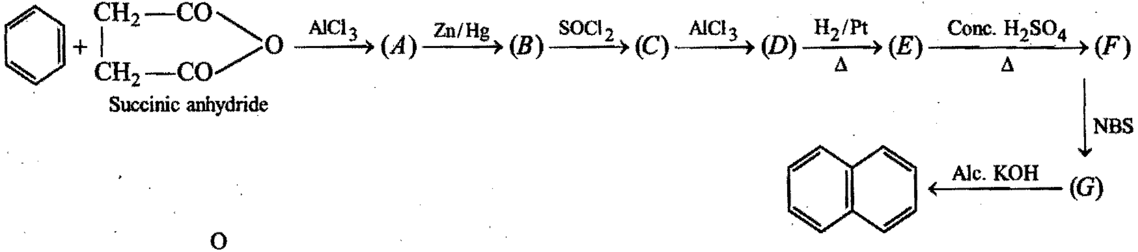
(*Y*) :



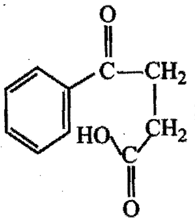
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOH$; (*Z*) : C_2H_5OH

(*X*) and (*Y*) have $CH_3-\overset{O}{\overset{\|}{C}}-$ group hence, they will show iodoform test. Alcohol (*Z*) on oxidation gives $CH_3-\overset{O}{\overset{\|}{C}}-$ group hence, it will also give iodoform test.]

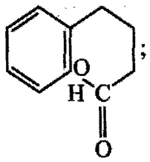
3. Formation of naphthalene takes place in the following steps. What are (*A*), (*B*), (*C*), (*D*), (*E*), (*F*) and (*G*) formed in between?



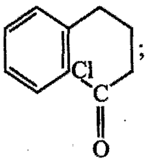
[**Ans.** (*A*)



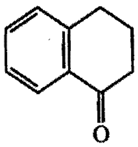
; (*B*)



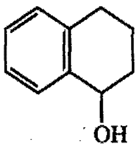
; (*C*)



; (*D*)

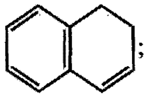


; (*E*)

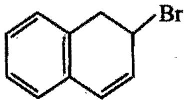


;

(*F*)



; (*G*)



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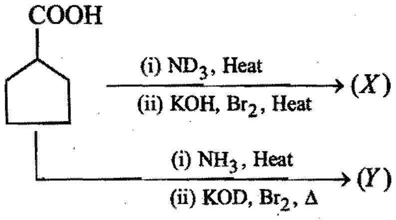
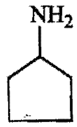
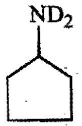
4. What are (*X*) and (*Y*) in the following reaction? Give the mechanism of formation of (*X*) and (*Y*).



[**Ans.** (*X*) ⟶

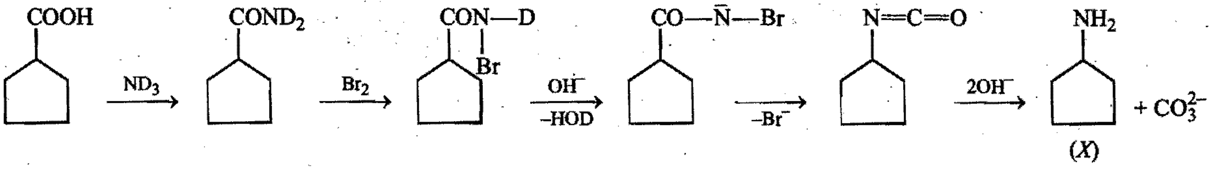


; (*Y*) ⟶

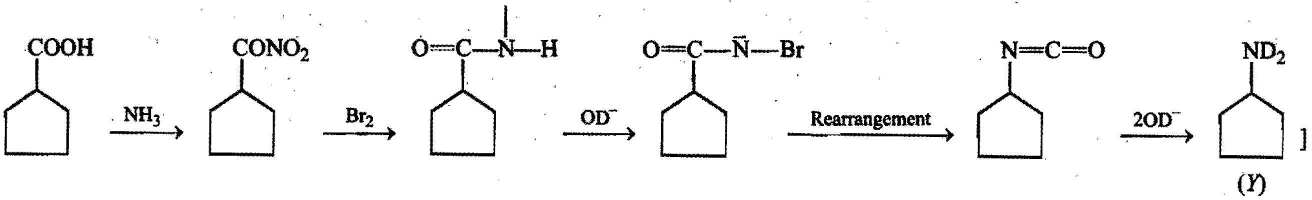


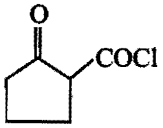
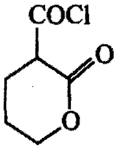
]

[**Hint :**

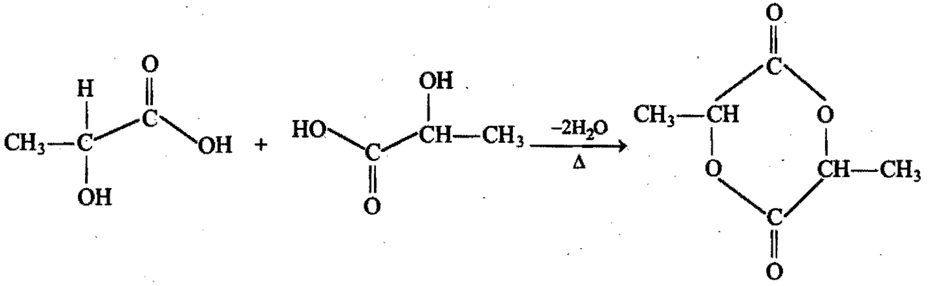


Both deuterium atoms are involved in the reaction hence do not appear in the final product.



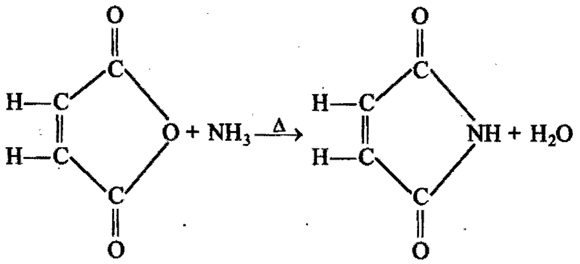
5. What happens when?
   (i) Lactic acid is heated,
   (ii) Cyclic amide is reduced with $LiAlH_4$,
   (iii) Maleic anhydride is treated with ammonia,
   (iv) Acid halide, C_2H_5COCl reacts with dimethyl cadmium,
   (v)  is reduced by $LiAlH_4$,
   (vi)  is reduced by using $LiAlH_4$ and by using Lindlar's catalyst.

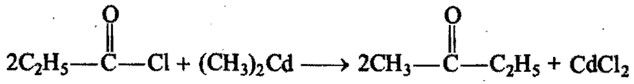
[**Ans.** (i) Dimerisation takes place to form lactide (Cyclic ester).



Lactide

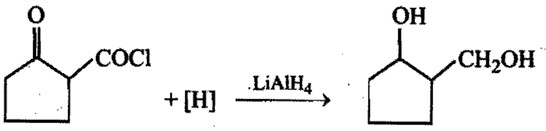
(ii) 

(iii) 

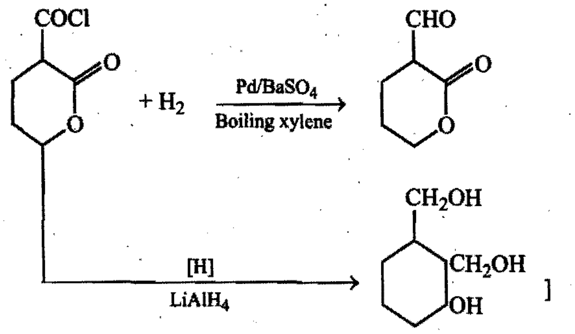
(iv) 

$$2C_2H_5-\overset{\overset{\large O}{\|}}{C}-Cl + (CH_3)_2Cd \longrightarrow 2CH_3-\overset{\overset{\large O}{\|}}{C}-C_2H_5 + CdCl_2$$

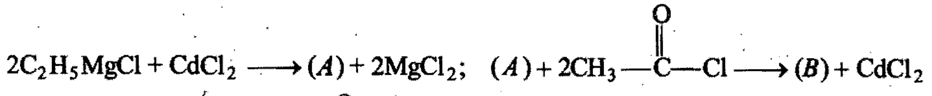
Butan-2-one

(v) 

(vi)

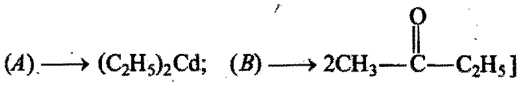


6. Complete the following reaction:



$$2C_2H_5MgCl + CdCl_2 \longrightarrow (A) + 2MgCl_2;\quad (A) + 2CH_3-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow (B) + CdCl_2$$

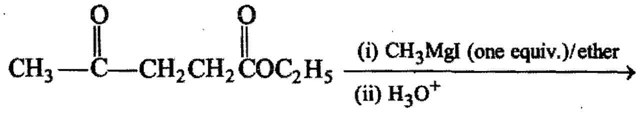
[**Ans.**



$(A) \longrightarrow (C_2H_5)_2Cd$; $(B) \longrightarrow 2CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5$]

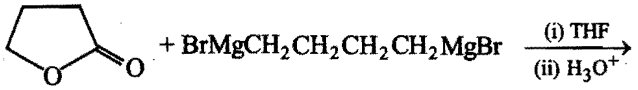
7. Predict the products expected of the following reactions:

(i)

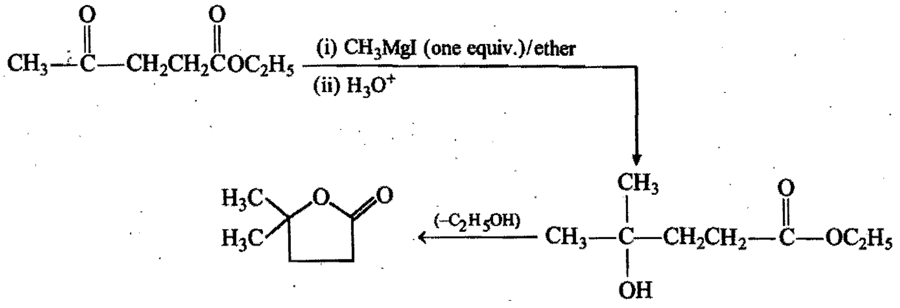


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgI \text{ (one equiv.)/ether}}$$

(ii)

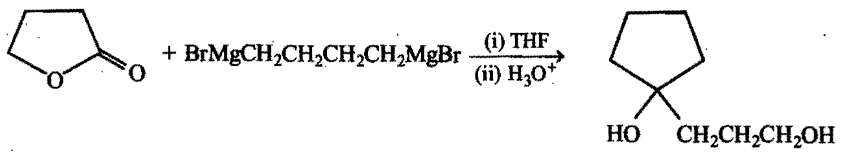


[**Ans.** (i)



(Ketonic carbonyl group is more reactive.)

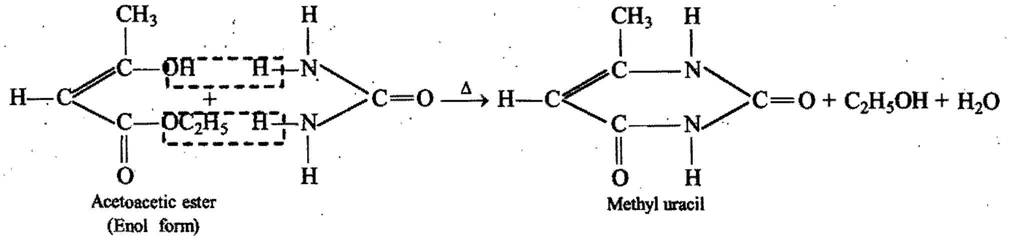
(ii)



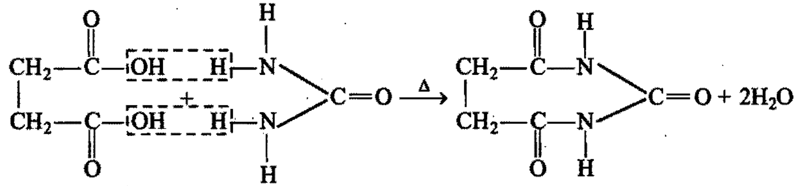
(Ester group reacts with both parts of Grignard reagent forming a diol.)]

8. What happens when?
- (i) Urea is heated with acetoacetic ester,
- (ii) Urea is heated with succinic acid,
- (iii) Urea is treated with sodium hypobromide in alkaline medium,
- (iv) Urea is treated with acetyl chloride.

[**Ans.** (i) Enolic form of acetoacetic ester reacts with urea to form methyl uracil,

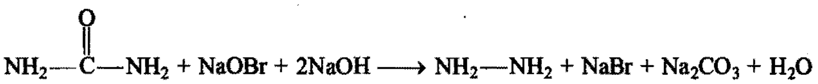


(ii)



Succinic acid Succinyl urea

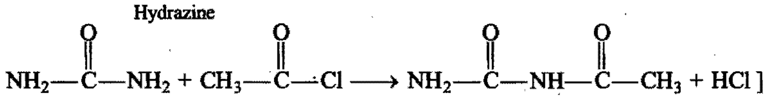
(iii)



$$NH_2-\overset{\overset{O}{\|}}{C}-NH_2 + NaOBr + 2NaOH \longrightarrow NH_2-NH_2 + NaBr + Na_2CO_3 + H_2O$$

$$\underset{\text{Hydrazine}}{NH_2-NH_2} + 2NaOBr \longrightarrow N_2 + 2NaBr + 2H_2O$$

(iv)



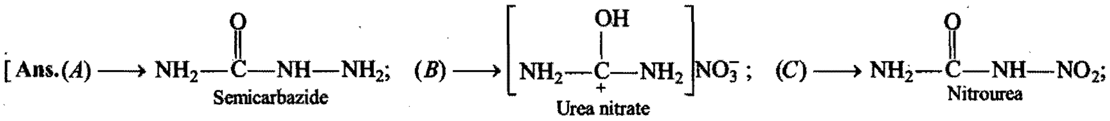
$$NH_2-\overset{\overset{O}{\|}}{C}-NH_2 + CH_3-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow NH_2-\overset{\overset{O}{\|}}{C}-NH-\overset{\overset{O}{\|}}{C}-CH_3 + HCl\,]$$

n-Acetyl urea (Ureide)

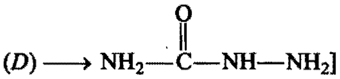
9. Complete the following set of reactions:

(i) $\text{Urea} + NH_2-NH_2 \xrightarrow[\text{Amyl alcohol}]{110°C} (A) + NH_3$

(ii) $\text{Urea} + HNO_3 \longrightarrow (B) \xrightarrow{\text{Conc. } H_2SO_4} (C) + H_2O;\quad (C) \xrightarrow[\text{[H]}]{Zn/CH_3COOH} (D)$



$$[\textbf{Ans.}(A) \longrightarrow \underset{\text{Semicarbazide}}{NH_2-\overset{\overset{O}{\|}}{C}-NH-NH_2};\ (B) \longrightarrow \underset{\text{Urea nitrate}}{\left[NH_2-\overset{\overset{OH}{|}}{\underset{+}{C}}-NH_2\right]NO_3^-};\ (C) \longrightarrow \underset{\text{Nitrourea}}{NH_2-\overset{\overset{O}{\|}}{C}-NH-NO_2};$$



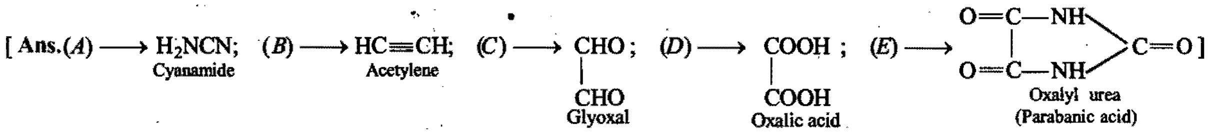
$$(D) \longrightarrow \underset{\text{Semicarbazide}}{NH_2-\overset{\overset{O}{\|}}{C}-NH-NH_2}]$$

10. Complete the following reactions: $CaCN_2 + H_2SO_4 \longrightarrow CaSO_4 + (A)$

$$(A) \xrightarrow{HOH} NH_2CONH_2$$

$$CaC_2 \xrightarrow{HOH} (B) + Ca(OH)_2$$

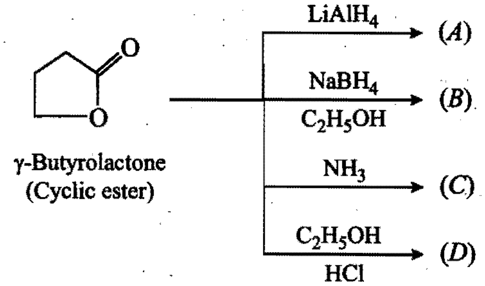
$$(B) \xrightarrow{O_3/H_2O} (C) \xrightarrow{H_2O_2} (D) \xrightarrow{\text{Urea}} (E)$$



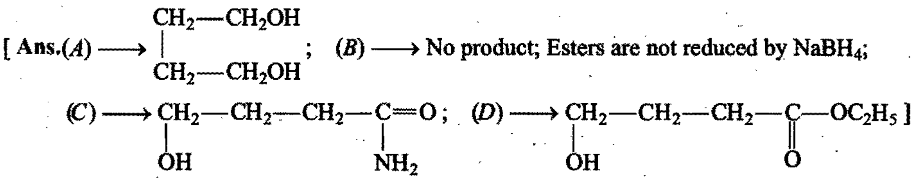
$$[\textbf{Ans.}(A) \longrightarrow \underset{\text{Cyanamide}}{H_2NCN};\ (B) \longrightarrow \underset{\text{Acetylene}}{HC{\equiv}CH};\ (C) \longrightarrow \underset{\text{Glyoxal}}{\begin{matrix}CHO\\|\\CHO\end{matrix}};\ (D) \longrightarrow \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}};\ (E) \longrightarrow$$

Oxalyl urea (Parabanic acid)]

11. Write down the products in the following reactions:



γ-Butyrolactone (Cyclic ester)



$$[\textbf{Ans.}(A) \longrightarrow \begin{matrix}CH_2-CH_2OH\\|\\CH_2-CH_2OH\end{matrix};\ (B) \longrightarrow \text{No product; Esters are not reduced by } NaBH_4;$$

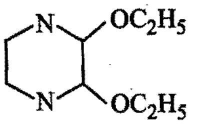
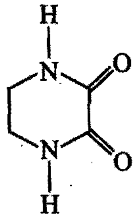
$$(C) \longrightarrow \underset{OH}{\underset{|}{CH_2}}-CH_2-CH_2-\underset{NH_2}{\underset{|}{C}}{=}O;\ (D) \longrightarrow \underset{OH}{\underset{|}{CH_2}}-CH_2-CH_2-\underset{O}{\underset{\|}{C}}-OC_2H_5\,]$$

12. Ketones [$R-\overset{\overset{O}{\|}}{C}-R_1$], where R and R_1 are alkyl groups, can be obtained in one step by:
(a) hydrolysis of ester ☐
(b) oxidation of primary alcohols ☐
(c) oxidation of tertiary alcohols ☐
(d) reaction of acid halides with dialkyl cadmium ☐

13. Which of the following has the highest melting point ?
(a) $(CH_3CO)_2O$ ☐ (b) CH_3CN ☐
(c) CH_3CONH_2 ☐ (d) CH_3COCl ☐

14. Which of the following is the most reactive towards nucleophilic substitution reaction ?
(a) RCl ☐ (b) $(RCO)_2O$ ☐
(c) $RCOCl$ ☐ (d) $RCONH_2$ ☐

15. $H_2N-CH_2-CH_2-NH_2$ when reacts with diethyl oxalate gives:

(a)

☐ (b)

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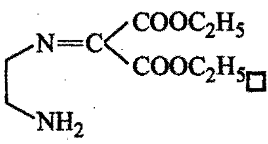
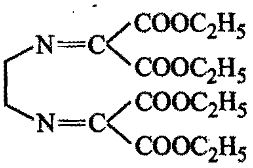
(c)

☐ (d)

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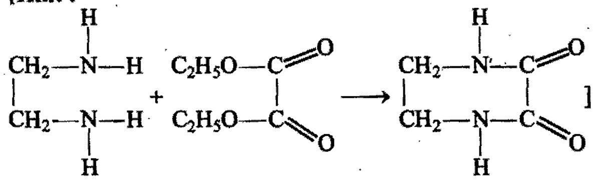
[Hint :

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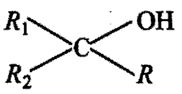
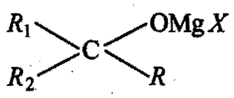
16. The boiling points of acetic anhydride (I), propionic anhydride (II) and butyric anhydride (III) follow the order :
(a) I < II < III ☐ (b) III < II < I ☐
(c) I < III < II ☐ (d) II < III < I ☐

17. The hydrolysis of which of the following takes the longest time ?
(a) CH_3COCl ☐ (b) $(CH_3CO)_2O$ ☐
(c) $CH_3COOC_2H_5$ ☐ (d) CH_3CONH_2 ☐

18. The product obtained in the following reaction,
$R_1COOR_2 + RMgX \longrightarrow$
is :

(a)

☐ (b) $R_1-\overset{\overset{O}{\|}}{C}-R$ ☐

(c) $R_1-\overset{\overset{O}{\|}}{C}-R_2$ ☐ (d)

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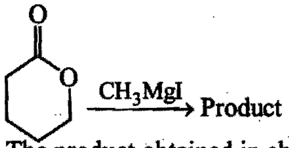
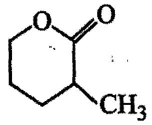
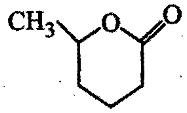
19.

The product obtained in above reaction will be :

(a) $CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_4-OMgI$ ☐

(b) $CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-MgI$ ☐

(c)

☐ (d)

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20. Reaction,

$$CH_3COOCH_3 + C_8H_{17}COOH \xrightarrow[\Delta]{C_8H_{17}COONa} CH_3COOC_8H_{17} + CH_3COOH$$

is called as :
(a) reverse esterification ☐ (b) *cis*-esterification ☐
(c) *trans*-esterification ☐ (d) both (a) and (c) ☐

21. $(A) \xrightarrow{PCl_5} RCOCl$; (A) may be :
(a) $RCOOH$ ☐ (b) $RCOOR$ ☐
(c) $RCONH_2$ ☐ (d) $(RCO)_2O$ ☐

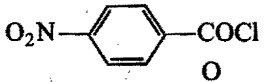
22. CH_3COCl is used to detect the number of amino groups in the organic compounds. When a compound of molecular mass 180 is acetylated, gives a compound of molecular mass 390. The number of amino groups in the compound is :
(a) 1 ☐ (b) 2 ☐
(c) 5 ☐ (d) 4 ☐

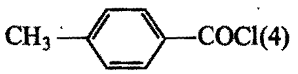
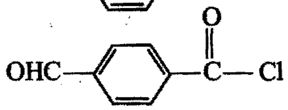
[Hint : $-NH_2 + CH_3-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow -\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-CH_3 + HCl$

Let the amino compound has $n(-NH_2)$ groups. Molecular mass of the product will be :

$$180 - n \times 1 + n \times 43 = 390$$
$$42n = 210$$
$$n = 5$$
]

23. Arrange the following compounds in the decreasing order of reactivity for hydrolysis reaction :

(1) C_6H_5COCl (2)


(3)

(4)


(a) 2 > 4 > 1 > 3 ☐ (b) 2 > 4 > 3 > 1 ☐
(c) 1 > 2 > 3 > 4 ☐ (d) 4 > 3 > 2 > 1 ☐

[Hint : Stronger is the (–*I*) effect of the group at *para*-position with respect to acid halide group, greater is the reactivity towards hydrolysis.**]**

24. Number of cross products in the given reaction,

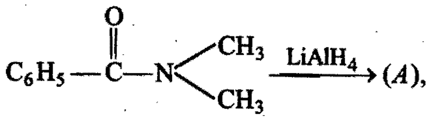
$$CH_3COOC_2H_5 + C_6H_5CH_2COOC_2H_5 \xrightarrow{C_2H_5ONa/\ C_2H_5OH}$$

will be :

(a) one ☐ (b) three ☐

(c) two ☐ (d) four ☐

25. In the following reaction,



the product (A) will be :

(a) $C_6H_5CH_2OH$ ☐ (b) C_6H_5COOH ☐

(c) $C_6H_5CONH_2$ ☐ (d) $C_6H_5CH_2N(CH_3)_2$ ☐

26. Which of the following compounds will give carboxylic acid with nitrous acid (HNO_2) ?

(a) $R—COCl$ ☐ (b) $R—CONH_2$ ☐

(c) $R—COOR$ ☐ (d) $(RCO)_2O$ ☐

27. Natural wax is :

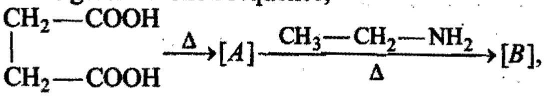
(a) oils and fats ☐

(b) long chain fatty acids ☐

(c) ester of long chain fatty acid and long chain alcohol ☐

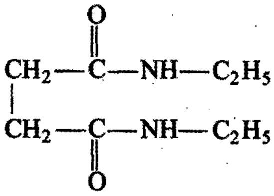
(d) long chain alcohol ☐

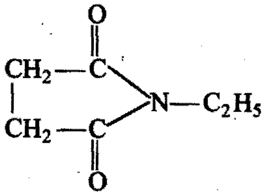
28. In the given reaction sequence,

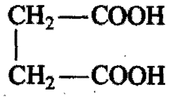


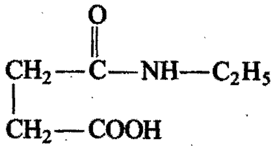
$$\begin{array}{l}CH_2—COOH\\ |\\ CH_2—COOH\end{array} \xrightarrow{\Delta} [A] \xrightarrow[\Delta]{CH_3—CH_2—NH_2} [B],$$

the final product [B] will be :

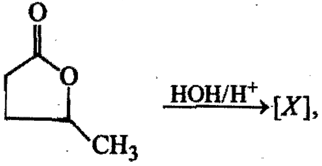
(a)  ☐

(b)  ☐

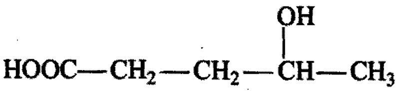
(c)  ☐

(d)  ☐

29. In the given reaction,



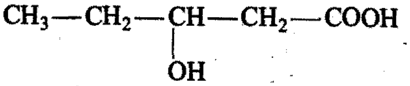
[X] will be :

(a) 

$HOOC—CH_2—CH_2—CH(OH)—CH_3$ ☐

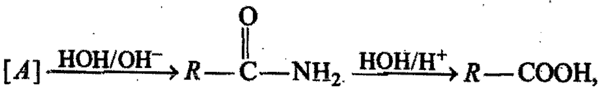
(b) $CH_3—CH_2—CH_2—CH_2—COOH$ ☐

(c) $HO—CH_2—CH_2—CH_2—COOH$ ☐

(d) 

$CH_3—CH_2—CH(OH)—CH_2—COOH$ ☐

30. In the reaction sequence,



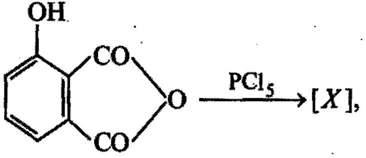
$$[A] \xrightarrow{HOH/OH^-} R—\overset{O}{\overset{\|}{C}}—NH_2 \xrightarrow{HOH/H^+} R—COOH,$$

[A] will be :

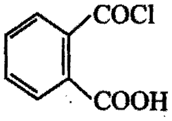
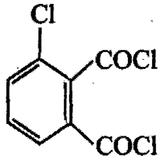
(a) RCN ☐ (b) RNC ☐

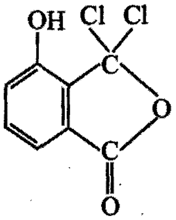
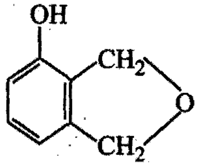
(c) $RCHO$ ☐ (d) R_2CO ☐

31. In the given reaction,

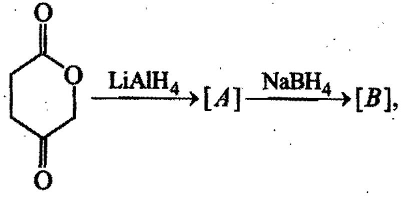


the product [X] will be :

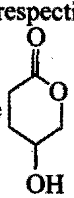
(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

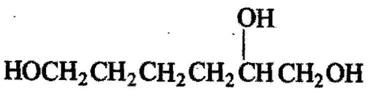
32. In the reaction,



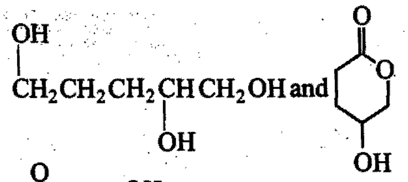
[A] and [B] respectively be :

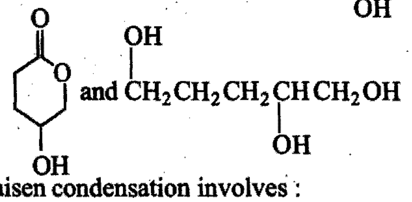
(a) both are  ☐

(b) both are ☐



$HOCH_2CH_2CH_2CH_2CH(OH)CH_2OH$

(c)  ☐

(d)  ☐

33. Claisen condensation involves :

(a) two molecules of ketone ☐

(b) two molecules of esters having no α-hydrogen ☐

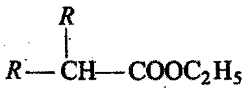
(c) two molecules of esters having α-hydrogen atoms ☐

(d) one molecule of ester having α-hydrogen and one molecule of ester having no α-hydrogen ☐

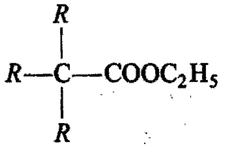
34. Which one of the following esters cannot undergo self Claisen condensation ?

(a) $CH_3COOC_2H_5$ ☐

(b) $R—CH_2—COOC_2H_5$ ☐

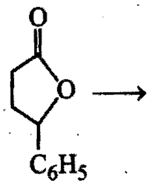
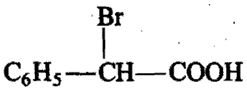
(c) 

$R—\overset{R}{\overset{|}{C}}H—COOC_2H_5$ ☐

(d) 

$R—\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}—COOC_2H_5$ ☐

35. Match the **List I** with **List II** and select the correct answer using the codes given below the lists:

List I	List II
A. $CH_3COOC_2H_5 \longrightarrow CH_3COCH_2COOC_2H_5$	1. Anhyd. $AlCl_3$
B.  $\longrightarrow$ $CH_2OH(CH_2)_2CHOHC_6H_5$	2. $LiAlH_4$
C. $C_6H_5CH_2COOH \longrightarrow$  $C_6H_5—\overset{Br}{\overset{|}{C}}H—COOH$	3. C_2H_5ONa
D. $C_6H_6 + CH_3COCl \longrightarrow C_6H_5COCH_3$	4. P/Br_2

Codes :	A	B	C	D
(a)	2	4	1	3
(b)	3	2	4	1
(c)	1	3	2	4
(d)	4	1	3	2

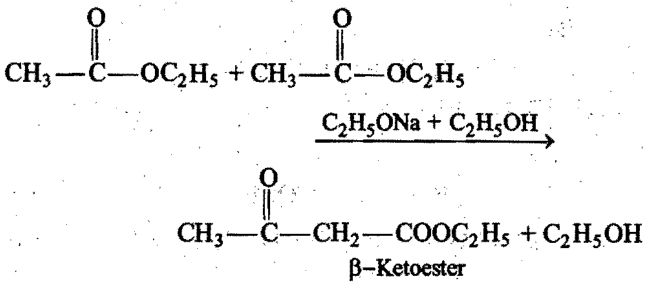
ANSWERS : BRAIN STORMING PROBLEMS

12. (d)	**13.** (a)	**14.** (c)	**15.** (b)	**16.** (b)	**17.** (d)	**18.** (b)	**19.** (a)	**20.** (c)	**21.** (a,b,d)
22. (c)	**23.** (a)	**24.** (c)	**25.** (d)	**26.** (b)	**27.** (c)	**28.** (b)	**29.** (a)	**30.** (a)	**31.** (b)
32. (c)	**33.** (c)	**34.** (d)	**35.** (b)						

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

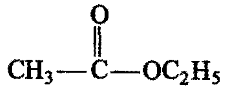
This reaction takes place between two molecules of esters (same or different). One ester should have atleast one α-hydrogen atom which behaves as a reagent. The reaction is catalysed by strong base like $C_2H_5\bar{O}Na^+$ in presence of C_2H_5OH. The product of this reaction is β-ketoester:



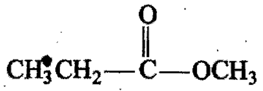
$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{C_2H_5ONa + C_2H_5OH} \underset{\beta\text{-Ketoester}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOC_2H_5} + C_2H_5OH$$

Answer the following questions :

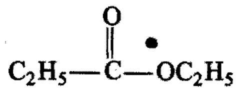
1. Which of the following esters will not undergo Claisen condensation ?

(a) 

$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5$

(b) 

$CH_3CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$

(c) 

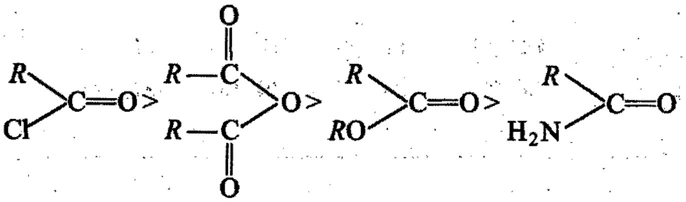
$C_2H_5-\overset{O}{\overset{\|}{C}}-OC_2H_5$

(d) $C_6H_5-COOC_2H_5$

2. Which of the following esters will undergo Claisen condensation to form acetoacetic ester ?
   (a) $CH_3COOC_2H_5$ (b) $C_6H_5COOC_2H_5$
   (c) $HCOOC_2H_5$ (d) None of these
3. When two esters having α-hydrogens are subjected to Claisen condensation then we get :
   (a) 4 cross products
   (b) 2 simple and 2 cross products
   (c) 3 cross products and 1 simple product
   (d) 4 simple products
4. When one ester has α-hydrogen and other has no α-hydrogen then Claisen condensation will give:
   (a) 1 product molecule (b) 2 product molecules
   (c) 3 product molecules (d) 4 product molecules
5. Which among the following is the most reactive towards Claisen condensation ?
   (a) $HCOOC_2H_5$ (b) $CH_3COOC_2H_5$
   (c) $C_2H_5COOC_2H_5$ (d) $HCOOCH_3$

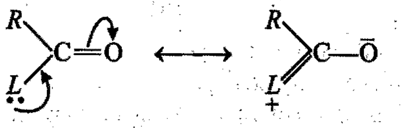
Passage 2

The reactivity of acid derivatives in general follows the order:



The above order of reactivity can be explained in terms of the:
(i) Basicity of leaving group (ii) Resonance effect
(iii) Inductive effect

Weaker is the basic character of leaving group, more is the reactivity of acid derivative. In general, all the acid derivatives show resonance as follows:



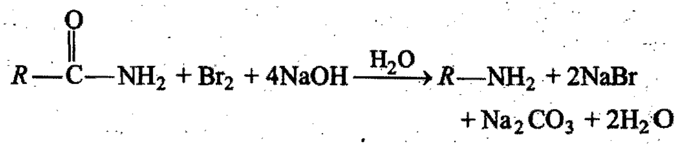
More is the stabilization, lesser is the reactivity and *vice-versa.*

Answer the following questions :

1. Which among the following anions is the most basic ?
   (a) $\bar{N}H_2$ (b) $\bar{O}R$
   (c) $R-CO\bar{O}$ (d) Cl^-
2. Which is the most reactive acid derivative?
   (a) $R-COCl$ (b) $(RCO)_2O$
   (c) $RCOOR$ (d) $RCONH_2$
3. Which among the following acid halides is the most reactive?
   (a) CH_3COBr (b) CH_3COCl
   (c) CH_3COI (d) All are equally reactive
4. Acid derivatives although contain $-\overset{O}{\overset{\|}{C}}-$ group, yet do not undergo the usual properties of carbonyl group. It is due to :
   (a) inductive effect (b) resonance
   (c) electromeric effect (d) all of these
5. Which of the following compounds will be the most easily hydrolysed ?
   (a) Acid halide (b) Acid amide
   (c) Ester (d) Acid anhydride

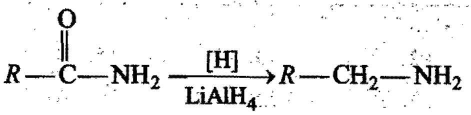
Passage 3

Amides with no substitution on nitrogen react with the solution of bromine or chlorine in NaOH or KOH to yield amines through a reaction called as Hofmann's degradation.



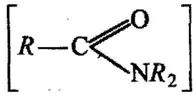
$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \xrightarrow{H_2O} R-NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

Amides can be reduced to amines having same number of carbon atoms.



$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[LiAlH_4]{[H]} R-CH_2-NH_2$$

Indicate whether the following statements are true or false :

1.  $\left[R-C\begin{smallmatrix}\nearrow O\\ \searrow NR_2\end{smallmatrix}\right]$ will undergo Hofmann's degradation.
   (a) True (b) False
2. Benzamide when treated with Br_2 in presence of NaOH gives aniline.
   (a) True (b) False
3. Iso-cyanates are formed as intermediate in the Hofmann's degradation.
   (a) True (b) False
4. Carbon dioxide gas is released in above mentioned reaction.
   (a) True (b) False
5. *N*-Methyl aniline can be obtained by using Hofmann's degradation.
   (a) True (b) False

Passage 4

Any compound formed by the reaction of a water-insoluble fatty acid with a metallic radical or with an organic base may be called as soap. Soaps used for cleaning purpose are sodium or potassium salts of long chain fatty acids, *e.g.*, palmitic, lauric, stearic and oleic acids. Soaps are generally obtained by the hydrolysis of oils and fats with aqueous alkali. This reaction is called saponification.

Synthetic detergents are cleansing agents which have all the properties of soaps, but they actually do not contain any soap. A synthetic detergent is the sodium salt of a long chain alkyl hydrogen sulphate or the sodium salt of a long chain benzene sulphonic acid.

Answer the following questions:

1. Sodium salts of higher fatty acids are known as:
   (a) soft soaps (b) hard soaps
   (c) detergents (d) lipids
2. The reaction between alkali and fat is called:
   (a) hydrolysis (b) dehydration
   (c) saponification (d) rancidity
3. Detergents have a common group:
   (a) $RONa$ (b) $RCOONa$
   (c) $R-C\equiv C-Na$ (d) $RC_6H_4SO_3Na$
4. Soaps can be classified as:
   (a) carbohydrates (b) lipids
   (c) salts of fatty acids (d) ethers
5. Which one is not a glyceride?
   (a) Soap (b) Fat
   (c) Oil (d) Phospholipid

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	**1.** (d)	**2.** (a)	**3.** (b)	**4.** (a)	**5.** (b)
Passage 2	**1.** (a)	**2.** (a)	**3.** (b)	**4.** (b)	**5.** (a)
Passage 3	**1.** (b)	**2.** (a)	**3.** (a)	**4.** (a)	**5.** (b)
Passage 4	**1.** (b)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (a)

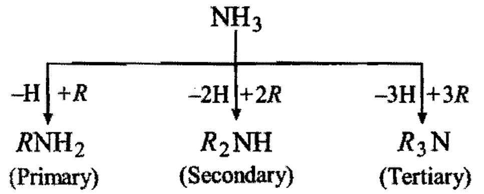
14

NITROGEN CONTAINING COMPOUNDS

1. ALIPHATIC AMINES

14.1 INTRODUCTION

Amines may be regarded as derivatives of ammonia formed by the replacement of one or more hydrogen atoms by corresponding number of alkyl groups.

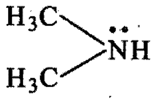


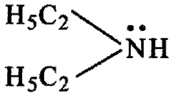
Classification

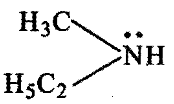
Amines are classified as primary (1°), secondary (2°) or tertiary (3°) depending on the number of alkyl groups attached to nitrogen atom. A **primary amine** has only one alkyl group directly attached to nitrogen atom, *i.e.*, it has **—NH_2** group which is known as **amino group.** Examples are:

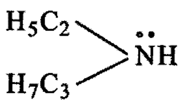
$$CH_3\ddot{N}H_2 \quad ; \quad C_2H_5\ddot{N}H_2 \quad ; \quad C_3H_7\ddot{N}H_2$$

A **secondary amine** has two alkyl groups directly attached to nitrogen, *i.e.*, it has **$>$NH** group which is known as **imino group.** These are further classified as simple or mixed. When both the alkyl groups are same, it is termed **simple secondary amine** and in case both the alkyl groups are different, it is called **mixed secondary amine.** Some examples are:

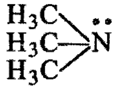

Simple

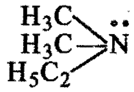

Simple

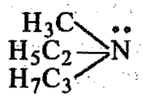

Mixed


Mixed

A **tertiary amine** has three alkyl groups directly attached to nitrogen, *i.e.*, it has **$>$N group** which is known as **tertiary nitrogen atom.** The three alkyl groups may be same or different. Examples are:

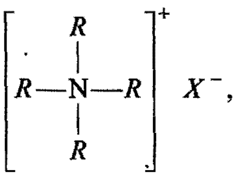

Simple


Mixed


Mixed

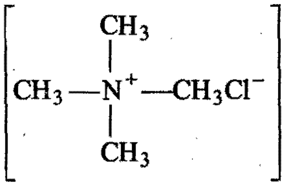
In addition to above amines, tetra-alkyl derivatives similar to ammonium salts also exist which are called **quaternary ammonium compounds.**

NH_4I	;	R_4NI	;	$(CH_3)_4NI$
		Quaternary ammonium iodide		Tetramethyl ammonium iodide

or 

$$\left[\begin{array}{c} R \\ | \\ R—N—R \\ | \\ R \end{array}\right]^+ X^-$$

Tetra-alkyl ammonium salt

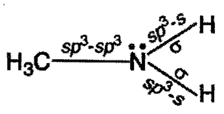


$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3—N^+—CH_3 \\ | \\ CH_3 \end{array}\right] Cl^-$$

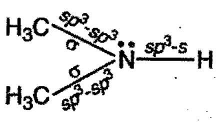
Tetramethyl ammonium chloride

Structure

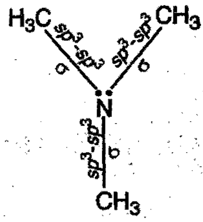
In amines, nitrogen is sp^3-hybridized and the molecules have **pyramidal** shape like that in NH_3. Three hybrid orbitals possess one electron each and form sigma bonds either with carbon atoms of the three alkyl groups or with two carbon atoms of two alkyl groups and one hydrogen atom or with one carbon atom of one alkyl group and two hydrogen atoms. One



(Primary amine)



(Secondary amine)

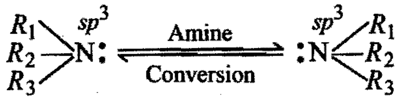


(Tertiary amine)

of the hybrid orbitals of nitrogen is completely filled with an electron pair and does not take part in bond formation.

All bond angles are approximately tetrahedral.

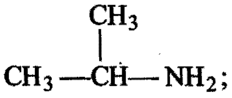
The amines of the type $R_1R_2R_3N$ (three different alkyl groups attached to chiral N) exist in the form of racemic mixture that cannot be resolved into enantiomers because of rapid inversion of an enantiomer to its mirror image. This inversion is called **amine inversion, nitrogen inversion** or **flipping.**



14.2 NOMENCLATURE

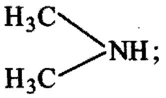
In common name system, amines are named by naming the alkyl groups attached to nitrogen atom followed by suffix -amine. The names are written in one word only. In the case of mixed amines, the names of the alkyl groups are written in alphabetical order. When two or three identical alkyl groups are attached to nitrogen atom, the prefix di- or tri- is added to the name of alkyl group.

CH_3NH_2 ; $C_2H_5NH_2$; $CH_3CH_2CH_2NH_2$;
Methylamine (1°) Ethylamine (1°) *n*-Propylamine (1°)

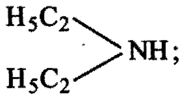


$$CH_3-\overset{CH_3}{\overset{|}{CH}}-NH_2;$$

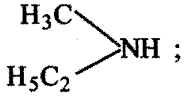
Isopropylamine
(1°)



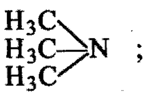
Dimethylamine
(2°)



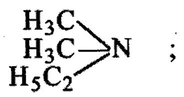
Diethylamine
(2°)



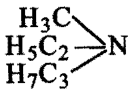
Ethyl methylamine
(2°)



Trimethylamine
(3°)



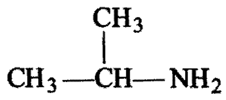
Ethyl dimethylamine
(3°)



Ethyl methyl propylamine
(3°)

In another system, amino group is considered as substituent and amines are named as amino derivatives of alkanes (aminoalkanes).

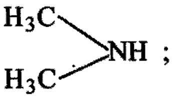
CH_3NH_2 ; $C_2H_5NH_2$;
Aminomethane Aminoethane



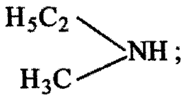
$$CH_3-\overset{CH_3}{\overset{|}{CH}}-NH_2$$

2-Aminopropane

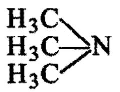
Secondary amines are named as alkyl aminoalkanes and tertiary as dialkyl aminoalkanes with highest rank to the aminoalkane (primary amine).



N-Methyl amino-methane



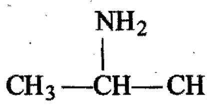
N-Methyl amino-ethane



N,N-Dimethyl amino-methane

In the **IUPAC system, primary amines** are named by replacing the final -e of the parent alkane by -amine (alkanamine). A number is added to indicate the position of $-NH_2$ group.

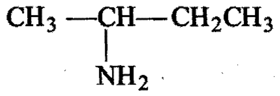
CH_3NH_2 ; $CH_3CH_2NH_2$;
Methanamine Ethanamine



$$CH_3-\overset{NH_2}{\overset{|}{CH}}-CH_3$$

Propan-2-amine

$CH_3CH_2CH_2NH_2$;
Propan-1-amine

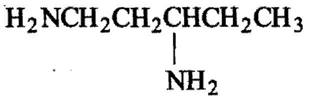


$$CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_2CH_3$$

Butan-2-amine

When two or more amino groups are present, words di-, tri-, etc., are used with position numbers.

$H_2NCH_2-CH_2NH_2$;
Ethane-1,2-diamine

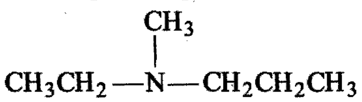


$$H_2NCH_2CH_2\underset{NH_2}{\underset{|}{CH}}CH_2CH_3$$

Pentane-1,3-diamine

Secondary or **tertiary amines** are named as *N*-substituted derivatives of primary amines. The largest group attached to nitrogen is taken as the alkyl group of the primary amine.

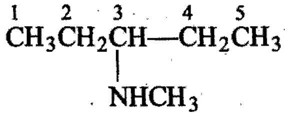
$CH_3CH_2NHCH_3$;
N-Methyl ethanamine



$$CH_3CH_2-\overset{CH_3}{\overset{|}{N}}-CH_2CH_2CH_3$$

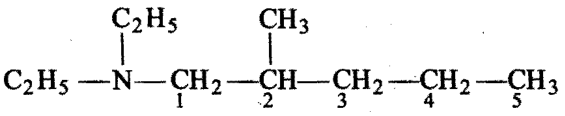
N-Ethyl-*N*-methyl propan-1-amine

$CH_3CH_2CH_2NH-CH_3$;
N-Methylpropan-1-amine



$$\overset{1}{CH_3}\overset{2}{CH_2}\underset{NHCH_3}{\underset{|}{\overset{3}{CH}}}-\overset{4}{CH_2}\overset{5}{CH_3}$$

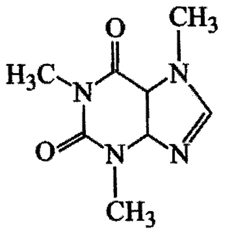
N-Methylpentan-3-amine



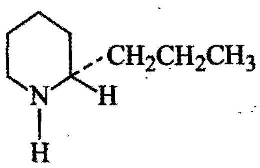
$$C_2H_5-\overset{C_2H_5}{\overset{|}{N}}-\underset{1}{CH_2}-\overset{CH_3}{\overset{|}{\underset{2}{CH}}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_3}$$

N,N-Diethyl-2-methyl pentan-1-amine

Caffeine and coniine are some of the naturally occurring amines.

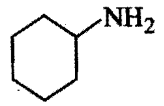


Caffeine

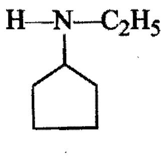


Coniine

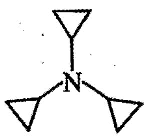
Cyclic primary, secondary and tertiary amines can be named as,



Cyclohexanamine



N-Ethyl cyclo-pentanamine



N,N-Dicyclopropyl cyclopropanamine

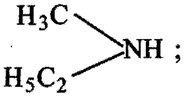
14.3 ISOMERISM

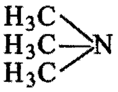
Amines are represented by a general formula, $C_nH_{2n+3}N$ and exhibit following types of isomerism:

1. Functional isomerism : This is due to the presence of different functional groups, *i.e.*, —NH_2 or >NH or ⋗N.

Molecular formula C_3H_9N represents three functional isomers.

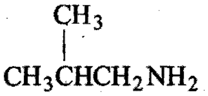
$CH_3CH_2CH_2NH_2$;
n-Propylamine
(Primary)1°


Ethyl methylamine
(Secondary)2°


Trimethylamine
(Tertiary)3°

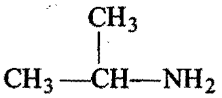
2. Chain isomerism : This is due to difference in the carbon skeleton of the alkyl group attached to the amino group.

$CH_3CH_2CH_2CH_2NH_2$;
Butan-1-amine
(*n*-Butylamine)

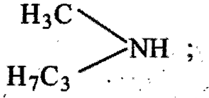

$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2NH_2$ $(C_4H_{11}N)$
2-Methyl propan-1-amine
(Isobutylamine)

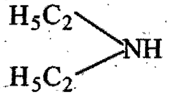
3. Position isomerism : This is due to the difference in the position of amino group in the carbon chain.

$CH_3CH_2CH_2NH_2$;
Propan-1-amine
(*n*-Propylamine)


$CH_3—\overset{CH_3}{\overset{|}{C}}H—NH_2$ (C_3H_9N)
Propan-2-amine
(Isopropylamine)

4. Metamerism : This is due to different alkyl groups attached to the same polyvalent functional group.


Methyl propylamine


Diethylamine

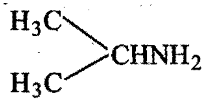
$(C_4H_{11}N)$

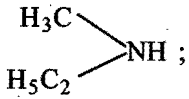
SOME SOLVED EXAMPLES

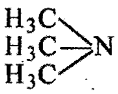
Problem 1. *Write the names and structures of four isomeric amines having the molecular formula* C_3H_9N.

Solution :

(i) $CH_3CH_2CH_2NH_2$;
n-Propylamine

(ii)

Isopropylamine

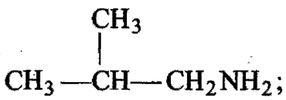
(iii)

Ethyl methylamine

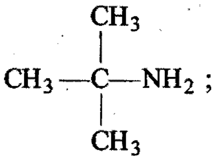
(iv)

Trimethylamine

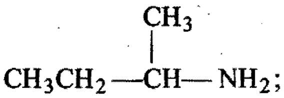
Problem 2. *Write the structures of eight isomeric amines having the molecular formula* $C_4H_{11}N$.

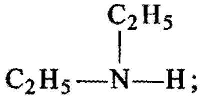
Solution :

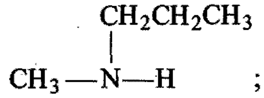
(i) $CH_3CH_2CH_2CH_2NH_2$;

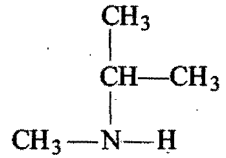
(ii)

$CH_3—\overset{CH_3}{\overset{|}{C}}H—CH_2NH_2$;

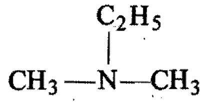
(iii)

$CH_3—\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}—NH_2$;

(iv)

$CH_3CH_2—\overset{CH_3}{\overset{|}{C}}H—NH_2$;

(v)

$C_2H_5—\overset{C_2H_5}{\overset{|}{N}}—H$;

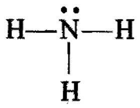
(vi)

$CH_3—\overset{CH_2CH_2CH_3}{\overset{|}{N}}—H$;

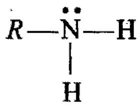
(vii)

$CH_3—\overset{\overset{CH_3}{|}}{\overset{CH—CH_3}{\overset{|}{N}}}—H$;

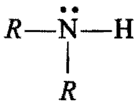
(viii)

$CH_3—\overset{C_2H_5}{\overset{|}{N}}—CH_3$

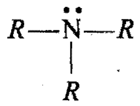
14.4 BASIC NATURE OF AMINES

Amines like ammonia are basic in nature. The basic nature is due to the presence of an unshared pair (lone pair) of electrons on nitrogen atom. This lone pair of electrons is available for the formation of a new bond with a proton or Lewis acids.


Ammonia


Primary amine (1°)


Secondary amine (2°)


Tertiary amine (3°)

Amines are weak bases as they combine partially with the water to form hydroxyl ions.

$$R—NH_2 + H_2O \rightleftharpoons R—\overset{+}{N}H_3 + OH^-$$

Alkyl ammonium ion

Applying law of mass action,

$$K_b = \frac{[R—\overset{+}{N}H_3][OH^-]}{[R—NH_2]}$$

(Where, K_b is equilibrium constant of the base or **basicity constant.**)

[Concentration of water is considered constant as it is present in large amounts.]

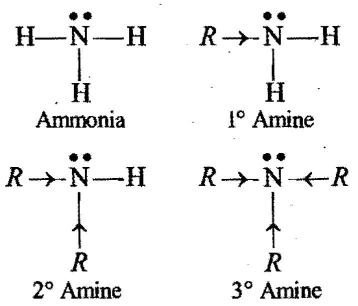
The value of K_b describes the relative strength of the bases. **Strong bases have higher values of K_b while weak bases have low values.**

A more convenient method of expressing the basic strength of amines is in terms of pK_b values ($pK_b = -\log K_b$). Smaller the value of pK_b, more is the basic strength of amine. The K_b and pK_b values of some amines are given below:

Basicity constants of some amines

Compound	K_b	pK_b
Ammonia, NH_3	1.8×10^{-5}	4.75
1° Amines		
Methylamine, CH_3NH_2	4.4×10^{-4}	3.35
Ethylamine, $C_2H_5NH_2$	5.1×10^{-4}	3.29
2° Amines		
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}	3.27
Diethylamine, $(C_2H_5)_2NH$	1.1×10^{-3}	2.95
3° Amines		
Trimethylamine, $(CH_3)_3N$	6.0×10^{-5}	4.22
Triethylamine, $(C_2H_5)_3N$	5.6×10^{-4}	3.25
Aromatic amines		
Aniline, $C_6H_5NH_2$	4.2×10^{-10}	9.38
N-Methylaniline, $C_6H_5NHCH_3$	5.0×10^{-10}	9.30
N,N-Dimethylaniline, $C_6H_5N(CH_3)_2$	11.5×10^{-10}	8.92
Benzylamine, $C_6H_5CH_2NH_2$	2.0×10^{-5}	4.70

(i) Alkylamines are stronger bases than ammonia: Alkylamines (1°, 2° and 3°) are stronger bases than ammonia. This can be explained in terms of electron releasing inductive effect of alkyl group. As a result, the electron density on the nitrogen atom increases and thus, they can donate the lone pair of electrons more easily than ammonia.



The electron releasing effect is maximum in tertiary amines and minimum in primary amines **(in gas phase).**

$$3° \text{ Amine} > 2° \text{ Amine} > 1° \text{ Amine} > NH_3$$

However, the actual order of basicity **(in aqueous solution)** in the case of lower members is found to be as:

$$2° \text{ Amine} > 1° \text{ Amine} > 3° \text{ Amine} > NH_3$$

$$i.e., (CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

If, however, the alkyl group is bigger than CH_3 group, *i.e.*, ethyl, propyl, etc., there will be some steric hindrance to H-bonding. As a result, the stability due to *+I* effect predominates over the stability due to H-bonding and hence 3° amines become more basic than 1° amines. In other words, the overall decreasing strength of ethylamine in aqueous medium is:

$$\underset{2°}{(C_2H_5)_2NH} > \underset{3°}{(C_2H_5)_3N} > \underset{1°}{C_2H_5NH_2}$$

In fact, the basic strength in aqueous solution depends not only upon electron releasing effect but also upon steric effect and hydration effect.

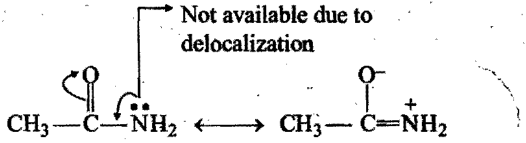
(a) Steric effect : The crowding of alkyl groups cover nitrogen atoms from all sides and thus, makes the approach and bonding by a proton relatively difficult which results the maximum steric strain in tertiary amines. The electrons are there but the path is blocked, resulting the reduced in its basicity.

The order of basic nature of various amines has been found to vary with the nature of alkyl groups.

Alkyl group	Relative strength
CH_3-	$R_2NH > RNH_2 > R_3N > NH_3$
C_2H_5-	$R_2NH > R_3N > RNH_2 > NH_3$

Note: 1. Aniline is less basic than ammonia. The phenyl group exerts *–I* (inductive) effect, *i.e.*, it withdraws electrons. This results to the lower availability of electrons on nitrogen for protonation.

2. Ethylamine and acetamide both contain an amino group but acetamide does not show basic nature. This is because lone pair of electrons on nitrogen is delocalised by resonance with the carbonyl group which makes it less available for protonation.



3. The compounds with least '*s*' character (sp^3-hybridized) is most basic and with more '*s*' character (*sp*-hybridized) is least basic. Examples in decreasing order of basicity are:

(i) $\underset{(sp^3)}{CH_3\ddot{N}H_2} > \underset{(sp^2)}{CH_3-\ddot{N}=CHCH_3} > \underset{(sp)}{CH_3-C\equiv\ddot{N}}$

(ii) $CH_3CH_2CH_2NH_2 > H_2C=CHCH_2NH_2 > HC\equiv CCH_2NH_2$

(iii) $(CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2$
Electron withdrawing (C_6H_5-) groups decreases electron density on nitrogen atom and thereby decreasing basicity.

(iv) $(CH_3)_2NH > CH_3NH_2 > C_6H_5NHCH_3 > C_6H_5NH_2$

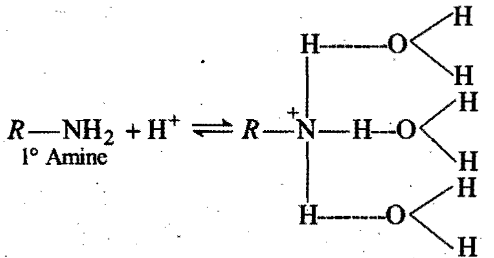
(v) $CH_3CH_2NH_2 > HO(CH_2)_3NH_2 > HO(CH_2)_2NH_2$
Electron withdrawing inductive effect of the —OH group decreases the electron density on nitrogen. This effect diminishes with distance from the amino group.

(vi) $CH_3CH_2NH_2 > C_6H_5CONH_2 > CH_3CONH_2$

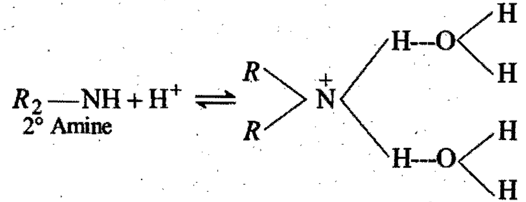
(b) Hydration effect : It also depends upon the stability of the conjugated acid formed by accepting a proton from the solution. The hydration effect refers to the stabilization of the protonated amine by water molecules. The water molecules form H-bonding with the protonated amine and release energy (called hydration energy).

Now greater the extent of H-bonding in protonated amine, more will be its stabilization, *i.e.*, 1° amine is the most stable since, it has three H-atoms which can form H-bonds with H_2O (maximum hydration) and consequently, greater will be the basic strength of the corresponding amine. The 2° amine is less stable since, it has two H-atoms (less hydration) while that of 3° amines is the least stable since, it has only one H-atom (least hydration) which can form H-bonds with H_2O. Therefore, the basic strength of amines in aqueous solution should follow the order.

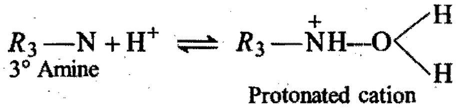
$R—NH_2$ (1° Amine) > R_2NH (2° Amine) > R_3N (3° Amine)



Protonated cation
of 1° amine (Most stable)



Protonated cation
of 2° amine (Less stable)



Protonated cation
of 3° amine (Least stable)

Thus, it was observed that 3° amine is least stable while it has maximum $+I$ effect and 1° amine is most stable inspite of minimum $+I$ effect. In actual practice, these two opposing factors balance each other in case of 2° amine. This makes 2° amine to be still more basic than 1° amine.

Hence, it may be concluded that it is a combination of electron releasing, H-bonding and steric factors that determine the stability of the ammonium cations in solution and thereby resulting in the basic strength order of aliphatic amines as:

Secondary > tertiary > primary amines

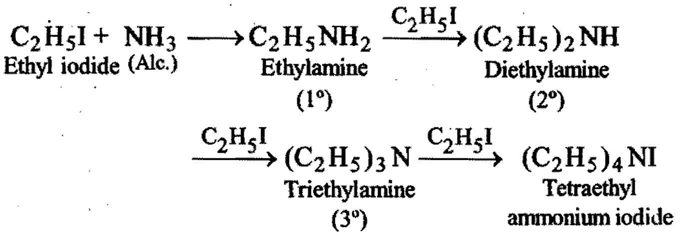
Problem 3. *Trimethylamine is less basic than dimethylamine or methylamine. Explain why it is so?*

Solution : Methyl groups are electron releasing groups. Although in trimethylamine, the electron density on nitrogen is more in comparison to dimethylamine or methylamine yet it is less basic because crowding of three methyl groups makes it difficult for a proton to approach the nitrogen in order to form a bond. Thus, the electrons are there in trimethylamine but the path is blocked.

14.5 GENERAL METHODS OF PREPARATION

Methods Yielding Mixture of Amines (Primary, Secondary and Tertiary)

1. Hofmann's ammonolysis method : A mixture of amines (primary, secondary and tertiary amines) along with quaternary compound is formed when alkyl halide is heated with alcoholic ammonia in a sealed tube at 100°C.

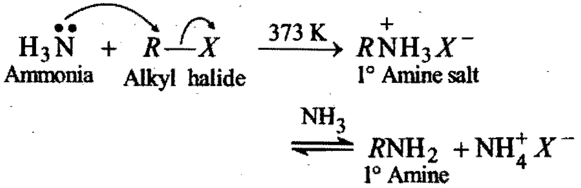


$$\underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{(Alc.)}}{NH_3} \longrightarrow \underset{\substack{\text{Ethylamine}\\(1°)}}{C_2H_5NH_2} \xrightarrow{C_2H_5I} \underset{\substack{\text{Diethylamine}\\(2°)}}{(C_2H_5)_2NH}$$

$$\xrightarrow{C_2H_5I} \underset{\substack{\text{Triethylamine}\\(3°)}}{(C_2H_5)_3N} \xrightarrow{C_2H_5I} \underset{\substack{\text{Tetraethyl}\\\text{ammonium iodide}}}{(C_2H_5)_4NI}$$

This reaction is a typical example of **nucleophilic substitution reaction.**

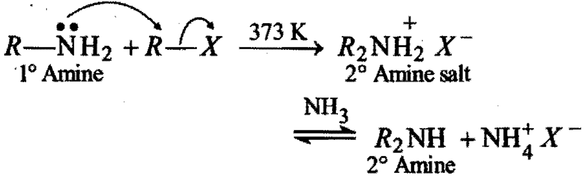
Mechanism : (a) The mechanism involves the nucleophilic attack of $\ddot{N}H_3$ molecule (through lone pair) on $R—X$. Primary (1°) amine salt is formed which reacts with ammonia to give 1° amines and ammonium halide as follows:



$$\underset{\text{Ammonia}}{H_3\ddot{N}} + \underset{\text{Alkyl halide}}{R—X} \xrightarrow{373\text{ K}} \underset{\text{1° Amine salt}}{R\overset{+}{N}H_3X^-}$$

$$\xrightleftharpoons{NH_3} \underset{\text{1° Amine}}{RNH_2} + NH_4^+X^-$$

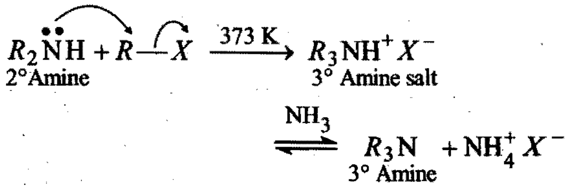
(b) The primary (1°) amine formed now acts as the nucleophile and reacts with another molecule of $R—X$ to form 2° (sec-) amine.



$$\underset{\text{1° Amine}}{R—\ddot{N}H_2} + R—X \xrightarrow{373\text{ K}} \underset{\text{2° Amine salt}}{R_2\overset{+}{N}H_2\,X^-}$$

$$\xrightleftharpoons{NH_3} \underset{\text{2° Amine}}{R_2NH} + NH_4^+X^-$$

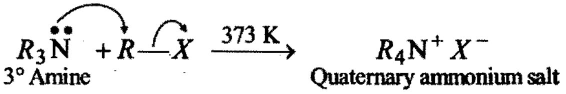
(c) The reaction is repeated to form tertiary (3°) and quaternary ammonium salt as follows:



$$\underset{\text{2°Amine}}{R_2\ddot{N}H} + R—X \xrightarrow{373\text{ K}} \underset{\text{3° Amine salt}}{R_3NH^+X^-}$$

$$\xrightleftharpoons{NH_3} \underset{\text{3° Amine}}{R_3N} + NH_4^+X^-$$

(d)



$$\underset{\text{3° Amine}}{R_3\ddot{N}} + R—X \xrightarrow{373\text{ K}} \underset{\text{Quaternary ammonium salt}}{R_4N^+X^-}$$

So, the ammonia molecule in the first step and amine molecules in the subsequent steps act as nucleophiles.

The primary amine may be obtained in a good yield by using a large excess of ammonia. The process is also termed as **ammonolysis of alkyl halides.** The amines being basic at once combine with HI produced during reaction to form salts.

The reactivity of various halides in this reaction is:

$R—I > R—Br > R—Cl$ and 1° > 2° > 3° alkyl halide.

Tertiary butyl bromide (3°) on treatment with NH_3 (base) prefers to undergo elimination rather than substitution.

2. Ammonolysis of alcohols : A mixture of amines is also obtained when the mixture containing vapours of alcohol and ammonia are passed over heated alumina (Al_2O_3) or thoria (ThO_2) at 350°C.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + NH_3 \longrightarrow \underset{\text{1°Amine}}{C_2H_5NH_2} \xrightarrow{C_2H_5OH}$$

$$\underset{\text{2°Amine}}{(C_2H_5)_2NH} \xrightarrow{C_2H_5OH} \underset{\text{3°Amine}}{(C_2H_5)_3N}$$

Primary amine may be obtained in a good yield by using a large excess of ammonia.

Methods Yielding Primary Amines

3. Reduction of nitro compounds : Primary amines can be obtained by the reduction of nitro alkanes with Sn/HCl; Zn/HCl; H_2/Ni; $LiAlH_4$ in dry ether; Raney Ni or Pt or Pd as catalyst at room temperature.

$$R—NO_2 + 6[H] \xrightarrow[\substack{\text{Zn/HCl or Ni}\\ \text{or } LiAlH_4}]{\text{Sn/HCl or}} RNH_2 + 2H_2O$$

$$\underset{\text{Nitroethane}}{C_2H_5—NO_2} + 6[H] \xrightarrow[\text{or Pt}]{\text{Sn/HCl}} \underset{\text{Ethanamine}}{C_2H_5NH_2} + 2H_2O$$

4. Reduction of nitriles (Mendius reaction) : Primary amines can be prepared by reduction of **nitriles.** The reduction is done either catalytically with H_2 and Raney Ni or with sodium in alcohol or sodium amalgam and alcohol or with $LiAlH_4$.

$$\underset{\text{Alkyl nitrile}}{R—C\equiv N} + 4[H] \xrightarrow[\text{or } LiAlH_4]{H_2/\text{Raney Ni}} \underset{\text{1°Amine}}{R—CH_2NH_2}$$

$$\underset{\substack{\text{Methyl cyanide}\\ \text{(Acetonitrile)}}}{CH_3C\equiv N} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Ethanamine}}{CH_3—CH_2NH_2}$$

The start can be made from alcohol or alkyl halide.

$$\underset{\text{Alcohol}}{R—OH} \xrightarrow{SOCl_2} \underset{\text{Alkyl chloride}}{R—Cl} \xrightarrow{KCN} \underset{\text{Alkyl nitrile}}{R—CN} \xrightarrow{LiAlH_4} \underset{\text{Primary amine}}{RCH_2NH_2}$$

This sequence gives an amine containing one more carbon atom than alcohol.

5. By reduction of amides : Primary amines having same number of carbon atoms can be obtained by the reduction of amides by $LiAlH_4$ or sodium and absolute alcohol.

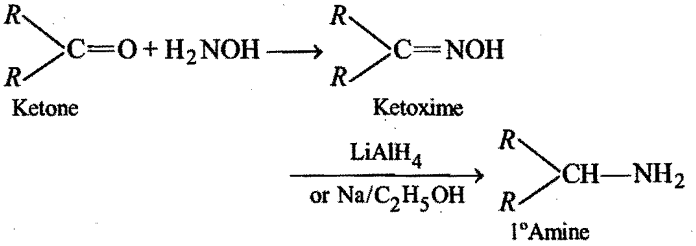
$$\underset{\text{1°Amide}}{RCONH_2} + 4[H] \xrightarrow[\text{or } Na + C_2H_5OH]{LiAlH_4/\text{ether}} \underset{\text{1°Amine}}{RCH_2NH_2}$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} + 4[H] \xrightarrow{LiAlH_4/\text{ether}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

6. By reduction of oximes : Primary amines can be formed by reduction of oximes. The reduction is done by H_2/Ni; sodium and absolute alcohol or $LiAlH_4$. The start can be made from an aldehyde or ketone.

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow{H_2NOH} \underset{\text{Aldoxime}}{RCH{=}NOH} \xrightarrow[\text{ether}]{LiAlH_4} \underset{\text{Primary amine}}{RCH_2NH_2}$$

$$\underset{\text{Acetaldoxime}}{CH_3CH{=}NOH} + 4[H] \xrightarrow[\text{or } LiAlH_4]{H_2/Ni} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$



7. Hofmann's bromamide reaction or degradation : By this method, the amide (—$CONH_2$) group is converted into primary amino (—NH_2) group. The amide is heated with bromine and concentrated aqueous or ethanolic KOH solution (or potassium hypobromite, KOBr).

$$\underset{\text{Amide}}{RCONH_2} + Br_2 + 4KOH \xrightarrow{\text{Heat}} \underset{\text{1°Amine}}{R—NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

For example,

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \xrightarrow{\text{Heat}} \underset{\text{Methylamine}}{CH_3NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

$$\underset{\text{Propanamide}}{CH_3CH_2CONH_2} + Br_2 + 4KOH \xrightarrow{\text{Heat}} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

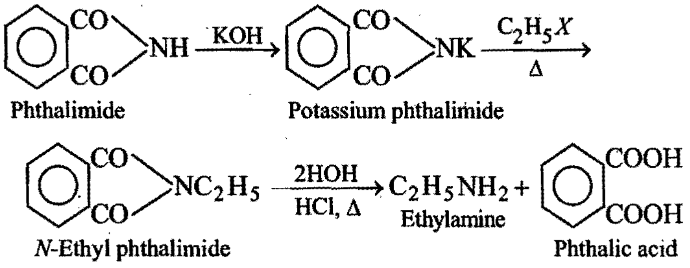
This is most convenient **laboratory method** to give pure amine containing one carbon atom less than amide (For mechanism see **Section 13.5**).

8. Gabriel phthalimide synthesis : This method involves the following three steps:

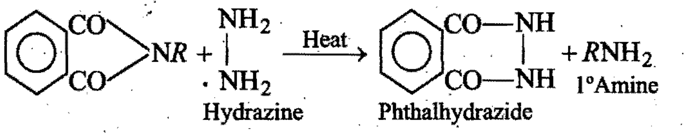
(a) Phthalimide is reacted with ethanolic solution of KOH to form potassium phthalimide.

(b) The potassium salt is treated with an alkyl halide.

(c) The product *N*-alkyl phthalimide is put to hydrolysis with dilute hydrochloric acid under pressure when pure primary amine is formed.

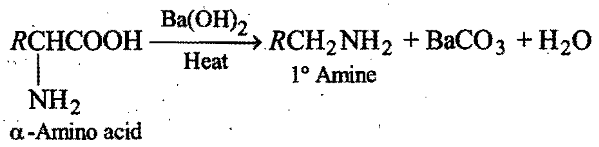


When hydrolysis is difficult, the *N*-alkyl phthalimide can be treated with hydrazine to give the required amine. This is called **hydrazinolysis** (cleavage by using hydrazine).

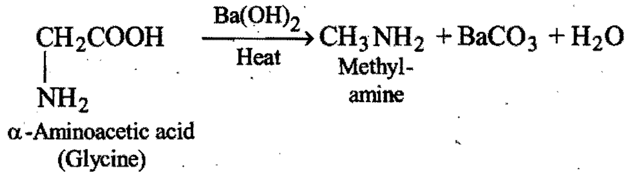


Note : (i) Only 1° amine (pure) can be prepared by Gabriel synthesis.
(ii) Aniline cannot be prepared by this synthesis because aryl halides (C_6H_5Cl or C_6H_5Br) do not undergo nucleophilic substitution (*i.e.*, the cleavage of C—*X* bond in haloarene is quite difficult) with potassium phthalimide under ordinary conditions to give *N*-phenyl phthalimide.

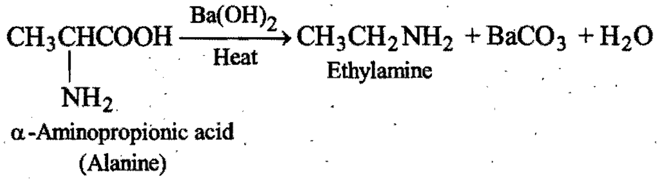
9. By decarboxylation of α-amino acids : Decarboxylation is done by distilling the amino acid with $Ba(OH)_2$.



$$\underset{\alpha\text{-Amino acid}}{R\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH} \xrightarrow[\text{Heat}]{Ba(OH)_2} \underset{1^\circ\text{ Amine}}{RCH_2NH_2} + BaCO_3 + H_2O$$



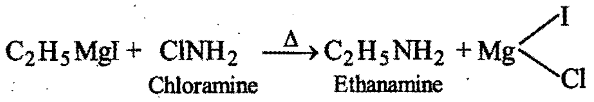
$$\underset{\substack{\alpha\text{-Aminoacetic acid}\\ \text{(Glycine)}}}{\underset{\displaystyle NH_2}{\underset{|}{CH_2}}COOH} \xrightarrow[\text{Heat}]{Ba(OH)_2} \underset{\text{Methyl-amine}}{CH_3NH_2} + BaCO_3 + H_2O$$



$$\underset{\substack{\alpha\text{-Aminopropionic acid}\\ \text{(Alanine)}}}{CH_3\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH} \xrightarrow[\text{Heat}]{Ba(OH)_2} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + BaCO_3 + H_2O$$

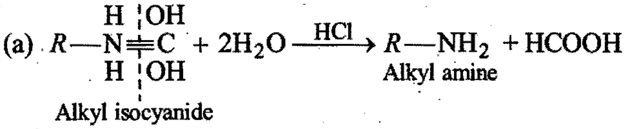
10. By double decomposition between Grignard reagent and chloramine :

$$RMgX + ClNH_2 \xrightarrow{\Delta} RNH_2 + MgXCl$$



$$C_2H_5MgI + \underset{\text{Chloramine}}{ClNH_2} \xrightarrow{\Delta} \underset{\text{Ethanamine}}{C_2H_5NH_2} + Mg\begin{matrix}I\\Cl\end{matrix}$$

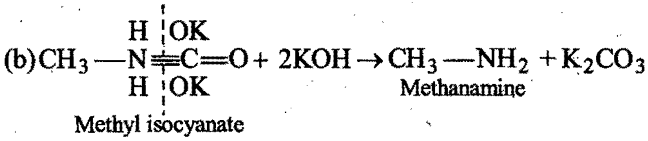
11. By hydrolysis of isocyanides or isocyanates :



$$\text{(a) } \underset{\text{Alkyl isocyanide}}{R—N\!\equiv\!C} \begin{matrix}H\,¦\,OH\\ \\ H\,¦\,OH\end{matrix} + 2H_2O \xrightarrow{HCl} \underset{\text{Alkyl amine}}{R—NH_2} + HCOOH$$

$$\underset{\text{Ethyl isocyanide}}{C_2H_5NC} + 2H_2O \xrightarrow{HCl} \underset{\text{Ethylamine}}{C_2H_5NH_2} + HCOOH$$

$$\underset{\text{Aceto isonitrile}}{CH_3—NC} + 2HOH \xrightarrow{H^+} \underset{\text{Methanamine}}{CH_3—NH_2} + HCOOH$$



$$\text{(b) } \underset{\text{Methyl isocyanate}}{CH_3—N\!=\!C\!=\!O} \begin{matrix}H\,¦\,OK\\ \\ H\,¦\,OK\end{matrix} + 2KOH \rightarrow \underset{\text{Methanamine}}{CH_3—NH_2} + K_2CO_3$$

$$\underset{\text{Ethyl isocyanate}}{C_2H_5—NCO} + 2KOH \longrightarrow \underset{\text{Ethanamine}}{C_2H_5—NH_2} + K_2CO_3$$

12. By Schmidt reaction :

$$\underset{\text{Acid}}{R—COOH} + \underset{\text{Hydrazoic acid}}{N_3H} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Alkyl amine}}{R—NH_2} + N_2 + CO_2$$

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} + N_3H \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + N_2 + CO_2$$

In this reaction, the acylazide ($R—CON_3$) and alkyl isocyanate ($R—NCO$) are formed as an intermediate.

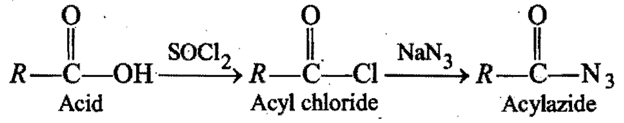
(i) $R—COOH + N_3H \longrightarrow \underset{\text{Acylazide}}{RCON_3} + H_2O$

(ii) $\underset{\text{Acylazide}}{RCON_3} \xrightarrow[\text{(curtius rearrangement)}]{C_6H_6 \text{ or } CHCl_3\ \Delta} \underset{\text{Alkyl isocyanate}}{R—N\!=\!C\!=\!O} + N_2$

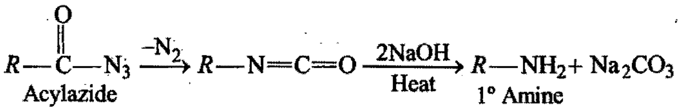
(iii) $\underset{\text{Alkyl isocyanate}}{R—N\!=\!C\!=\!O} + H_2O \longrightarrow \underset{\text{Alkyl amine}}{R—NH_2} + CO_2$

The overall reaction which proceeds by the elimination of nitrogen from acylazide followed by acidic or alkaline hydrolysis to yield primary amine containing one carbon less, is called **Curtius degradation.**

This method uses acid chloride to prepare primary amine through acylazide.

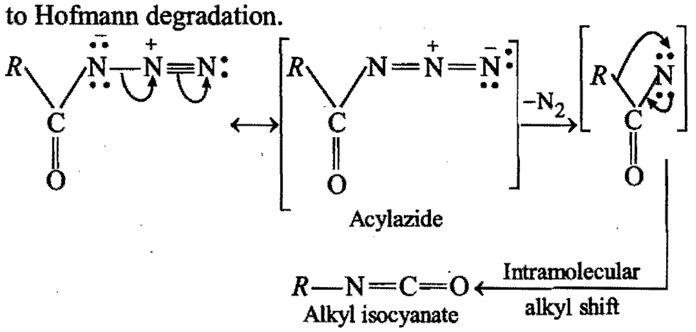


$$\underset{\text{Acid}}{R—\overset{\overset{\displaystyle O}{\|}}{C}—OH} \xrightarrow{SOCl_2} \underset{\text{Acyl chloride}}{R—\overset{\overset{\displaystyle O}{\|}}{C}—Cl} \xrightarrow{NaN_3} \underset{\text{Acylazide}}{R—\overset{\overset{\displaystyle O}{\|}}{C}—N_3}$$

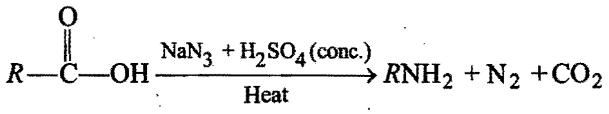


$$\underset{\text{Acylazide}}{R—\overset{\overset{\displaystyle O}{\|}}{C}—N_3} \xrightarrow{-N_2} R—N\!=\!C\!=\!O \xrightarrow[\text{Heat}]{2NaOH} \underset{1^\circ\text{ Amine}}{R—NH_2} + Na_2CO_3$$

The mechanism of **Curtius rearrangement** is very similar to Hofmann degradation.

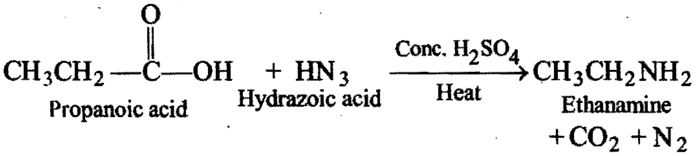


Schmidt reaction converts $R—COOH$ to $R—NH_2$, which is a modification of curtius degradation. In this reaction a carboxylic acid is warmed with sodium azide ($Na^+N_3^-$) and conc. H_2SO_4. The carboxylic acid is directly converted to the primary amine without the necessity of isolating alkyl azide.



$$R—\overset{\overset{\displaystyle O}{\|}}{C}—OH \xrightarrow[\text{Heat}]{NaN_3 + H_2SO_4\text{(conc.)}} RNH_2 + N_2 + CO_2$$

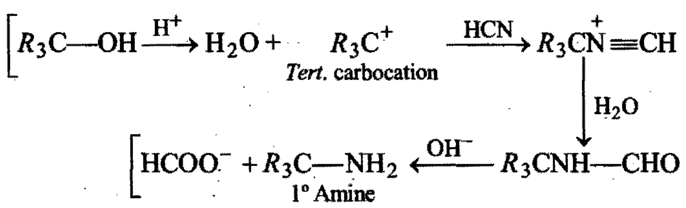
$(NaN_3 + H_2SO_4 \longrightarrow N_3H + NaHSO_4)$



$$\underset{\text{Propanoic acid}}{CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Hydrazoic acid}}{HN_3} \xrightarrow[\text{Heat}]{\text{Conc. } H_2SO_4} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + CO_2 + N_2$$

13. By Ritter reaction : It is a good method for preparing primary amines having a tertiary alkyl group. Thus, tertiary butyl alcohol (or alkene) is treated with hydrocyanic acid (or alkyl cyanide) in the presence of conc. sulphuric acid to give *tert*. butylamine.

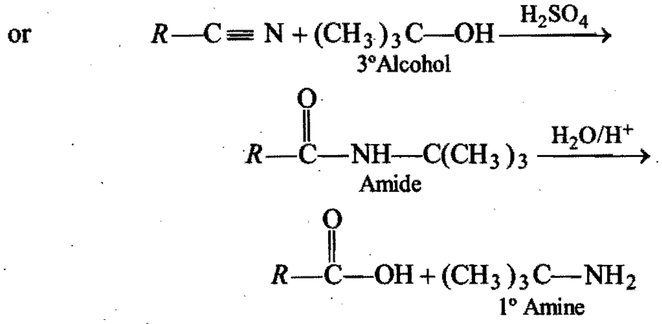
$$\underset{\substack{\textit{Tert.}\text{ butyl alcohol}\\(3^\circ\text{ Alcohol})}}{(CH_3)_3C-OH} + H_2SO_4 + HCN \longrightarrow \underset{\substack{\textit{Tert.}\text{ butylamine}\\(1^\circ\text{ Amine})}}{(CH_3)_3C-NH_2}$$



$$\left[R_3C-OH \xrightarrow{H^+} H_2O + \underset{\textit{Tert.}\text{ carbocation}}{R_3C^+} \xrightarrow{HCN} R_3C\overset{+}{N}{\equiv}CH\right.$$

$$\Big\downarrow H_2O$$

$$\left[HCOO^- + \underset{1^\circ\text{ Amine}}{R_3C-NH_2} \xleftarrow{OH^-} R_3CNH-CHO\right.$$

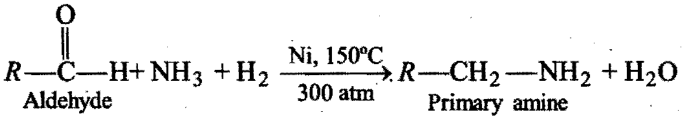


or $$R-C\equiv N + \underset{3^\circ\text{Alcohol}}{(CH_3)_3C-OH} \xrightarrow{H_2SO_4}$$

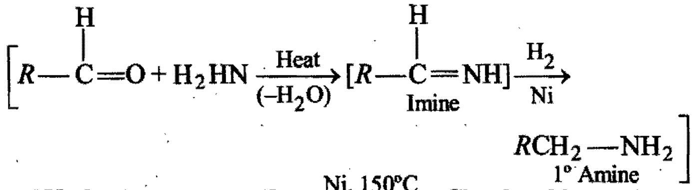
$$\underset{\text{Amide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-NH-C(CH_3)_3} \xrightarrow{H_2O/H^+}$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + \underset{1^\circ\text{ Amine}}{(CH_3)_3C-NH_2}$$

14. Reductive amination of aldehydes and ketones : Aldehyde or ketone when reduced catalytically with nickel, H_2/Raney Ni or $NaBH_3CN$ (sodium cyanoborohydride) in presence of excess of ammonia at about 150°C under pressure (300 atm) forms primary amine through the intermediate formation of an imine.

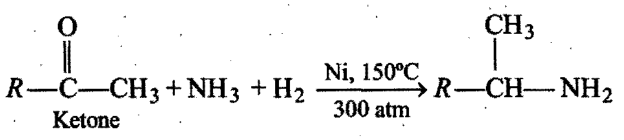


$$\underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H} + NH_3 + H_2 \xrightarrow[\text{300 atm}]{\text{Ni, 150°C}} \underset{\text{Primary amine}}{R-CH_2-NH_2} + H_2O$$

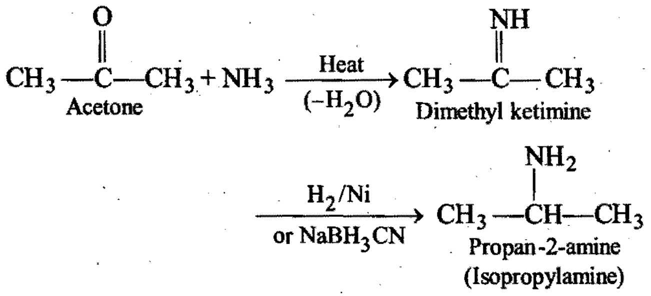


$$\left[R-\overset{\overset{\displaystyle H}{|}}{C}{=}O + H_2HN \xrightarrow[(-H_2O)]{\text{Heat}} \underset{\text{Imine}}{[R-\overset{\overset{\displaystyle H}{|}}{C}{=}NH]} \xrightarrow[\text{Ni}]{H_2} \underset{1^\circ\text{ Amine}}{RCH_2-NH_2}\right]$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + NH_3 + H_2 \xrightarrow[\text{atm. pressure}]{\text{Ni, 150°C}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$



$$\underset{\text{Ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + NH_3 + H_2 \xrightarrow[\text{300 atm}]{\text{Ni, 150°C}} R-\overset{\overset{\displaystyle CH_3}{|}}{CH}-NH_2$$



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + NH_3 \xrightarrow[(-H_2O)]{\text{Heat}} \underset{\text{Dimethyl ketimine}}{CH_3-\overset{\overset{\displaystyle NH}{\|}}{C}-CH_3}$$

$$\xrightarrow[\text{or } NaBH_3CN]{H_2/Ni} \underset{\substack{\text{Propan-2-amine}\\\text{(Isopropylamine)}}}{CH_3-\overset{\overset{\displaystyle NH_2}{|}}{CH}-CH_3}$$

This reaction probably takes place through the formation of an imine (Schiff's base).

The primary amines can also be converted into secondary or tertiary amines by the following steps:

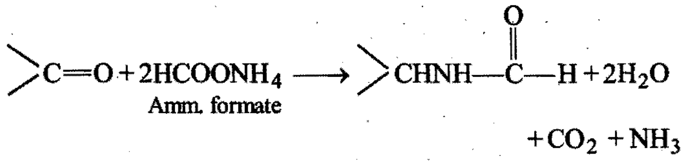
$$R-CHO + R'NH_2 \xrightarrow[NaBH_3CN]{H_2/\text{Ni or}} \underset{2^\circ\text{ Amine}}{RCH_2NHR'}$$

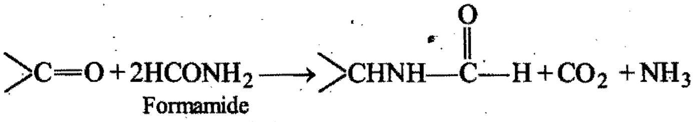
$$RNH_2 + 2H_2C{=}O + 2HCOOH \rightarrow \underset{3^\circ\text{ Amine}}{RN(CH_3)_2} + 2H_2O + 2CO_2$$

15. By reduction of azide with $NaBH_4$:

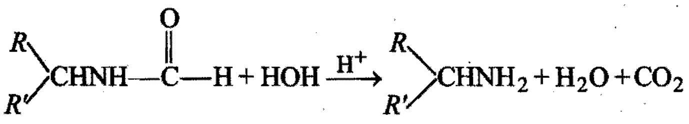
$$\underset{\substack{\text{Alkyl halide}\\(1^\circ\text{ or }2^\circ)}}{R-X} + \underset{\substack{\text{Sodium}\\\text{azide}}}{NaN_3} \longrightarrow \underset{\substack{\text{Alkyl}\\\text{azide}}}{RN_3} \xrightarrow[H_2O]{NaBH_4} \underset{(1^\circ)\text{ Amine}}{RNH_2}$$

16. By Leuckart reaction : Aldehydes or ketones react with ammonium formate or with formamide to give formyl derivative of primary amine.

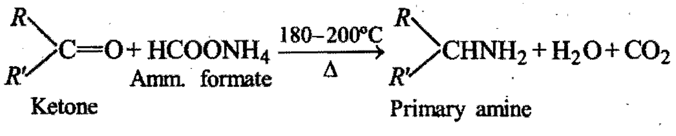




These formyl derivatives are readily hydrolysed by acid to yield primary amine.



This is called Leuckart reaction, *i. e.*,



17. By the action of ammonia on alkenes : Ethylamine is obtained by heating a mixture of ethylene and ammonia at 450°C under 20 atmospheric pressure in presence of cobalt catalyst **(commercial preparation).**

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + NH_3 \xrightarrow[\text{450°C, 20 atm.}]{\text{Cobalt catalyst}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

Methods Yielding Secondary Amines

1. Reaction of primary amines with alkyl halides : A primary amine is heated with calculated quantity of alkyl halide when dialkyl ammonium salt is formed. It is then treated with NaOH solution to recover free secondary amine.

$$R—NH_2 + R—X \longrightarrow R_2NH + HX \longrightarrow R_2\overset{+}{N}H_2\overset{-}{X}$$

$$R_2\overset{+}{N}H_2\overset{-}{X} + NaOH \longrightarrow \underset{\text{Secondary amine}}{R_2NH} + H_2O + NaX$$

$$\underset{\text{Methylamine}}{CH_3NH_2} + CH_3I \xrightarrow{\Delta} \underset{\text{Dimethylamine}}{CH_3NHCH_3} + HI$$

2. Reduction of *N*-substituted amides : Reduction of *N*-substituted amides with $LiAlH_4$ yield secondary amines.

Alkyl β-amino ketones are formed by the action of ketone with formaldehyde and NH_3 (or primary or secondary amines).

The product is referred to as Mannich base and the reaction is called **Mannich Reaction.**

$$CH_3COCH_3 + HCHO + RNH_2 \xrightarrow{\text{Heat}} CH_3COCH_2CH_2NHR$$

Which can be reduced to alkyl amines.

$$\underset{N\text{-Alkyl acid amide}}{R—CONHR'} + 4[H] \xrightarrow{LiAlH_4} \underset{2^\circ\text{ Amine}}{RCH_2NHR'} + H_2O$$

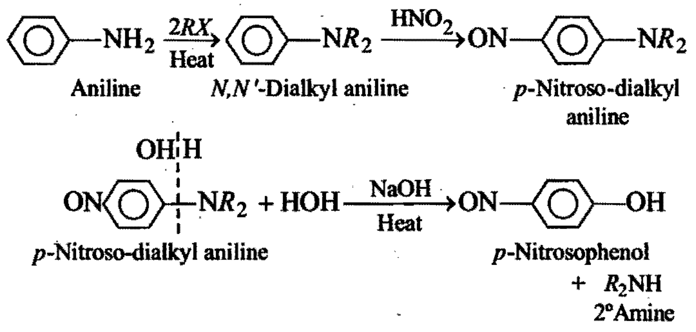
3. Reduction of isonitriles : Secondary amines are formed when isonitriles are reduced with hydrogen in presence of Pt-catalyst or sodium in presence of alcohol or Raney Ni or $LiAlH_4$.

$$\underset{\text{Alkyl isocyanide}}{RN{\equiv}C} + 4[H] \xrightarrow[LiAlH_4]{\text{Pt or}} \underset{2^\circ\text{ Amine}}{RNHCH_3}$$

$$\underset{\text{Ethyl isocyanide}}{CH_3CH_2N \overset{\rightarrow}{=} C} + 4[H] \xrightarrow[\text{or } LiAlH_4]{\text{Raney Ni}} \underset{N\text{-Methyl ethanamine}}{CH_3CH_2NHCH_3}$$

Secondary amine formed by this method always possesses one $—CH_3$ group linked directly to nitrogen.

4. Reaction of *p*-nitroso dialkyl aniline with strong alkali solution : Pure secondary amine is formed when *p*-nitroso-dialkyl aniline is heated with NaOH or KOH solution.



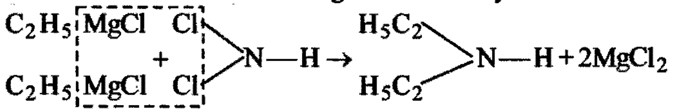
This is one of the best methods for preparing pure secondary amines.

5. Hydrolysis of dialkyl cyanamide : Pure secondary amine may be obtained by the hydrolysis of a dialkyl cyanamide with an acid or alkali.

$$[\underset{\text{Calcium cyanamide}}{CaN—CN} \xrightarrow{2NaOH} \underset{\text{Sodium cyanamide}}{Na_2N—CN} \xrightarrow{2RX} \underset{\text{Dialkyl cyanamide}}{R_2N—CN}]$$

$$R_2N—CN + 2HOH \xrightarrow{H^+} \underset{\text{Dialkylamine}}{R_2NH} + CO_2 + NH_3$$

6. Using Grignard reagent : Grignard reagent on treatment with dichloroamine gives secondary amine.



Methods Yielding Tertiary Amines

1. Reaction of alkyl halides with ammonia : When an alcoholic solution of ammonia is heated with excess of alkyl halide, a trialkyl ammonium salt is formed. This on treatment with dilute NaOH solution gives tertiary amine.

$$3RX + NH_3 \longrightarrow R_3N + 3HX \longrightarrow R_3\overset{+}{N}H\overset{-}{X}$$

$$R_3\overset{+}{N}H\overset{-}{X} + NaOH \longrightarrow R_3N + NaX + H_2O$$

2. Reduction of *N,N*-disubstituted amides : Reduction with $LiAlH_4$ is done. *N,N*-disubstituted amides on reduction form tertiary amines. The carbonyl group is converted into $—CH_2$ group.

$$RCONR'_2 \xrightarrow[4[H]]{LiAlH_4} RCH_2NR'_2 + H_2O$$

3. Decomposition of tetra-ammonium hydroxides : The tetra-alkyl ammonium hydroxides are formed when corresponding halides are treated with moist silver oxide.

$$R_4\overset{+}{N}\overset{-}{I} + AgOH \longrightarrow R_4\overset{+}{N}\overset{-}{O}H + AgI$$

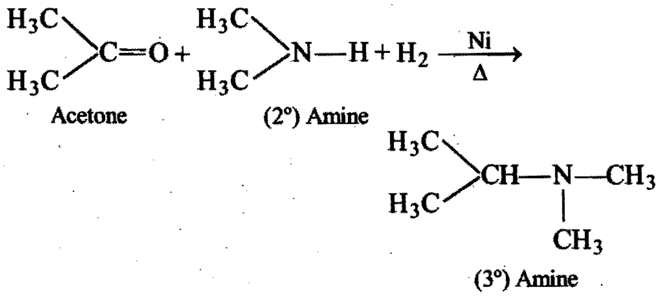
The hydroxides thus formed on heating decompose into tertiary amines. Tetramethyl ammonium hydroxide gives methyl alcohol as one of the products while all other tetra-alkyl ammonium hydroxides give an olefin and water besides tertiary amines.

$$(CH_3)_4NOH \xrightarrow{\Delta} (CH_3)_3N + CH_3OH$$

$$\underset{\text{Tetra ethyl ammonium hydroxide}}{(C_2H_5)_4NOH} \xrightarrow{\Delta} \underset{3^\circ\text{ Amine}}{(C_2H_5)_3N} + \underset{\text{Ethene}}{H_2C{=}CH_2} + H_2O$$

4. By reductive amination : This method is suitable for synthesis of both, secondary and tertiary amines.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{(1^\circ)\text{ Amine}}{C_2H_5NH_2} + H_2 \xrightarrow[\Delta]{Ni} \underset{(2^\circ)\text{ Amine}}{CH_3CH_2NHC_2H_5}$$



Separation of Mixture of Amines (1°, 2° and 3°)

When the mixture consists of salts of primary, secondary and tertiary amines along with quaternary salt, it is first distilled with KOH solution. The mixture of three amines distil over leaving behind non-volatile quaternary salt in the distillation flask.

$$R\mathrm{NH_2{\cdot}HI} \text{ or } R\overset{+}{\mathrm{N}}\mathrm{H_3}-\overset{-}{\mathrm{I}}+\overset{+}{\mathrm{K}}\overset{-}{\mathrm{OH}} \xrightarrow{\Delta} \underset{\substack{\text{Primary amine}\\ \text{(Volatile), Distillate}}}{R\mathrm{NH_2}}+\mathrm{KI}+\mathrm{H_2O}$$

$$R_2\mathrm{NH{\cdot}HI} \text{ or } R_2\overset{+}{\mathrm{N}}\mathrm{H_2}-\overset{-}{\mathrm{I}}+\overset{+}{\mathrm{K}}\overset{-}{\mathrm{OH}} \xrightarrow{\Delta} R_2\mathrm{NH}+\mathrm{KI}+\mathrm{H_2O}$$

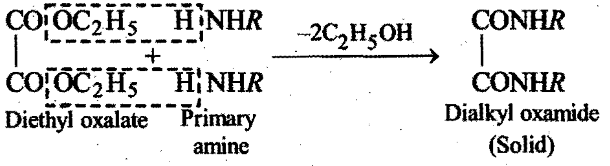
$$R_3\mathrm{N{\cdot}HI} \text{ or } R_3\overset{+}{\mathrm{N}}\mathrm{H}-\overset{-}{\mathrm{I}}+\overset{+}{\mathrm{K}}\overset{-}{\mathrm{OH}} \xrightarrow{\Delta} R_3\mathrm{N}+\mathrm{KI}+\mathrm{H_2O}$$

$R_4\overset{+}{\mathrm{N}}\overset{-}{\mathrm{I}}$ (non-volatile tetra-alkyl ammonium salt) has no reaction with KOH, however remains as residue.

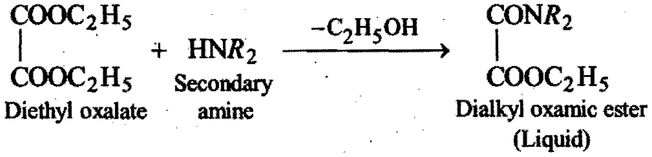
This mixture is separated into primary, secondary and tertiary amines by the application of following methods:

1. Fractional distillation : The boiling points of primary, secondary and tertiary amines are quite different, *i.e.*, the boiling point of $\mathrm{C_2H_5NH_2}$ is 17°C, $\mathrm{(C_2H_5)_2NH}$ is 56°C and $\mathrm{(C_2H_5)_3N}$ is 95°C and thus, these can be separated by fractional distillation. This method is used satisfactorily in industry.

2. Hofmann's method : The mixture of three amines is treated with diethyl oxalate (Hofmann's reagent). The primary amine forms a solid dialkyl oxamide, a secondary amine gives a liquid oxamic ester while tertiary amine does not react.

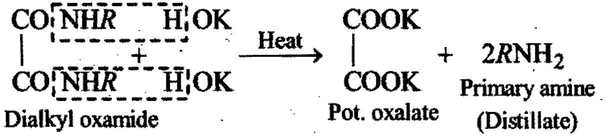


$$\underset{\text{Diethyl oxalate}}{\begin{array}{l}\mathrm{CO\,OC_2H_5}\\ |\\ \mathrm{CO\,OC_2H_5}\end{array}} + \underset{\text{Primary amine}}{\begin{array}{l}\mathrm{H\,NH}R\\ \\ \mathrm{H\,NH}R\end{array}} \xrightarrow{-2\mathrm{C_2H_5OH}} \underset{\substack{\text{Dialkyl oxamide}\\ \text{(Solid)}}}{\begin{array}{l}\mathrm{CONH}R\\ |\\ \mathrm{CONH}R\end{array}}$$



$$\underset{\text{Diethyl oxalate}}{\begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{COOC_2H_5}\end{array}} + \underset{\substack{\text{Secondary}\\ \text{amine}}}{\mathrm{HN}R_2} \xrightarrow{-\mathrm{C_2H_5OH}} \underset{\substack{\text{Dialkyl oxamic ester}\\ \text{(Liquid)}}}{\begin{array}{l}\mathrm{CON}R_2\\ |\\ \mathrm{COOC_2H_5}\end{array}}$$

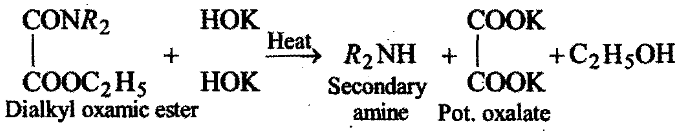
Primary amine is recovered when solid oxamide is heated with caustic potash solution and collected as distillate on distilling the reaction mixture.



$$\underset{\text{Dialkyl oxamide}}{\begin{array}{l}\mathrm{CO\,NH}R\\ |\\ \mathrm{CO\,NH}R\end{array}} + \begin{array}{l}\mathrm{H\,OK}\\ \\ \mathrm{H\,OK}\end{array} \xrightarrow{\text{Heat}} \underset{\text{Pot. oxalate}}{\begin{array}{l}\mathrm{COOK}\\ |\\ \mathrm{COOK}\end{array}} + \underset{\substack{\text{Primary amine}\\ \text{(Distillate)}}}{2R\mathrm{NH_2}}$$

The liquid (mixture of oxamic ester + tertiary amine) is subjected to fractional distillation when tertiary amine distils over.

The remaining liquid is distilled with KOH to recover secondary amine.



$$\underset{\text{Dialkyl oxamic ester}}{\begin{array}{l}\mathrm{CON}R_2\\ |\\ \mathrm{COOC_2H_5}\end{array}} + \begin{array}{l}\mathrm{HOK}\\ \\ \mathrm{HOK}\end{array} \xrightarrow{\text{Heat}} \underset{\substack{\text{Secondary}\\ \text{amine}}}{R_2\mathrm{NH}} + \underset{\text{Pot. oxalate}}{\begin{array}{l}\mathrm{COOK}\\ |\\ \mathrm{COOK}\end{array}} + \mathrm{C_2H_5OH}$$

3. Hinsberg's method : It involves the treatment of the mixture with benzene sulphonyl chloride, *i.e.*, **Hinsberg's reagent** ($\mathrm{C_6H_5SO_2Cl}$). The solution is then made alkaline with aqueous alkali to form sodium or potassium salt of monoalkyl benzene sulphonamide (soluble in alkali).

$$\underset{\substack{\text{Benzene}\\ \text{sulphonyl}\\ \text{chloride}}}{\mathrm{C_6H_5SO_2Cl}} + \underset{\text{Primary amine}}{\mathrm{HNH}R} \xrightarrow[-\mathrm{HCl}]{} \underset{\substack{N\text{-Alkyl benzene}\\ \text{sulphonamide}}}{\mathrm{C_6H_5SO_2NH}R} \xrightarrow{\mathrm{KOH}} \underset{\text{Soluble salt}}{\mathrm{C_6H_5SO_2N(K)}R}$$

The secondary amine forms *N,N*-dialkyl benzene sulphonamide which does not form any salt with KOH and remains as insoluble in alkali solution.

$$\mathrm{C_6H_5SO_2Cl} + \underset{\text{Sec. amine}}{\mathrm{HN}R_2} \xrightarrow[-\mathrm{HCl}]{} \underset{\substack{N,N\text{-Dialkyl}\\ \text{benzene}\\ \text{sulphonamide}}}{\mathrm{C_6H_5SO_2N}R_2} \xrightarrow{\mathrm{KOH}} \underset{\text{(Insoluble in alkali)}}{\text{No reaction}}$$

Tertiary amine does not react.

The above alkaline mixture of the amines is extracted with ether.

Two distinct layers are formed. Lower layer, the aqueous layer consists of potassium salt of *N*-alkyl benzene sulphonamide (primary amine) and upper layer, the etheral layer consists of *N,N*-dialkyl benzene sulphonamide (secondary amine) and tertiary amine.

Two layers are separated. The upper layer is fractionally distilled. One fraction obtained is tertiary amine and the other fraction is hydrolysed with concentrated HCl to recover secondary amine hydrochloride which gives free secondary amine on distillation with KOH.

$$\mathrm{C_6H_5SO_2N}R_2+\mathrm{HCl}+\mathrm{H_2O}\xrightarrow{\Delta}\mathrm{C_6H_5SO_2{\cdot}OH}+R_2\mathrm{NH{\cdot}HCl}$$

$$R_2\mathrm{NH{\cdot}HCl}+\mathrm{KOH}\xrightarrow{\Delta}\underset{\text{Sec. amine}}{R_2\mathrm{NH}}+\mathrm{KCl}+\mathrm{H_2O}$$

The aqueous layer is acidified with dil. HCl and hydrolysed by heating with conc. HCl. The hydrochloride formed is then distilled with KOH when primary amine distils over and collected.

$$\mathrm{C_6H_5SO_2N(K)}R + \underset{\text{(Dil.)}}{\mathrm{HCl}} \longrightarrow \underset{\substack{\text{Sulphonamide of}\\ \text{primary amine}}}{\mathrm{C_6H_5SO_2NH}R} + \mathrm{KCl}$$

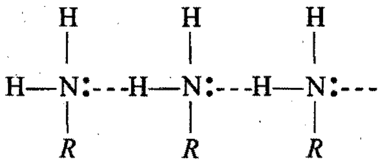
$$C_6H_5SO_2NHR + \underset{\text{(Conc.)}}{HCl} + H_2O \longrightarrow C_6H_5SO_2{\cdot}OH + \underset{\text{Primary amine hydrochloride}}{RNH_2{\cdot}HCl}$$

$$RNH_2\cdot HCl + KOH \xrightarrow{\Delta} RNH_2 + KCl + H_2O$$

Recently benzene sulphonyl chloride is replaced by *p*-toluene sulphonyl chloride (tosyl chloride) since, the substituted sulphonamides thus formed are stable solids which can be easily purified by crystallization.

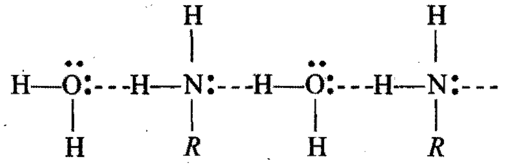
Physical properties : (i) Lower amines are gases or low boiling point liquids and possess a characteristic ammonia like smell (fishy odour). Higher members are solids.

(ii) The boiling points rise gradually with increase of molecular mass. Amines are polar compounds like NH_3 and have comparatively higher boiling points than non-polar compounds of similar molecular masses. This is due to the presence of intermolecular hydrogen bonding (except tertiary amines).



Hydrogen bonding in amines

(iii) Amines are soluble in water. This is due to hydrogen bonding between amine and water molecules. Amines are also soluble in benzene and ether.



Hydrogen bonding between amine and water molecules

Solubility decreases with increase of molecular mass.

Chemical properties : The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom. Amines are nucleophilic reagents as the lone pair of electrons can be donated to electron seeking reagents, (*i.e.*, electrophiles).

(i) Salt formation : Amines, being basic in nature, combine with mineral acids to form salts. The amine salts when treated with NaOH liberates parent amine.

$$\underset{\substack{\text{Alkylamine}\\(1^\circ)}}{R\text{—}NH_2} + HCl \longrightarrow RNH_2\cdot HCl \text{ or } \underset{\text{(Alkyl ammonium chloride)}}{R\overset{+}{N}H_3\overset{-}{Cl}}$$

$$RNH_3Cl + NaOH \longrightarrow RNH_2 + NaCl + H_2O$$

$$\underset{2^\circ\text{ amine}}{R_2NH} + HCl \rightarrow R_2\overset{+}{N}H_2Cl^- \xrightarrow{NaOH} R_2NH + NaCl + H_2O$$

$$\underset{\text{Dialkylamine}}{R_2NH} + H_2SO_4 \longrightarrow \underset{\text{Dialkyl ammonium sulphate}}{(R_2\overset{+}{N}H_2)_2SO_4^-}$$

$$\underset{3^\circ\text{ Amine}}{R_3N} + HCl \rightarrow R_3\overset{+}{N}HCl^- \xrightarrow{NaOH} R_3N + NaCl + H_2O$$

$$\underset{\text{Trialkylamine}}{R_3N} + HNO_3 \longrightarrow \underset{\text{Trialkyl ammonium nitrate}}{(R_3\overset{+}{N}H)NO_3^-}$$

Further, amine hydrochlorides, on heating undergo dialkylation.

$$\underset{\text{Trialkylamine hydrochloride}}{R_3N\cdot HCl} \xrightarrow{\Delta} \underset{\text{Dialkylamine}}{R_2NH} + RCl$$

$$R_2NH\cdot HCl \xrightarrow{\Delta} RNH_2 + RCl$$

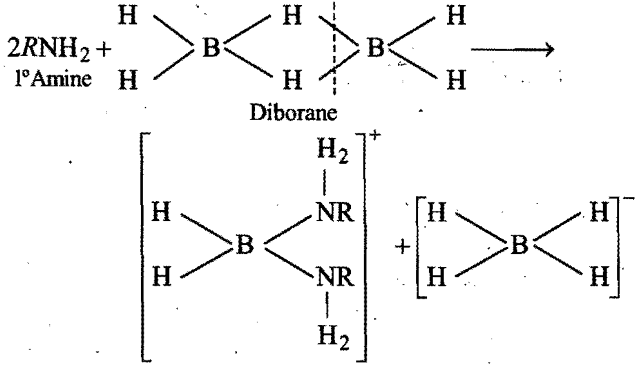
$$RNH_2\cdot HCl \xrightarrow{\Delta} NH_3 + RCl$$

$$2R\text{—}NH_2 + H_2SO_4 \longrightarrow \underset{\text{(Alkyl ammonium sulphate)}}{(R\overset{+}{N}H_3)_2SO_4^-}$$

With chlorauric acid, chloroplatinic acid and chlorostanic acid, amines form double salts:

$$RNH_2 + HAuCl_4 \longrightarrow RNH_2\cdot HAuCl_4$$
$$2RNH_2 + H_2PtCl_6 \longrightarrow (RNH_2)_2\cdot H_2PtCl_6$$
$$2RNH_2 + H_2SnCl_6 \longrightarrow (RNH_2)_2\cdot H_2SnCl_6$$

The reaction of diborane $(BH_3)_2$ with NH_3, 1° and 2° amines yield an ionic compound.



However, 3° amine forms an adduct with diborane.

$$\underset{3^\circ\text{Amine}}{(CH_3)_3N} + BH_3 \longrightarrow \underset{\text{Adduct}}{(CH_3)_3N \rightarrow BH_3}$$

All the amines are basic and they are stronger bases than ammonia (see **Section 14.4**).

(ii) Nature of aqueous solution : Amines combine with water to form alkyl ammonium hydroxides. These ionise to give hydroxide ions in solution, *i.e.*, the aqueous solutions of amines are **basic in nature.**

$$\underset{1^\circ\text{Amine}}{RNH_2} + HOH \rightleftharpoons R\overset{+}{N}H_3OH^- \rightleftharpoons [RNH_3]^+ + OH^-$$

$$\underset{2^\circ\text{Amine}}{R_2NH} + HOH \rightleftharpoons R_2\overset{+}{N}H_2OH^- \rightleftharpoons [R_2NH_2]^+ + OH^-$$

$$\underset{3^\circ\text{Amine}}{R_3N} + HOH \rightleftharpoons R_3\overset{+}{N}HOH^- \rightleftharpoons [R_3NH]^+ + OH^-$$

The aqueous solutions of amines behave like NH_4OH and give precipitates of iron, chromium and aluminium as hydroxides when their salts are treated with it and also blue solution with copper sulphate.

$$3RNH_3OH + FeCl_3 \longrightarrow \underset{\text{Brown ppt.}}{Fe(OH)_3} + 3RNH_3Cl$$

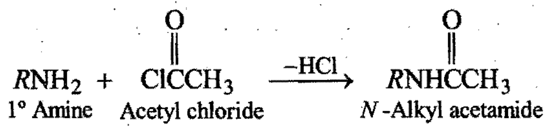
(iii) Reaction with alkyl halides (Alkylation) : The hydrogen atoms of the amino group are successively replaced by alkyl groups when amines are treated with alkyl halides. Finally, tertiary amine adds one more molecule of alkyl halide to form a quaternary compound.

$$\underset{\text{Pri. amine}}{RNH_2} \xrightarrow[-HX]{R'X} \underset{\text{Sec. amine}}{RNHR'} \xrightarrow[-HX]{R'X} \underset{\text{Tert. amine}}{R-NR'_2} \xrightarrow{R'X} \underset{\text{Quaternary salt}}{(R-\overset{+}{N}R'_3)X^-}$$

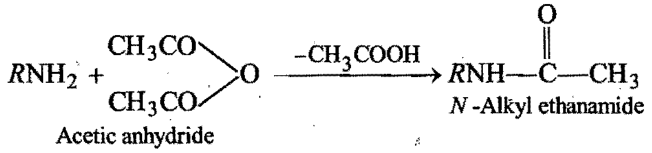
Quaternary ammonium halides on treatment with moist silver oxide (AgOH) or methanolic KOH are converted into their corresponding hydroxides which are strongly basic as NaOH or KOH.

$$\underset{\substack{\text{Quaternary}\\\text{amm. halide}}}{[R_4N]^+X^-} + AgOH \longrightarrow \underset{\substack{\text{Quaternary}\\\text{amm. hydroxide}}}{[R_4N]^+OH^-} + AgX$$

(iv) Reaction with acid chlorides and acid anhydrides (Acylation or acetylation) : (a) Acid chlorides or acid anhydrides react with primary amines and form *N*-substituted amides.

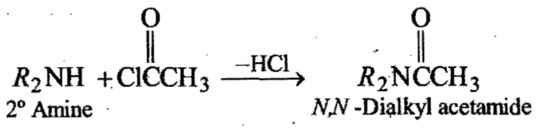


$$\underset{\text{1° Amine}}{RNH_2} + \underset{\text{Acetyl chloride}}{Cl\overset{O}{\overset{\|}{C}}CH_3} \xrightarrow{-HCl} \underset{N\text{-Alkyl acetamide}}{RNH\overset{O}{\overset{\|}{C}}CH_3}$$



$$RNH_2 + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \xrightarrow{-CH_3COOH} \underset{N\text{-Alkyl ethanamide}}{RNH-\overset{O}{\overset{\|}{C}}-CH_3}$$

(b) Secondary amines react with acid chlorides to form *N,N*-disubstituted amides.



$$\underset{\text{2° Amine}}{R_2NH} + Cl\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{-HCl} \underset{N,N\text{-Dialkyl acetamide}}{R_2N\overset{O}{\overset{\|}{C}}CH_3}$$

(c) Tertiary amines do not react, since they do not have replaceable hydrogen on nitrogen.

Therefore, all these above reactions are used to distinguish between primary, secondary and tertiary amines.

(v) Action of sodium : Primary and secondary amines form sodium salts when heated with sodium.

$$2RNH_2 + 2Na \xrightarrow{\text{Heat}} 2[RNH]^- Na^+ + H_2\uparrow$$

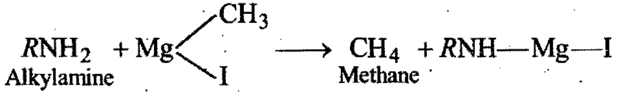
$$2R_2NH + 2Na \xrightarrow{\text{Heat}} 2[R_2N]^- Na^+ + H_2\uparrow$$

(vi) Action of halogens : Primary and secondary amines react with halogens on heating in the presence of alkali solution to form halogeno-amines.

$$\underset{\text{Alkylamine}}{RNH_2} \xrightarrow[NaOH]{X_2} RNHX \xrightarrow[NaOH]{X_2} \underset{\text{Dihaloalkylamine}}{RNX_2}$$

$$\underset{\text{Dialkylamine}}{R_2NH} \xrightarrow[NaOH]{X_2} \underset{\text{Halodialkylamine}}{R_2NX}$$

(vii) Reaction with Grignard reagents : Primary and secondary amines (tertiary amines have no H-atom) form alkanes with Grignard reagents by providing hydrogen atom of amines to alkyl group of Grignard reagents.



$$\underset{\text{Alkylamine}}{RNH_2} + Mg\begin{matrix}CH_3\\I\end{matrix} \longrightarrow \underset{\text{Methane}}{CH_4} + RNH-Mg-I$$

$$C_2H_5N\boxed{H_2 + 2CH_3}MgBr \longrightarrow 2CH_4 + C_2H_5N(MgBr)_2$$

$$\underset{\text{Dialkylamine}}{R_2NH} + CH_3-Mg-I \longrightarrow CH_4 + R_2N-Mg-I$$

(viii) Carbylamine reaction : This reaction is shown by only **primary amines (1°).** Primary amines on heating with chloroform in presence of alcoholic KOH to form isocyanides (or carbylamines) which possess bad smell. This is a test of primary amines and is used to distinguish primary amines from secondary and tertiary amines.

$$\underset{\text{Alkylamine (1°)}}{RNH_2} + CHCl_3 + \underset{\text{(Alc.)}}{3KOH} \xrightarrow{\text{Heat}} \underset{\text{Alkyl isocyanide}}{RNC} + 3KCl + 3H_2O$$

$$CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} CH_3-\overset{+}{N}\equiv\overset{-}{C} + 3KCl + 3H_2O$$

(ix) Reaction with nitrous acid : (a) Primary amines form alcohols with nitrous acid ($NaNO_2 + HCl$). Nitrogen gas (with brisk effervescence) is eliminated and a clear solution is obtained **(Lab test of primary amine).**

$$(NaNO_2 + HCl \longrightarrow HNO_2 + NaCl)$$

$$RNH_2 + HNO_2 \xrightarrow{(NaNO_2 + HCl)} \underset{\substack{\text{Diazonium salt}\\\text{(Unstable)}}}{[RN{=}NCl]} \xrightarrow{H_2O} R-OH + N_2\uparrow + HCl$$

or $$\underset{\text{1° Amine}}{RNH_2} + \underset{\text{Nitrous acid}}{HONO} \longrightarrow \underset{\text{Alcohol}}{ROH} + N_2\uparrow + H_2O$$

Methylamine is an exception to this reaction. It does not yield methyl alcohol only but can also form methyl nitrite or dimethyl ether, *i.e.*,

$$CH_3NH_2 + 2HONO \longrightarrow \underset{\text{Methyl nitrite}}{CH_3ON{=}O} + N_2 + 2H_2O$$

$$2CH_3NH_2 + 2HONO \longrightarrow \underset{\text{Dimethyl ether}}{CH_3OCH_3} + 2N_2 + 3H_2O$$

(b) Secondary amines form nitrosoamines which are yellow oily liquids insoluble in water.

$$\underset{\text{2° Amine}}{R_2NH} + HONO \longrightarrow \underset{N\text{-Nitrosodialkylamine}}{R_2NNO} + H_2O$$

On heating with conc. HCl, they give back secondary amines.

$$R_2N—NO + HCl \longrightarrow R_2NH + NOCl$$

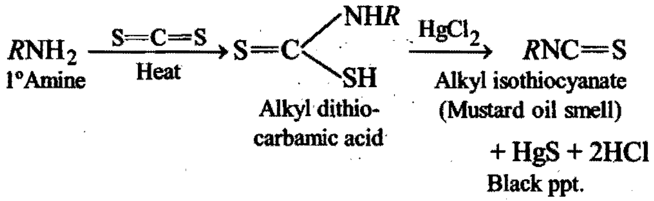
[Nitrosoamines on warming with phenol and a few drops of conc. H_2SO_4 give a brown or red colour which soon changes to blue green. The colour changes to red on dilution and further changes to blue or violet with alkali. This colour change is referred to **Liebermann's nitroso reaction** and is used for the test of secondary amines.]

(c) Tertiary amines react with nitrous acid to form nitrite salts which are soluble in water. These salts on heating give alcohols and nitrosoamines.

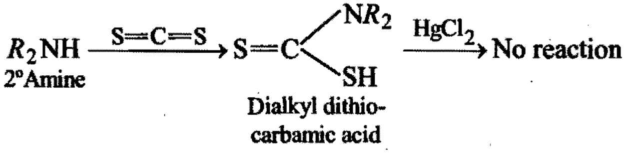
$$\underset{\text{3° Amine}}{R_3N} + HONO \longrightarrow \underset{\text{Trialkyl ammonium nitrite}}{[R_3NH]^+NO_2^-} \xrightarrow{\text{Heat}} \underset{\text{Alcohol}}{R—OH} + \underset{\text{Nitrosoamine}}{R_2N—N{=}O}$$

This reaction (nitrous acid test) is used to make distinction between primary, secondary and tertiary amines.

(x) Reaction with carbon disulphide : (a) Primary amines react with carbon disulphide to form alkyl derivative of dithiocarbamic acid which is decomposed by mercuric chloride to give alkyl isothiocyanate. This is **Hofmann's mustard oil reaction** and is used as **a test for primary amines.**



(b) Secondary amines form dialkyl of dithiocarbamic acid which is not decomposed by mercuric chloride.



(xi) Reaction with benzene sulphonyl chloride (Sulphonylation) : See separation of mixture of amines.

(xii) Oxidation : All the three types of amines undergo oxidation. The product depends upon the nature of oxidising agent, class of amine and the nature of the alkyl group present.

(a) Primary amines are oxidised with potassium permanganate into aldimine or ketimine which on hydrolysis form aldehydes or ketones respectively.

$$\underset{\text{1° Amine}}{RCH_2NH_2} \xrightarrow[\text{KMnO}_4]{[O]} \underset{\text{Aldimine}}{RCH{=}NH} \xrightarrow{H_2O/H^+} \underset{\text{Aldehyde}}{RCHO} + NH_3$$

$$\underset{\text{1° Amine}}{R_2CHNH_2} \xrightarrow[\text{KMnO}_4]{[O]} \underset{\text{Ketimine}}{R_2C{=}NH} \xrightarrow{H_2O/H^+} \underset{\text{Ketone}}{R_2CO} + NH_3$$

Note: Primary amines can also undergo oxidation to nitro compounds through the following sequence of reactions.

$$\underset{\text{1° Amine}}{R—NH_2} \xrightarrow{[O]} \underset{\text{Alkyl hydroxylamine}}{R—NHOH} \xrightarrow[-H_2O]{[O]} \underset{\text{Nitroso compound}}{R—N{=}O} \xrightarrow{[O]} \underset{\text{Nitroalkane}}{R—NO_2}$$

But tertiary alkylamine on oxidation with $KMnO_4$ gives corresponding nitro compound.

$$\underset{\text{1° Amine}}{R_3CNH_2} + 3[O] \xrightarrow{\text{KMnO}_4} \underset{\text{Tert. nitroalkane}}{R_3C \cdot NO_2} + H_2O$$

(b) Secondary amines on oxidation with $KMnO_4$ form tetra-alkyl hydrazine and with Caro's acid (H_2SO_5) or H_2O_2 form dialkyl hydroxylamine.

$$\underset{\text{2° Amine}}{R_2NH} \xrightarrow[\text{KMnO}_4]{[O]} \underset{\text{Tetra-alkyl hydrazine}}{R_2N—NR_2}$$

$$\underset{\text{2° Amine}}{R_2NH} \xrightarrow[H_2SO_5]{[O]} \underset{\text{Dialkyl hydroxylamine}}{R_2NOH}$$

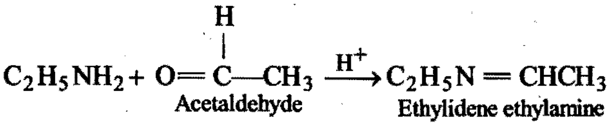
(c) Tertiary amines are not oxidised by potassium permanganate but are oxidised by Caro's acid or H_2O_2 or O_3 or Fenton's reagent to amine oxides.

$$\underset{\text{3° Amine}}{R_3N} + [O] \xrightarrow[\text{or } H_2O_2]{H_2SO_5} \underset{\text{Amine } N\text{-oxide}}{[R_3N \rightarrow O]}$$

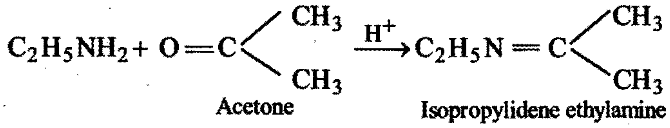
(xiii) Reaction with other electrophilic reagents :

(a) Aldehydes and ketones react with primary amines in the presence of trace of an acid as catalyst to form azomethines called **Schiff's base** or **anils.**

$$\underset{\text{Alkylamine}}{RNH_2} + \underset{\text{Aldehyde}}{O{=}HCR'} \xrightarrow{H^+} \underset{\text{Schiff's base (Aldimine)}}{RN{=}HCR'}$$



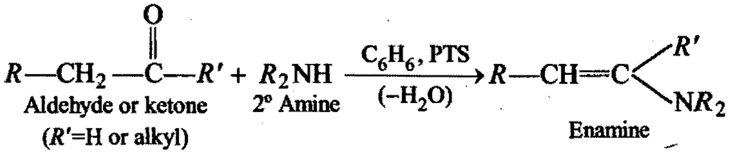
$$C_2H_5NH_2 + \underset{\text{Acetaldehyde}}{O{=}\overset{\overset{\displaystyle H}{|}}{C}—CH_3} \xrightarrow{H^+} \underset{\text{Ethylidene ethylamine}}{C_2H_5N = CHCH_3}$$



$$C_2H_5N\boxed{H_2 + O}{=}HCC_6H_5 \xrightarrow{H^+} C_2H_5N{=}CHC_6H_5$$

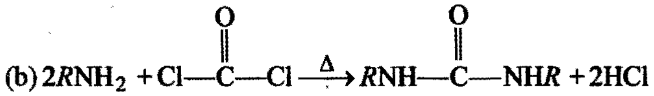
Ethylamine Benzaldehyde Benzal ethylimine

Aldehydes and ketones that have α-hydrogen atoms react with secondary amines to form stable **enamines** (α,β-unsaturated tertiary amine).



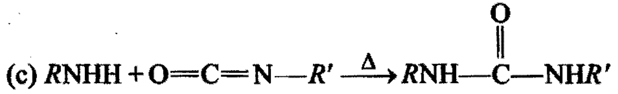
(PTS = p-Toluene sulphonic acid)

The double bond in enamines can also be catalytically reduced to corresponding amines.



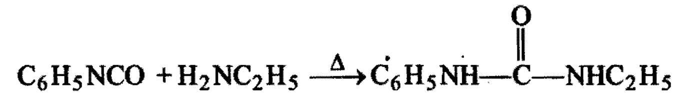
$$\text{(b)}\ 2RNH_2 + Cl-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{\Delta} RNH-\overset{\overset{O}{\|}}{C}-NHR + 2HCl$$

Carbonyl chloride; Dialkyl urea (Symmetrical)



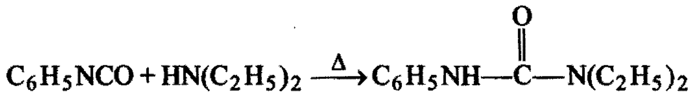
$$\text{(c)}\ RNHH + O{=}C{=}N-R' \xrightarrow{\Delta} RNH-\overset{\overset{O}{\|}}{C}-NHR'$$

1°Amine; Isocyanate; Dialkyl urea (Unsymmetrical)



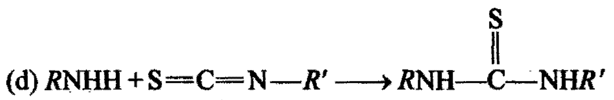
$$C_6H_5NCO + H_2NC_2H_5 \xrightarrow{\Delta} C_6H_5NH-\overset{\overset{O}{\|}}{C}-NHC_2H_5$$

Phenyl isocyanate; 1° Amine; *N*-Ethyl-*N*′-phenyl urea



$$C_6H_5NCO + HN(C_2H_5)_2 \xrightarrow{\Delta} C_6H_5NH-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$$

2° Amine; *N,N*-Diethyl-*N*′-phenyl urea



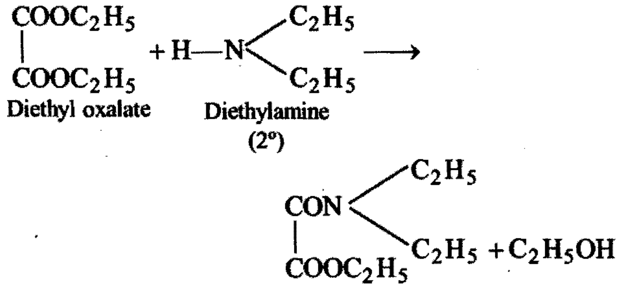
$$\text{(d)}\ RNHH + S{=}C{=}N-R' \longrightarrow RNH-\overset{\overset{S}{\|}}{C}-NHR'$$

Isothiocyanate; Dialkyl thiourea

$$\text{(e)}\ C_2H_5NH_2 + \overset{+}{N}\overset{-}{O}Cl \rightarrow C_2H_5Cl + N_2 + H_2O$$

Nitrosyl chloride; Ethyl chloride

(xiv) 2° Amines react with diethyl oxalate to form oxamic ester in liquid state.



Diethyl oxalate; Diethylamine (2°)

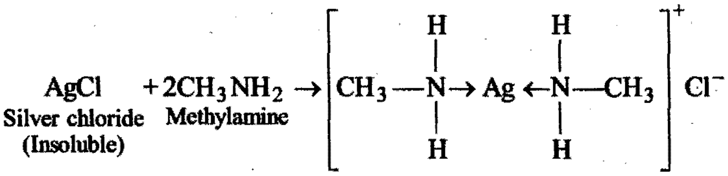
Oxamic ester

(xv) Reaction with HCHO and HCOOH (Methylation): Both primary and secondary amines are methylated by heating with formaline solution and excess of formic acid at 100°C.

$$R-NH_2 + CH_2O + HCOOH \xrightarrow{100°C} RNHCH_3 + CO_2 + H_2O$$

$$R_2NH + CH_2O + HCOOH \xrightarrow{100°C} R_2N-CH_3 + CO_2 + H_2O$$

(xvi) Reaction with metal ions : Lower aliphatic amines form soluble coordination complexes with transition metal ions like Ag^+ and Cu^{2+}, etc. For example, silver chloride dissolves in aqueous solution of methylamine.



$$AgCl + 2CH_3NH_2 \rightarrow \left[CH_3-\underset{H}{\overset{H}{N}}\rightarrow Ag \leftarrow \underset{H}{\overset{H}{N}}-CH_3\right]^+ Cl^-$$

Silver chloride (Insoluble); Methylamine

Bis (methylamine) Silver (I) chloride (soluble complex)

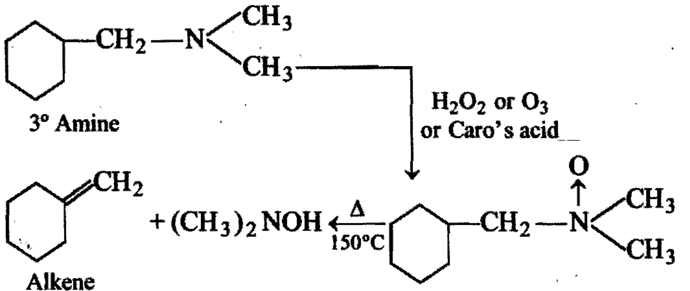
Similarly, like NH_3, lower amines react with Cu^{2+} ions to form a deep blue solution of soluble coordination complex.

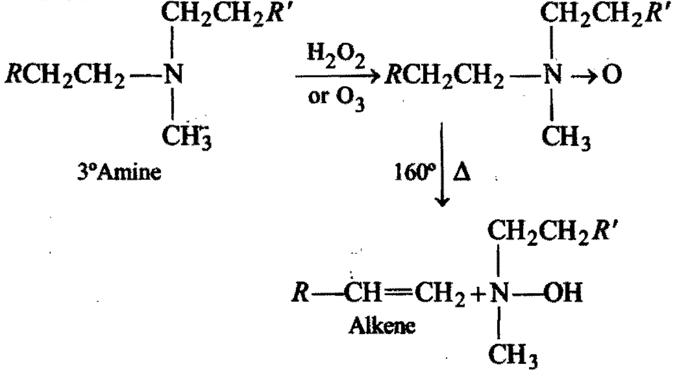
$$CuSO_4 + 4C_2H_5NH_2 \longrightarrow [Cu(C_2H_5NH_2)_4]^{2+}SO_4^{2-}$$

Ethylamine; Tetrakis (ethylamine) Copper (II) Sulphate (Deep blue colour)

$$(\text{Cf.}\ CuCl_2 + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}Cl^{2-})$$

(xvii) Cope reaction : Tertiary amine oxides on heating form an alkene and N, N-disubstituted hydroxylamine if and only there is β-hydrogen atom in it.





Uses : Lower aliphatic amines are used
(i) as solvent in laboratory and industry.
(ii) as a stabilizer for rubber latex.
(iii) in petroleum refining.
(iv) in the manufacture of detergents.
(v) as reagents in organic synthesis.

Tests for Ethylamine (Tests for Primary Amines)

(i) Carbylamine test

Note : This test is also shown by aniline.

(ii) Hofmann's mustard oil test

Note : This test is not shown by aniline but alkyl primary amines respond to this test.

(iii) Nitrous acid test

Note : Aniline does not form alcohol with nitrous acid but it forms benzene diazonium chloride which shows dye test.

14.6 DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY AMINES

Test	Primary amines	Secondary amines	Tertiary amines
1. Action of $CHCl_3$ and alcoholic KOH. (Carbylamine test)	Bad smelling carbylamine (Isocyanide) is formed.	No action.	No action.
2. Action of CS_2 and $HgCl_2$. (Mustard oil test)	Alkyl isothiocyanate is formed which has pungent smell like mustard oil.	No action.	No action.
3. Action of nitrous acid.	Alcohol is formed with evolution of nitrogen.	Forms nitrosoamine which gives green colour with phenol and conc. H_2SO_4 (Liebermann's test).	Forms nitrite in cold which on heating gives nitrosoamine which responds to Liebermann's test.
4. Action of acetyl chloride.	Acetyl derivative is formed.	Acetyl derivative is formed.	No action.
5. Action of Hinsberg's reagent.	Monoalkyl sulphonamide is formed which is soluble in KOH.	Dialkyl sulphonamide is formed which is insoluble in KOH.	No action.
6. Action of methyl iodide.	3 molecules (moles) of CH_3I to form quaternary salt with one mole of primary amine.	2 moles of CH_3I to form quaternary salt with one mole of secondary amine.	One mole of CH_3I to form quaternary salt with one mole of tertiary amine.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Which of the following would undergo Hofmann's reaction to give a primary amine? **[CET (Karnataka) 2006]**
(a) $RCONH_2$ (b) $RCONHCH_3$
(c) $RCOCl$ (d) $RCOOR$
[Ans. (a)]

2. Hinsberg's reagent is used to distinguish between: **[PMT (Raj) 2004]**
(a) 1° and 2° amines (b) 2° and 3° amines
(c) (a) and (b) (d) none of these
[Ans. (c)]

3. Which on reduction does not give primary amine? **[PMT (Raj) 2004]**
(a) CH_3CN (b) C_2H_5NC
(c) CH_3CONH_2 (d) All of these
[Ans. (b)]

4. Primary amine + aldehyde $\longrightarrow X$, what is X?
(a) Nitro (b) Nitroso
(c) Amino (d) Imino
[Ans. (d)]

5. Complete the following reaction:
$$RNH_2 + H_2SO_4 \longrightarrow ?$$
(a) $[RNH_3]^+HSO_4^-$ (b) $[RNH_3]_2^+SO_4^{2-}$
(c) $RNH_2 \cdot H_2SO_4$ (d) no reaction
[Ans. (b)]

6. Ethylamine and acetamide are distinguished by reacting with:
(a) Br_2 water (b) acidic $KMnO_4$
(c) aq. NaOH and heat (d) aq. HCl and heat
[Ans. (c)]

7. Which of the following compounds gives secondary amine on reduction? **[DCE 2004]**
(a) Alkyl nitrile
(b) Carbylamine
(c) Primary amine
(d) Secondary nitro compound
[Ans. (b)]

8. The basicity of compounds I, II, III and IV
$$\underset{\text{I}}{CH_3NH_2},\quad \underset{\text{II}}{(CH_3)_2NH},\quad \underset{\text{III}}{(CH_3)_3N},\quad \underset{\text{IV}}{C_6H_5CH_2NH_2},$$
varies in the order: **[AMU (Engg.) 2004; AMU (Med.) 2010]**
(a) I > II > III > IV (b) II > I > III > IV
(c) III > I > II > IV (d) IV > I > II > III
[Ans. (b)]

9. Tertiary alcohol on treatment with cyanide in presence of conc. H_2SO_4 gives corresponding primary amine. This reaction is called as:
(a) Schmidt reaction (b) Curtius degradation
(c) Leuckart reaction (d) Ritter reaction
[Ans. (d)]

10. The end product of the reaction,
$$\text{Ethylamine} \xrightarrow{HNO_2} (A) \xrightarrow{PCl_5} (B) \xrightarrow{KCN} (C), \text{ is:}$$
(a) propane nitrile (b) triethylamine
(c) diethylamine (d) propylamine
[Ans. (a)]

14.7 CONVERSIONS

1. Conversion of methylamine to ethylamine. (Ascent)

$$\underset{\text{Methyl-amine}}{CH_3NH_2} \xrightarrow{HNO_2} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{PI_3} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{NaCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

2. Conversion of ethylamine to methylamine. (Descent)

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow{NH_3}$$

$$\underset{\text{Methylamine}}{CH_3NH_2} \xleftarrow[KOH]{Br_2} \underset{\text{Acetamide}}{CH_3CONH_2}$$

3. Conversion of ethylamine to acetone.

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} \xrightarrow{HNO_2} \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{Heat} \underset{\text{Acetone}}{CH_3COCH_3}$$

4. Conversion of propionic acid to :
(a) Ethylamine, (b) *n*-Butylamine.

(a) $$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow{SOCl_2} \underset{\text{Propionyl chloride}}{CH_3CH_2COCl} \xrightarrow{NH_3} \underset{\text{Propionamide}}{CH_3CH_2CONH_2} \xrightarrow[KOH]{Br_2} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

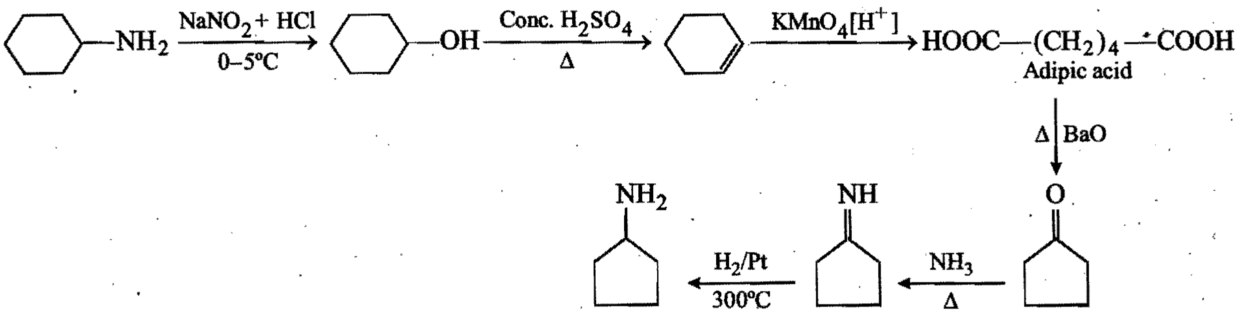
or $$C_2H_5COOH \xrightarrow[H_2SO_4\,(\text{conc.})]{N_3H} C_2H_5NH_2$$

(b) $$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow[\text{Ether}]{LiAlH_4} \underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{PBr_5} \underset{\text{Propyl bromide}}{CH_3CH_2CH_2Br} \xrightarrow{KCN} \underset{\text{Propyl cyanide}}{CH_3CH_2CH_2CN} \xrightarrow[\text{or } LiAlH_4]{Na + C_2H_5OH} \underset{n\text{-Butylamine}}{CH_3CH_2CH_2CH_2NH_2}$$

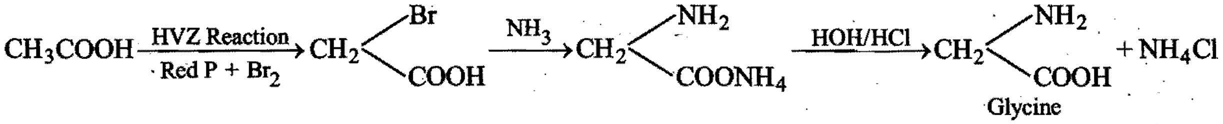
5. Conversion of ethylene to 1,4-diamino butane.

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} \xrightarrow[CCl_4]{Br_2} \underset{\text{Ethylene bromide}}{CH_2Br{-}CH_2Br} \xrightarrow{NaCN} \underset{\text{Ethylene cyanide}}{NCCH_2CH_2CN} \xrightarrow{LiAlH_4} \underset{\text{1,4-Diamino butane}}{NH_2CH_2CH_2CH_2CH_2NH_2}$$

6. Cyclohexylamine into cyclopentylamine.

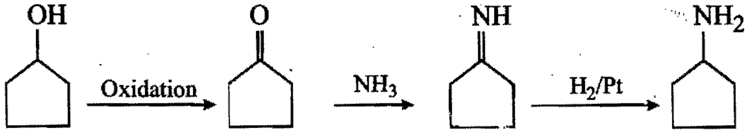


7. Acetic acid into glycine.

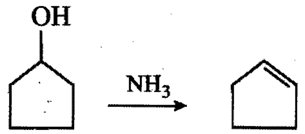


$$CH_3COOH \xrightarrow[\text{Red P + } Br_2]{\text{HVZ Reaction}} CH_2\!\begin{cases} Br \\ COOH \end{cases} \xrightarrow{NH_3} CH_2\!\begin{cases} NH_2 \\ COONH_4 \end{cases} \xrightarrow{HOH/HCl} \underset{\text{Glycine}}{CH_2\!\begin{cases} NH_2 \\ COOH \end{cases}} + NH_4Cl$$

8. Cyclopentanol into cyclopentylamine.

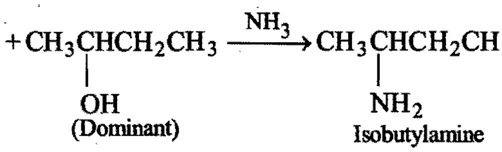


Note: Cyclopentanol on direct treatment of ammonia undergoes dehydration to give cycloalkene.



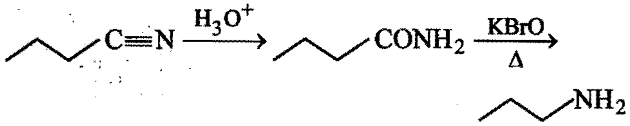
9. *n*-butylamine into isobutylamine.

$$CH_3CH_2CH_2CH_2NH_2 \xrightarrow[0\text{–}5°C]{NaNO_2 + HCl} CH_3CH_2CH_2CH_2OH$$



$$+\underset{\substack{OH\\(\text{Dominant})}}{CH_3\underset{|}{C}HCH_2CH_3} \xrightarrow{NH_3} \underset{\substack{NH_2\\\text{Isobutylamine}}}{CH_3\underset{|}{C}HCH_2CH_3}$$

10. *n*-Propyl cyanide to *n*-propylamine.



2. CYANIDES AND ISOCYANIDES

14.8 INTRODUCTION

Hydrogen cyanide is known to exist as a tautomeric mixture.

$$H—C{\equiv}N \rightleftharpoons H—N\overset{\rightarrow}{=}C$$

Hence, it forms two types of alkyl derivatives which are known as alkyl cyanides and alkyl isocyanides.

$$\underset{\text{Alkyl cyanide}}{R—C{\equiv}N} \quad \underset{\text{Alkyl isocyanide}}{R—N\overset{\rightarrow}{=}C}$$

Compounds having the formula *R*CN are called alkyl cyanides or as nitriles of the acid which they produce on hydrolysis by the replacement of terminal '*ic acid*' with suffix 'onitrile'. According to IUPAC system, cyanides are named as **Alkane nitrile,** *i.e.*, in the name of parent hydrocarbon 'nitrile' is suffixed. In naming the hydrocarbon part, carbon of the —CN group is also counted.

Formula	As cyanide (Common name)	IUPAC name
CH_3CN	Methyl cyanide (Acetonitrile)	Ethane nitrile
C_2H_5CN	Ethyl cyanide (Propiononitrile)	Propane nitrile
C_3H_7CN	Propyl cyanide (Butyronitrile)	Butane nitrile
C_4H_9CN	Butyl cyanide	Pentane nitrile

The compounds having the formula $R\overset{+\,-}{NC}$ are called isocyanides or isonitriles. The nomenclature of isocyanides is similar to cyanides.

Formula	As isocyanide (Common name)	IUPAC name
CH_3NC	Methyl isocyanide (Methyl isonitrile)	Methyl carbylamine (Carbylamino methane)
C_2H_5NC	Ethyl isocyanide (Ethyl isonitrile)	Ethyl carbylamine (Carbylamino ethane)
C_3H_7NC	Propyl isocyanide (Propyl isonitrile)	Propyl carbylamine (Carbylamino propane)

In IUPAC system, the isocyanides are also named as alkane isonitrile.

$CH_3\overset{+\,-}{NC}$	Methane isonitrile
$C_2H_5\overset{+\,-}{NC}$	Ethane isonitrile
$C_3H_7\overset{+\,-}{NC}$	Propane isonitrile

14.9 ALKYL CYANIDES

Methods of Preparation

1. From alkyl halides : The alkyl cyanides are prepared by refluxing an alcoholic solution of an alkyl halide with potassium cyanide at 100°C. The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.

$$\underset{\substack{\text{Alkyl}\\\text{halide}}}{RX} + \underset{(\text{Alc.})}{KCN\ (\text{or } NaCN)} \xrightarrow{100°C} \underset{\substack{\text{Nitrile}\\(\text{Major product})}}{RCN} + \underset{\substack{\text{Isonitrile}\\(\text{Minor product})}}{RNC}$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + NaCN\ (\text{alc.}) \xrightarrow{\text{Heat}} \underset{\substack{\text{Propanenitrile}\\(\text{Major product})}}{C_2H_5CN} + NaBr$$

This method gives satisfactory results for primary and secondary halides. However, with tertiary halides, a considerable amount of an alkene is also formed due to β-elimination of halides.

2. From acid amides : Pure nitriles are obtained by dehydration of **primary acid amides** with phosphorus pentoxide or thionyl chloride ($SOCl_2$) or $POCl_3$, etc. Amides are distilled with phosphorus pentoxide, P_2O_5.

$$\underset{\text{Acid amide}}{RCONH_2} \xrightarrow[-H_2O]{P_2O_5,\ \text{Heat}} \underset{\text{Alkyl cyanide}}{RCN}$$

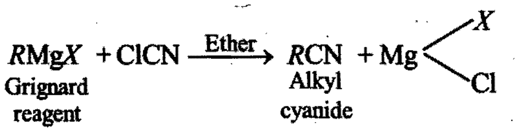
$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Methyl cyanide}}{CH_3CN} + H_2O$$

Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at 500°C.

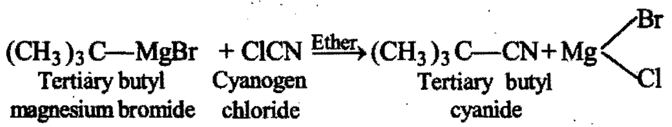
$$\underset{\text{Acid}}{RCOOH} + NH_3 \longrightarrow \underset{\substack{\text{Ammonium}\\\text{salt}}}{RCOONH_4} \xrightarrow[-H_2O]{Al_2O_3,\ 500°C}$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[-H_2O]{Al_2O_3} \underset{\text{Alkyl cyanide}}{RCN}$$

3. From Grignard reagents : Grignard reagents react with cyanogen chloride or cyanogen $(CN)_2$ to form alkyl cyanides.



$$\underset{\text{Grignard reagent}}{RMgX} + ClCN \xrightarrow{\text{Ether}} \underset{\text{Alkyl cyanide}}{RCN} + Mg\begin{smallmatrix}X\\Cl\end{smallmatrix}$$



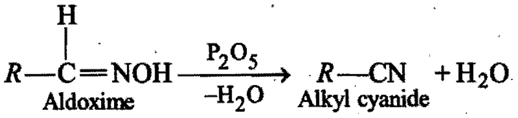
$$\underset{\text{Tertiary butyl magnesium bromide}}{(CH_3)_3C—MgBr} + \underset{\text{Cyanogen chloride}}{ClCN} \xrightarrow{\text{Ether}} \underset{\text{Tertiary butyl cyanide}}{(CH_3)_3C—CN} + Mg\begin{smallmatrix}Br\\Cl\end{smallmatrix}$$

4. From primary amines : Primary amines are dehydrogenated when passed over copper or nickel at high temperature to form alkyl cyanides. This is also a commercial method.

$$\underset{\text{Primary amine}}{RCH_2NH_2} \xrightarrow[500°C]{\text{Cu or Ni}} \underset{\text{Alkyl cyanide}}{RCN} + 2H_2$$

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[500°C]{\text{Cu or Ni}} \underset{\text{Methyl cyanide}}{CH_3CN} + 2H_2$$

5. From oximes : Aldoximes are converted into alkyl cyanides when distilled with phosphorus pentoxide or acetic anhydride. The dehydration of aldoximes occurs.



$$\underset{\text{Aldoxime}}{R—\overset{\overset{H}{|}}{C}=NOH} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Alkyl cyanide}}{R—CN} + H_2O$$

6. From alkanes : Another industrial method is the ammoxidation of alkanes.

$$\underset{\text{Ethane}}{2CH_3CH_3} + 2NH_3 + 3O_2 \xrightarrow[500\text{-}600°C]{\text{Catalyst}} \underset{\text{Ethane nitrile}}{2CH_3CN} + 6H_2O$$

Physical properties : (i) Alkyl cyanides are neutral substances with pleasant odour, similar to bitter almonds.

The anion derived by deprotonation of a nitrile is resonance stabilized.

$$CH_3—C\equiv N \rightleftharpoons H^+ + [^-CH_2—C\equiv N \leftrightarrow CH_2=C=\overset{-}{N}]$$

However, the negative charge on anion is shared by C and N, since nitrogen is not as electro negative as oxygen, hence nitriles are weaker acid than aldehydes and ketones.

(ii) Lower members containing upto 15 carbon atoms are liquids, while higher members are solids.

(iii) They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the molecule.

(iv) They are soluble in organic solvents.

(v) They are poisonous but less poisonous than HCN.

Chemical properties : (i) Hydrolysis : Alkyl cyanides are hydrolysed by both acids and alkalies. On partial hydrolysis by using alkaline H_2O_2, amides are formed while on complete hydrolysis carboxylic acids are obtained.

$$\underset{\text{Alkyl cyanide}}{RCN} \xrightarrow[\text{Alk. }H_2O_2]{H_2O} \underset{\text{Amide}}{RCONH_2} \xrightarrow[H^+]{H_2O} \underset{\text{Carboxylic acid}}{RCOOH} + NH_3$$

$$\underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[\text{Alk. }H_2O_2]{H_2O} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[H^+]{H_2O} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

(ii) Reduction : When reduced with hydrogen in presence of Pt or Ni, or $LiAlH_4$ (Lithium aluminium hydride) or sodium and alcohol, alkyl cyanides yield primary amines.

$$\underset{\text{Alkyl cyanide}}{RCN} + 4[H] \xrightarrow{Na + C_2H_5OH} \underset{\text{Primary amine}}{RCH_2NH_2}$$

Chemical reduction of alkyl (or aryl) cyanide using $LiAlH_4$ or Na/alcohol to form primary amine is named as **Mendius reduction.**

$$\underset{\text{Ethane nitrile}}{CH_3CN} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

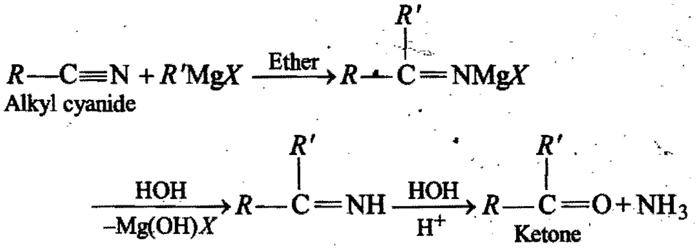
However, when a solution of alkyl cyanides in ether is reduced with stannous chloride and hydrochloric acid at room temperature, imine hydrochloride is obtained which on subsequent hydrolysis with boiling water, an aldehyde is formed **(Stephen's reaction).**

$$R—C\equiv N \xrightarrow[\text{[2H]}]{SnCl_2/HCl} \underset{\text{Imine hydrochloride}}{RCH=NH\cdot HCl} \xrightarrow{H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_4Cl$$

$$R—C\equiv N + 2[H] \xrightarrow[-78°C]{\text{DIBAL}} \underset{\text{Aldimine}}{RCH=NH} \xrightarrow{H_2O/H^+} \underset{\text{Aldehyde}}{RCHO}$$

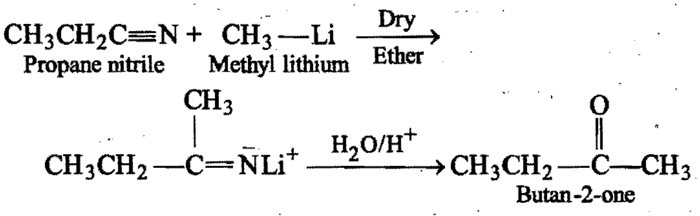
Note : Reduction with **DIBAL** (Di isobutyl aluminium hydride) is a selective method because this reagent reduces only —C≡N (and —COOR) group and has no effect on any reducing groups.

(iii) Reaction with Grignard reagents : With Grignard reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.

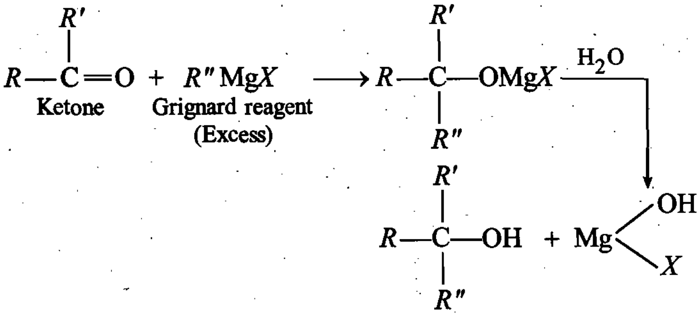


$$\underset{\text{Alkyl cyanide}}{R—C\equiv N} + R'MgX \xrightarrow{\text{Ether}} R—\overset{\overset{R'}{|}}{C}=NMgX \xrightarrow[-Mg(OH)X]{HOH} R—\overset{\overset{R'}{|}}{C}=NH \xrightarrow[H^+]{HOH} \underset{\text{Ketone}}{R—\overset{\overset{R'}{|}}{C}=O} + NH_3$$

It may be noted that like Grignard reagents, organo lithium compounds (R—Li), (due to their high reactivity) also react with cyanides to form ketone.



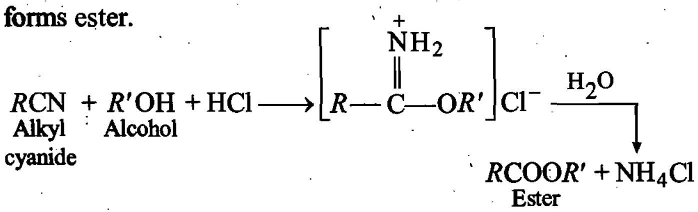
$$\underset{\text{Propane nitrile}}{CH_3CH_2C\equiv N} + \underset{\text{Methyl lithium}}{CH_3—Li} \xrightarrow[\text{Ether}]{\text{Dry}} CH_3CH_2—\overset{\overset{CH_3}{|}}{C}=\overset{-}{N}Li^+ \xrightarrow{H_2O/H^+} \underset{\text{Butan-2-one}}{CH_3CH_2—\overset{\overset{O}{\|}}{C}—CH_3}$$



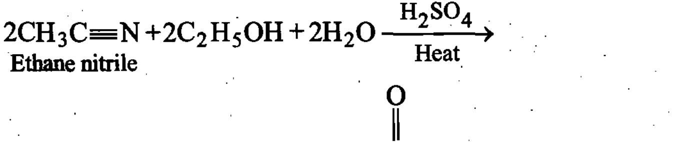
$$\underset{\text{Ketone}}{R-\overset{R'}{\overset{|}{C}}=O} + \underset{\substack{\text{Grignard reagent}\\\text{(Excess)}}}{R''MgX} \longrightarrow R-\overset{R'}{\underset{R''}{C}}-OMgX \xrightarrow{H_2O} R-\overset{R'}{\underset{R''}{C}}-OH + Mg\begin{matrix}OH\\X\end{matrix}$$

Tertiary alcohol (3°)

(iv) Alcoholysis : When an alkyl cyanide is refluxed with an anhydrous alcohol in presence of conc. H_2SO_4 or dry HCl, an imido ester is formed, which on hydrolysis with water forms ester.



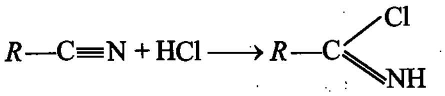
$$\underset{\substack{\text{Alkyl}\\\text{cyanide}}}{RCN} + \underset{\text{Alcohol}}{R'OH} + HCl \longrightarrow \left[R-\overset{\overset{+}{NH_2}}{\overset{\|}{C}}-OR'\right]Cl^- \xrightarrow{H_2O} \underset{\text{Ester}}{RCOOR'} + NH_4Cl$$



$$\underset{\text{Ethane nitrile}}{2CH_3C{\equiv}N} + 2C_2H_5OH + 2H_2O \xrightarrow[\text{Heat}]{H_2SO_4} 2CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + (NH_4)_2SO_4$$

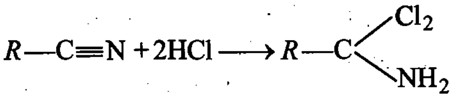
Ethyl ethanoate

(v) Addition of dry HCl gas : Imino and amino chlorides are obtained.



$$R-C{\equiv}N + HCl \longrightarrow R-C\begin{matrix}Cl\\NH\end{matrix}$$

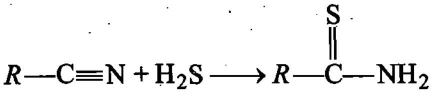
Imino chloride



$$R-C{\equiv}N + 2HCl \longrightarrow R-C\begin{matrix}Cl_2\\NH_2\end{matrix}$$

Amino chloride

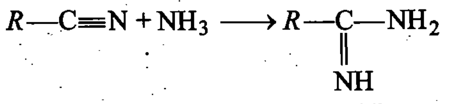
(vi) Addition of hydrogen sulphide : Thioamides are obtained.



$$R-C{\equiv}N + H_2S \longrightarrow R-\overset{S}{\overset{\|}{C}}-NH_2$$

Thio acid amide

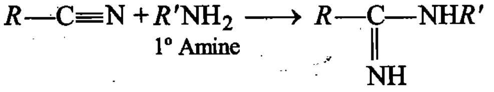
(vii) Reaction with ammonia and primary amines : Amidines are obtained.



$$R-C{\equiv}N + NH_3 \longrightarrow R-\underset{NH}{\underset{\|}{C}}-NH_2$$

Amidine

If amino cyanide (H_2N-CN) is taken in place of alkyl cyanide, the product will be **guanidine.**



$$R-C{\equiv}N + \underset{1^\circ\text{ Amine}}{R'NH_2} \longrightarrow R-\underset{NH}{\underset{\|}{C}}-NHR'$$

Substituted amidine

Uses : (i) Alkyl cyanides are important intermediates in the laboratory synthesis of a large number of compounds like acids, amides, esters, amines, etc.

(ii) Nitriles are also used in textile industry in the manufacture of nitrile rubber and also as a solvent particularly in perfume industry.

14.10 ALKYL ISOCYANIDES

Methods of Preparation

1. From alkyl halides : The isocyanides are prepared by refluxing an alkyl halide solution in alcohol with silver cyanide. The isonitrile is the main product but small amount of nitrile is also formed.

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{(Alc.)}}{AgCN} \xrightarrow[\text{Heat}]{C_2H_5OH} \underset{\substack{\text{Isocyanide}\\\text{(Isonitrile)}\\\text{(Main product)}}}{RNC} + \underset{\substack{\text{Cyanide}\\\text{(Nitrile)}\\\text{(Minor product)}}}{RCN}$$

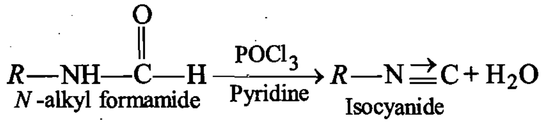
$$\underset{\text{Methyl chloride}}{CH_3Cl} + \underset{\text{(Alc.)}}{AgCN} \xrightarrow[\text{Heat}]{C_2H_5OH} \underset{\substack{\text{Methyl isocyanide}\\\text{(Main product)}}}{CH_3NC} + CH_3CN$$

This method is, thus, not suitable for preparing isocyanides and CN^- is an ambident nucleophile.

2. From primary amines (Carbylamine reaction) : Alkyl isocyanides may be prepared by heating primary amines with chloroform and alcoholic potash.

$$\underset{\text{Primary amine}}{RNH_2} + \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{(Alc.)}}{3KOH} \xrightarrow{\text{Heat}} \underset{\text{Isocyanide}}{RNC} + 3KCl + 3H_2O$$

3. From *N*-alkyl formamides : *N*-alkyl formamides when dehydrated on heating with $POCl_3$ in presence of pyridine give isocyanides.



$$\underset{N\text{-alkyl formamide}}{R-NH-\overset{O}{\overset{\|}{C}}-H} \xrightarrow[\text{Pyridine}]{POCl_3} \underset{\text{Isocyanide}}{R-N \overset{\rightarrow}{=} C} + H_2O$$

Physical properties : (i) Alkyl isocyanides are colourless, unpleasant smelling liquids.

(ii) The boiling points of isonitriles are lower than corresponding alkyl cyanides.

(iii) They are insoluble in water but freely soluble in organic solvents.

(iv) Isonitriles are much more poisonous than isomeric cyanides.

Chemical properties : (i) Hydrolysis : Alkyl isocyanides are hydrolysed by dilute mineral acids (but not by alkalies) to form primary amines.

$$\underset{\text{Alkyl isocyanide}}{RN\overset{\rightarrow}{=}C} + 2H_2O \xrightarrow{H^+} \underset{\text{Primary amine}}{RNH_2} + \underset{\text{Formic acid}}{HCOOH}$$

In alkyl isocyanide ($R-\overset{+}{N}{\equiv}\overset{-}{C}:$), the carbon atom being negatively charged, initially attracts electrophile (*i.e.*, H^+) in acidic medium but repels nucleophiles (*i.e.*, $-OH^-$ ions). As a result, isocyanides are hydrolysed only by acids but not by alkalies.

(ii) Reduction : When reduced with nascent hydrogen or hydrogen in presence of nickel or platinum or Na/alcohol or metal/acid or $LiAlH_4$, isocyanides form secondary amines containing methyl as one of the alkyl groups.

$$\underset{\text{Alkyl isocyanide}}{R\text{—}N \overset{\rightarrow}{\equiv} C} + 4H \xrightarrow[\text{or Ni or Pt}]{Na/C_2H_5OH} \underset{\text{Secondary amine}}{RNHCH_3}$$

$$\underset{\text{Methyl isocyanide}}{CH_3\text{—}N \overset{\rightarrow}{\equiv} C} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Dimethylamine}}{CH_3NHCH_3}$$

Reduction with Na/C_2H_5OH is known as **Mandius reduction.**

(iii) Action of heat : When heated for sometime at 250°C, a small amount of isonitrile changes into isomeric nitrile.

$$RNC \xrightarrow{\text{Heat}} RCN$$

(iv) Addition reaction : Alkyl isocyanide give addition reactions due to presence of unshared electron pair on carbon atom.

$$R:N:::C: \quad \text{or} \quad R\text{—}\overset{+}{N}\equiv\overset{-}{C}$$

The following are some of the addition reactions shown by alkyl isocyanides.

$$RNC + \underset{\text{(Halogen)}}{X_2} \longrightarrow RNCX_2 \quad \text{Alkyl iminocarbonyl halide}$$

$$RNC + S \longrightarrow RNCS \quad \text{Alkyl isothiocyanate}$$

$$CH_3NC + S \longrightarrow CH_3NCS$$

$$RNC + HgO \longrightarrow \underset{\substack{\text{Alkyl}\\ \text{isocyanate}}}{RNCO} + Hg$$

$$CH_3NC + 2HgO \longrightarrow CH_3\text{—}N{=}C{=}O + Hg_2O$$

$$\underset{\text{Ethyl isocyanide}}{C_2H_5NC} + O_3 \longrightarrow \underset{\text{Ethyl isocyanate}}{C_2H_5\text{—}N{=}C{=}O}$$

The famous Bhopal tragedy in Dec., 1984 was caused by extremely poisonous, methyl isocyanate (MIC).

Methyl isocyanate is industrially prepared by the action of methylamine with phosgene.

$$CH_3NH_2 + COCl_2 \xrightarrow{-HCl} [CH_3\text{—}NH\text{—}COCl] \xrightarrow[-HCl]{\text{Heat}} \underset{\text{Methyl isocyanate}}{CH_3\text{—}N{=}C{=}O}$$

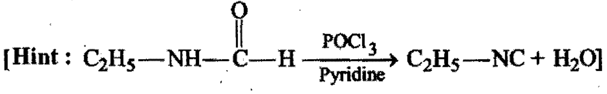
Distinction between Ethyl Cyanide and Ethyl Isocyanide

Test	Ethyl cyanide, C_2H_5CN	Ethyl isocyanide, C_2H_5NC
1. Odour	Not unpleasant	Extremely unpleasant
2. Solubility in water	Soluble	Insoluble
3. Hydrolysis by acid	Yields propionic acid $C_2H_5CN \rightarrow C_2H_5COOH$	Produces ethylamine $C_2H_5NC \rightarrow C_2H_5NH_2$
4. Hydrolysis by alkali	Same as in test 3	No action
5. Reduction	Gives propylamine (Primary amine)	Gives ethyl methylamine (Secondary amine)
6. Heating at 250°C	No effect	Changes to ethyl cyanide

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

11. Which one of the following functional groups undergoes hydrolysis with alkali to yield an acid group? **[EAMCET (Engg.) 2004]**
(a) —CHO (b) —CN
(c) $—COCH_3$ (d) —Br
[Ans. (b)]

12. *N*-ethyl formamide on dehydration with $POCl_3$ in presence of pyridine gives:
(a) ethylamine (b) ethyl cyanide
(c) ethyl isocyanide (d) methyl isocyanide
[Ans. (c)]



$$\text{[Hint: } C_2H_5\text{—}NH\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}H \xrightarrow[\text{Pyridine}]{POCl_3} C_2H_5\text{—}NC + H_2O]$$

13. Ethyl isocyanide on reduction with sodium and alcohol gives:
(a) ethylamine (b) propylamine
(c) dimethylamine (d) ethyl methylamine
[Ans. (d)]

14. Cyanide is an:
(a) Zwitter ion (b) cation
(c) ambident nucleophile (d) electrophile
[Ans. (c)]

15. Acid hydrolysis of methyl isocyanide gives:
(a) $CH_3NH_2 + HCOOH$
(b) $CH_3NH_2 + CH_3COOH$
(c) $C_2H_5NH_2 + HCOOH$
(d) $CH_3NH_2 + CH_3CH_2COOH$
[Ans. (a)]

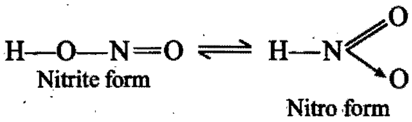
16. Which of the following reagents can be used to prepare ethyl carbylamine from ethyl iodide?
(a) KCN (b) AgCN
(c) CuCN (d) HCN
[Ans. (b)]

17. Acetaldoxime reacts with phosphorus pentoxide to give:
(a) methyl cyanide (b) methyl cyanate
(c) ethyl cyanide (d) none of these
[Ans. (a)]

18. Which of the following products is obtained when methyl isocyanide reacts with chlorine?
(a) $CH_3N{=}CCl_2$ (b) $CH_3NCl{-}CCl_2$
(c) $ClCH_2NC$ (d) Cl_2CHNC
[Ans. (a)]

14.11 ALKYL NITRITES AND NITROALKANES

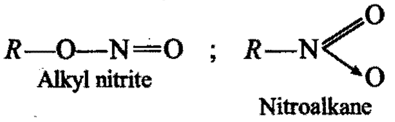
Nitrous acid exists in two tautomeric forms.



$$H{-}O{-}N{=}O \rightleftharpoons H{-}N\begin{smallmatrix}{=}O\\ \to O\end{smallmatrix}$$

Nitrite form Nitro form

Corresponding to these two forms, nitrous acid gives two types of derivatives, *i.e.*, alkyl nitrites and nitro alkanes.



$$R{-}O{-}N{=}O \quad ; \quad R{-}N\begin{smallmatrix}{=}O\\ \to O\end{smallmatrix}$$

Alkyl nitrite Nitroalkane

The most important alkyl nitrite is ethyl nitrite.

ETHYL NITRITE, $C_2H_5ON{=}O$

Methods of Preparation

1. It is prepared by adding concentrated hydrochloric acid or sulphuric acid to aqueous solution of sodium nitrite and ethyl alcohol at very low temperature (0°C).

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

$$C_2H_5OH + HNO_2 \longrightarrow \underset{\text{Ethyl nitrite}}{C_2H_5ONO} + H_2O$$

2. **From Ethyl iodide:**

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Pot. nitrite}}{KONO} \longrightarrow \underset{\text{Ethyl nitrite}}{C_2H_5ONO} + KI$$

3. It is also prepared by the action of nitrogen trioxide, N_2O_3, on ethyl alcohol.

$$2C_2H_5OH + N_2O_3 \longrightarrow 2C_2H_5ONO + H_2O$$

Properties : Ethyl nitrite is a gas at ordinary conditions. It has a characteristic smell of apples. It is insoluble in water.

It is hydrolysed by aqueous alkalies or acids into ethyl alcohol.

$$C_2H_5ONO + H_2O \xrightarrow{NaOH} C_2H_5OH + HNO_2$$

When reduced with tin and HCl, it produces ethyl alcohol and ammonia.

$$\underset{\text{Ethyl nitrite}}{C_2H_5ONO} + 6H \xrightarrow[HCl]{Sn} C_2H_5OH + NH_3 + H_2O$$

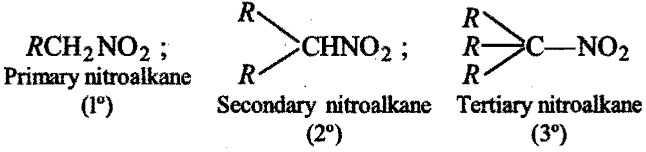
Small amount of hydroxylamine is also formed.

$$C_2H_5ONO + 4H \longrightarrow C_2H_5OH + NH_2OH$$

It accelerates pulse rate and lowers blood pressure and reduces hypertension and severe pain of angina pictoris so it is used as a medicine for the treatment of asthma and heart diseases. Its 4% solution (alcoholic) commonly known as "sweet spirit of nitre" is used as diuretic.

NITRO COMPOUNDS

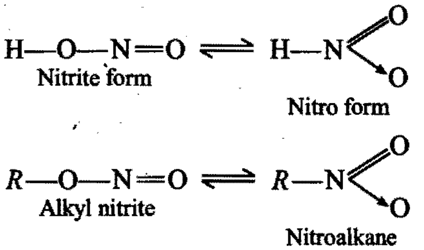
Nitro alkanes are the derivatives of alkanes. They are isomeric to nitrites (esters). They are classified as primary, secondary and tertiary depending on the nature of carbon atom to which nitro group is linked.



RCH_2NO_2 ; Primary nitroalkane (1°)
R_2CHNO_2 ; Secondary nitroalkane (2°)
$R_3C{-}NO_2$ Tertiary nitroalkane (3°)

It may be noted that $-NO_2$ group is **ambident group** and is capable of getting attached to the carbon chain through nitrogen ($R{-}N\begin{smallmatrix}{=}O\\ \to O\end{smallmatrix}$, nitroalkane) as well as through oxygen ($R{-}O{-}N{=}O$, alkyl nitrite) atom. The chemical properties of nitroalkanes and alkyl nitrites (isomeric compounds) are quite different and nitro compounds are much more stable than alkyl nitrites.

Both are alkyl derivatives of nitrous acid (HNO_2) which exhibits tautomerism as the two forms are in dynamic equilibrium.



$$H{-}O{-}N{=}O \rightleftharpoons H{-}N\begin{smallmatrix}{=}O\\ \to O\end{smallmatrix} \quad \text{(Nitrous acid)}$$

Nitrite form Nitro form

$$R{-}O{-}N{=}O \rightleftharpoons R{-}N\begin{smallmatrix}{=}O\\ \to O\end{smallmatrix}$$

Alkyl nitrite Nitroalkane

General Methods of Preparation (Nitroalkanes)

1. **From alkyl halides :** They are prepared by heating an alkyl halide with aqueous ethanolic solution of silver nitrite.

$$R{-}X + \underset{\text{(Alc.)}}{AgNO_2} \xrightarrow{\text{Heat}} \underset{\text{Nitroalkane}}{R{-}NO_2} + AgX$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + \underset{\text{Silver nitrite}}{AgNO_2\,(\text{alc.})} \xrightarrow{\text{Heat}} \underset{\substack{\text{Nitroethane}\\ (70\text{–}80\%)}}{C_2H_5NO_2} + \underset{\substack{\text{Ethyl nitrite}\\ (10\text{–}15\%)}}{C_2H_5{-}O{-}N{=}O}$$

Some quantity of alkyl nitrite is also formed in this reaction. It can be removed by fractional distillation since alkyl nitrites have much lower boiling points as compared to nitro alkanes.

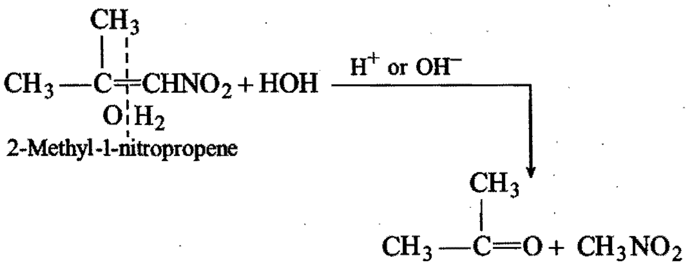
2. **Nitration :** Paraffins (alkanes) after hexane can be nitrated directly with concentrated nitric acid.

The nitration in lower members is carried out in liquid phase or **with fuming HNO_3** in vapour phase at about 400°C.

3. By boiling aqueous solution of sodium nitrite with α-halogeno acids. α-nitro substituted acids are first formed which lose CO_2 to form nitroalkanes.

$$\underset{\alpha\text{-Chloroacetic acid}}{CH_2ClCOOH} \xrightarrow[-NaCl]{NaNO_2} \underset{\alpha\text{-Nitroacetic acid}}{CH_2NO_2COOH} \xrightarrow{Heat} \underset{\text{Nitromethane}}{CH_3NO_2} + CO_2$$

4. A recent method is by the hydrolysis of α-nitroalkene with water or acid or alkali.



$$\underset{\text{2-Methyl-1-nitropropene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CHNO_2} + HOH \xrightarrow{H^+ \text{ or } OH^-} \underset{\text{Acetone}}{CH_3-\overset{CH_3}{\overset{|}{C}}=O} + \underset{\text{Nitromethane}}{CH_3NO_2}$$

Physical properties : Nitroalkanes are colourless pleasant smelling liquids. Their boiling points are much higher than isomeric alkyl nitrites. They are less soluble in water but readily soluble in organic solvents.

Chemical properties : (i) Reduction : Nitroalkanes are reduced to corresponding primary amines with Sn and HCl or iron and HCl or catalytic hydrogenation using nickel as catalyst.

$$\underset{\text{Nitroalkane}}{RNO_2} + 6H \xrightarrow{Sn/HCl} \underset{\text{Alkanamine}}{RNH_2} + 2H_2O$$

However, when reduced with a neutral reducing agent (zinc dust + NH_4Cl); nitroalkanes form substituted hydroxylamines.

$$R-NO_2 + 4H \xrightarrow{Zn + NH_4Cl} \underset{N\text{-Alkyl hydroxylamine}}{R-NHOH} + H_2O$$

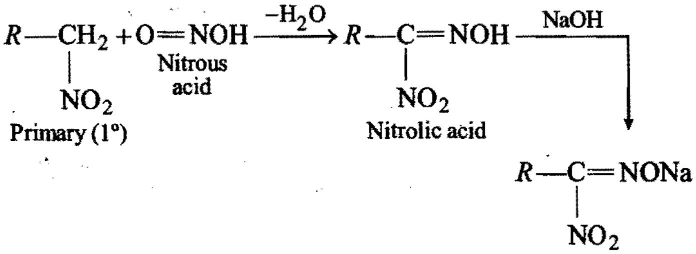
(ii) Hydrolysis : Primary nitroalkanes on hydrolysis with HCl or 80% H_2SO_4 produce hydroxylamine and carboxylic acid.

$$RCH_2NO_2 + H_2O \longrightarrow RCOOH + NH_2OH$$

Secondary nitroalkanes on hydrolysis form ketones

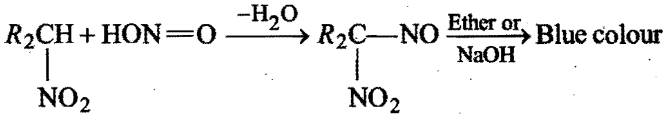
$$2R_2CHNO_2 \xrightarrow[Boiling]{HCl} \underset{\text{Ketone}}{2R_2CO} + N_2O + H_2O$$

(iii) Action of nitrous acid : Nitrous acid reacts with primary, secondary and tertiary nitroalkanes differently. **Primary nitro** compound forms nitrolic acid which dissolves in alkali to give red solution.



$$\underset{\text{Primary (1°)}}{\underset{NO_2}{\underset{|}{R-CH_2}}} + \underset{\text{Nitrous acid}}{O=NOH} \xrightarrow{-H_2O} \underset{\text{Nitrolic acid}}{\underset{NO_2}{\underset{|}{R-C=NOH}}} \xrightarrow{NaOH} \underset{\text{Red coloured sodium salt}}{\underset{NO_2}{\underset{|}{R-C=NONa}}}$$

Secondary nitro compounds give pseudo nitrols which are colourless solids and give blue colouration which does not dissolve in alkali.



$$\underset{\text{Secondary (2°)}}{\underset{NO_2}{\underset{|}{R_2CH}}} + HON=O \xrightarrow{-H_2O} \underset{\text{Pseudo nitrol}}{\underset{NO_2}{\underset{|}{R_2C-NO}}} \xrightarrow[NaOH]{\text{Ether or}} \text{Blue colour}$$

Tertiary nitro alkanes do not react with nitrous acid.

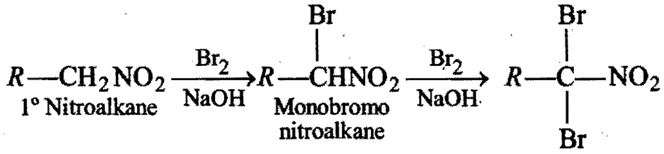
The different behaviour of nitrous acid with pri., sec. and tert. nitroalkanes forms the bases of the **Victor Meyer's Test** for the distinction of pri., sec. and tert. alcohols.

(iv) Thermal decomposition : Upon rapid heating, nitroalkanes decompose with great violence. Advantage is taken of this reaction in the commercial use of nitroalkanes as explosives.

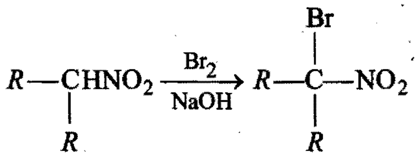
$$CH_3NO_2 \xrightarrow{Heat} \frac{1}{2}N_2 + CO_2 + \frac{3}{2}H_2$$

(v) Halogenation : Primary and secondary nitroalkanes are readily halogenated in the α-position by treatment with chlorine or bromine. Chloropicrin is formed when nitromethane reacts with excess of Cl_2 in presence of NaOH. Chloropicrin is an important insecticide.

$$CH_3-NO_2 \xrightarrow[3NaOH]{3Cl_2} \underset{\text{Chloropicrin}}{CCl_3NO_2} + 3NaCl + 3H_2O$$

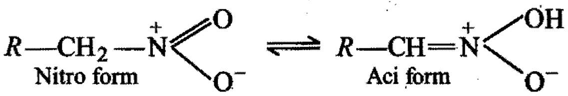


$$\underset{\text{1° Nitroalkane}}{R-CH_2NO_2} \xrightarrow[NaOH]{Br_2} \underset{\text{Monobromo nitroalkane}}{R-\overset{Br}{\overset{|}{C}}HNO_2} \xrightarrow[NaOH]{Br_2} \underset{\text{Dibromo nitroalkane}}{R-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-NO_2}$$



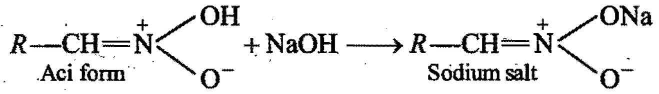
$$\underset{\text{2° Nitroalkane}}{\underset{R}{\underset{|}{R-CHNO_2}}} \xrightarrow[NaOH]{Br_2} \underset{\alpha\text{-Bromoderivative}}{R-\overset{Br}{\overset{|}{\underset{R}{\underset{|}{C}}}}-NO_2}$$

(vi) Acidic nature of α-hydrogen atoms (action of alkali) : The α-hydrogen atoms in aliphatic primary and secondary nitroalkanes become acidic due to the electron withdrawing nature of nitro group. In strong alkaline medium, they behave as acid and forms salts. Consequently, they are called pseudo acids. The acidic character is explained on the basis of tautomerism.



$$\underset{\text{Nitro form}}{R-CH_2-\overset{+}{N}\begin{smallmatrix}\nearrow O\\ \searrow O^-\end{smallmatrix}} \rightleftharpoons \underset{\text{Aci form}}{R-CH=\overset{+}{N}\begin{smallmatrix}\nearrow OH\\ \searrow O^-\end{smallmatrix}}$$

The aci form is weak acid and can form salt with strong alkali.



$$\underset{\text{Aci form}}{R—CH=\overset{+}{N}\langle^{OH}_{O^-}} + NaOH \longrightarrow \underset{\text{Sodium salt}}{R—CH=\overset{+}{N}\langle^{ONa}_{O^-}}$$

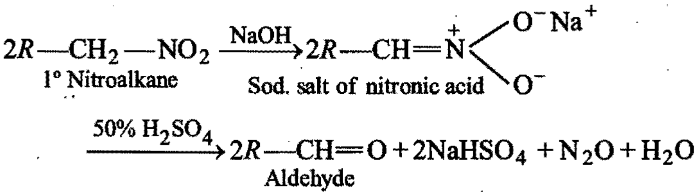
Therefore, primary (1°) and secondary (2°) nitroalkanes dissolve in aqueous solution of NaOH or KOH to form salts. The tertiary (3°) nitroalkanes do not have α-H atom and therefore, they do not exhibit tautomerism. The main reasons for acidic nature of nitroalkanes are:

(i) The strong electron-withdrawing inductive effect of $—NO_2$ group.

(ii) The resonance stabilization of the carbanion formed by the treatment with alkali (removal of proton).

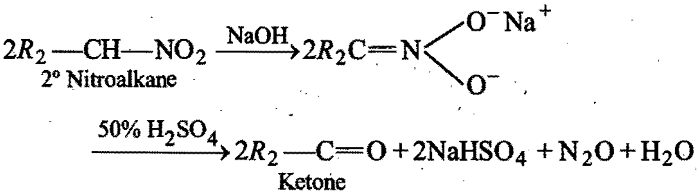
Nitroalkanes are neutral to litmus, although 1° and 2° nitroalkanes are weakly acidic as compared to aldehydes and ketones, they are twice as strong. For example, pK_a of nitromethane is 10.2 while that of acetone is 20.

Applications : Sodium salts of 1° and 2° nitroalkanes give aldehydes and ketones respectively on acidification with 50% H_2SO_4 at room temperature. This reaction is called **Nef-Carbonyl synthesis.**



$$\underset{\text{1° Nitroalkane}}{2R—CH_2—NO_2} \xrightarrow{NaOH} \underset{\text{Sod. salt of nitronic acid}}{2R—CH=\overset{+}{N}\langle^{O^-Na^+}_{O^-}}$$

$$\xrightarrow{50\%\ H_2SO_4} \underset{\text{Aldehyde}}{2R—CH=O} + 2NaHSO_4 + N_2O + H_2O$$



$$\underset{\text{2° Nitroalkane}}{2R_2—CH—NO_2} \xrightarrow{NaOH} 2R_2C=N\langle^{O^-Na^+}_{O^-}$$

$$\xrightarrow{50\%\ H_2SO_4} \underset{\text{Ketone}}{2R_2—C=O} + 2NaHSO_4 + N_2O + H_2O$$

Aqueous $TiCl_3$ can also be used to form aldehydes and ketones in better yield.

$$\underset{\text{1° Nitroalkane}}{RCH_2NO_2} \xrightarrow{\text{Aq. } TiCl_3} \underset{\text{Aldehyde}}{R—CHO}$$

$$\underset{\text{2° Nitroalkane}}{R_2CHNO_2} \xrightarrow{\text{Aq. } TiCl_3} \underset{\text{Ketone}}{R_2CO}$$

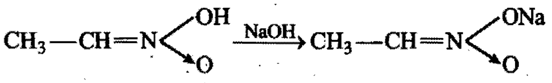
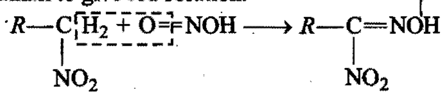
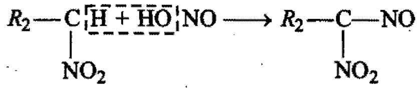
Uses : Nitroalkanes are used:

(i) as solvents for polar substances such as cellulose acetate, synthetic rubber, etc.

(ii) as explosives.

(iii) for the preparation of amines, hydroxylamines, etc.

Distinction between Ethyl Nitrite and Nitroethane

Test	Ethyl nitrite, (C_2H_5ONO) (Alkyl nitrite, *RONO*)	Nitroethane ($C_2H_5NO_2$) (Nitroalkane, RNO_2)
1. Boiling point	Low, 17°C.	Much higher, 115°C.
2. Reduction with metal and acid (Sn/HCl) or with $LiAlH_4$.	Give alcohol + hydroxyl amine or NH_3. $C_2H_5ONO + 4H \longrightarrow C_2H_5OH + NH_2OH$ $RONO + 6H \longrightarrow ROH + NH_3 + H_2O$	Gives corresponding primary amine. $C_2H_5NO_2 + 6H \longrightarrow C_2H_5NH_2 + 2H_2O$ $RNO_2 + 6H \longrightarrow RNH_2 + 2H_2O$
3. Action of NaOH (alkalies).	Readily hydrolysed to give corresponding alcohol and sodium nitrite (decomposition). $C_2H_5ONO + NaOH \longrightarrow C_2H_5OH + NaNO_2$ $RONO + NaOH \longrightarrow ROH + NaNO_2$	Not decomposed, *i.e.*, alcohols are not produced. But it may form soluble sodium salt, because in presence of alkali the nitro form changes into aci form, which dissolves in alkalies to form sodium salt.  $CH_3—CH=N\langle^{OH}_{\rightarrow O} \xrightarrow{NaOH} CH_3—CH=N\langle^{ONa}_{\rightarrow O}$
4. Action of HNO_2 ($NaNO_2$ + HCl).	No action with nitrous acid.	Primary nitroalkanes forms nitrolic acid, which dissolve in alkali to give red solution.  $R—\underset{NO_2}{\underset{\mid}{C}}\boxed{H_2 + O}=NOH \longrightarrow R—\underset{NO_2}{\underset{\mid}{C}}=NOH$ Secondary nitroalkanes yields pseudo-nitrol, which dissolves in alkali to give blue solution.  $R_2—\underset{NO_2}{\underset{\mid}{C}}\boxed{H + HO}NO \longrightarrow R_2—\underset{NO_2}{\underset{\mid}{C}}—NO$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. Nitroethane on reduction with zinc dust and ammonium chloride gives:

(a) ethanamine (b) *N*-ethyl hydroxyl amine
(c) ethyl nitrite (d) nitroso ethane
[Ans. (b)]

20. Hydrolysis of $CH_3CH_2NO_2$ with 85% H_2SO_4 gives:

(a) CH_3CH_2OH (b) C_2H_6
(c) $CH_3CH{=}NOH$ (d) CH_3COOH
[Ans. (d)]

21. 2-Nitropropane on hydrolysis with boiling concentrated solution of HCl gives:

(a) propane (b) propanal
(c) propanone (d) propanoic acid
[Ans. (c)]

22. Primary nitro compounds react with nitrous acid to form nitrolic acids which dissolve in sodium hydroxide to give: **[CET (Tamil Nadu) 2001]**

(a) yellow solution (b) blue solution
(c) colourless solution (d) red solution
[Ans. (d)]

23. The different behaviour of nitrous acid with 1°, 2° and 3° nitroalkanes forms the bases of:

(a) Victor Meyer's test (b) Lucas test
(c) Baker-Mulliken's test (d) Nef-Carbonyl synthesis
[Ans. (a)]

24. In Nef-Carbonyl synthesis, primary nitroalkanes on treatment with NaOH followed by acidification with 50% H_2SO_4 gives:

(a) aldehydes (b) ketones
(c) ketoacids (d) esters
[Ans. (a)]

25. Ethyl nitrite on reduction with Sn/HCl gives:

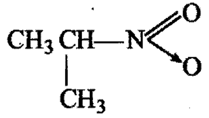
(a) $C_2H_5NH_2 + HNO_2$ (b) $C_2H_5NH_2 + H_2O$
(c) $C_2H_5OH + NH_4OH$ (d) $C_2H_5OH + NaNO_2$
[Ans. (c)]

26. Which of the following isomerism is exhibited in nitroethane? **[DCE 2004]**

(a) Geometrical isomerism (b) Optical isomerism
(c) Functional isomerism (d) Space isomerism
[Ans. (c)]

27. Which of the following is not nitroproduct? **[DCE 2004]**

(a) $C_6H_5NO_2$ (b) CH_3CH_2ONO

(c) 
$CH_3\underset{\substack{|\\ CH_3}}{CH}-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$
(d) $C_6H_4(OH)NO_2$

[Ans. (b)]

IMPORTANT POINTS TO REMEMBER (SUMMARY)

ALIPHATIC AMINES

☐ Amines are derivatives of ammonia in which one or more H atoms have been replaced by corresponding number of alkyl groups.

Primary (1°) amines :

$R—\ddot{N}H_2, CH_3\ddot{N}H_2, CH_3CH_2\ddot{N}H_2, C_3H_7\ddot{N}H_2$

Secondary (2°) amines :

$R_2\ddot{N}H, CH_3\ddot{N}HCH_3, C_2H_5\ddot{N}HCH_3, C_2H_5\ddot{N}HC_2H_5$

Tertiary (3°) amines :

$R_3\ddot{N}, (CH_3)_3\ddot{N}, (C_2H_5)_2\ddot{N}CH_3, (CH_3)_2\ddot{N}—C_2H_5$

☐ In addition to the above amines, tetra alkyl derivatives similar to ammonium salts also exist which are called **quaternary ammonium salts.** For example,

$R_4N^+X^-$, $[(CH_3)_4N^+]I^-$, $(C_2H_5)_3N^+C_2H_5Cl^-$, $[(CH_3)_4N^+]OH^-$

Preparation of primary (1°) amines

☐ **Ammonolysis of alkyl halides (Hofmann's method) :** By heating an alkyl halide with an excess of aqueous or alcoholic ammonia in a sealed tube at 100°C.

☐ **Ammonolysis of alcohol :** By passing a mixture of alcohol and excess of ammonia vapours over heated alumina or thoria at 350°C.

☐ **Reduction of nitroalkanes :** By the reduction of nitroalkanes with Sn/HCl or Zn/HCl or $LiAlH_4$, the $—NO_2$ group gets reduced into $—NH_2$ group.

☐ **Reduction of alkane nitriles (Mendius reaction) :** When an alkyl cyanide (nitrile) is reduced by Na/C_2H_5OH or H_2/Raney Ni or $LiAlH_4$ (LAH) or catalytically, the —CN group gets reduced to $—CH_2NH_2$ group.

☐ **Reduction of amides :** By $LiAlH_4$ or Na/alcohol amides give *p*-amine containing same number of carbon atoms.

☐ **Reduction of oximes :** By Na/alcohol or $LiAlH_4$ or H_2/Ni gives 1° amine.

☐ **Hofmann's bromamide reaction (Hofmann's degradation of amides) :** By this method an amide is converted into *p*-amine containing one carbon atom less. The amide is heated with Br_2 and concentrated aqueous KOH solution.

☐ **Gabriel phthalimide reaction :** Phthalimide is reacted with ethanolic solution of KOH to form potassium phthalimide which on heating with *RX* gives *N*-alkyl phthalimide. It is put to hydrolysis with dilute HCl to form pure primary amine.

☐ **Decarboxylation of α-amino acids :** By heating with $Ba(OH)_2$ gives 1° amine.

☐ **By double decomposition between Grignard reagents and chloramine ($Cl—NH_2$).**

☐ **Hydrolysis of isocyanides or isocyanates :** By boiling with aqueous solution of KOH or NaOH gives primary amine.

☐ **Schmidt reaction :** By treating a mixture of carboxylic acid and hydrazoic acid (N_3H) with cold conc. H_2SO_4, a primary amine is obtained.

☐ **Ritter reaction :** It is a good method for preparing *p*-amines having a tertiary alkyl group. This reaction occurs between a tertiary alcohol (or alkene) and alkyl cyanide (or HCN) in presence of conc. H_2SO_4 to form tert. butylamine through the intermediate formation of carbocation.

☐ **Reductive amination of aldehydes and ketones :** Aldehydes or ketones when reduced with Ni or H_2/Raney Ni in presence of excess of NH_3 at about 150°C under pressure forms 1° amine through the intermediate formation of an imine.

☐ **Leuckart reaction :** Aldehydes and ketones react with ammonium formate or with formamide to give formyl derivative of primary amine which are readily hydrolysed by acid to yield primary amine.

Preparation of secondary amines

☐ By heating a primary amine with calculated amount of *RX*.

☐ By reduction of *N*-substituted amides with $LiAlH_4$.

☐ By reduction of alkyl isocyanides (*R*NC) with H_2 in presence of Pt catalyst or Na/C_2H_5OH or Raney Ni or $LiAlH_4$.

☐ By heating two moles of alkyl halide with one mole of NH_3 in a sealed tube.

☐ By hydrolysis of *p*-nitroso dialkyl aniline with boiling NaOH or KOH solution.

☐ By hydrolysis of a dialkyl cyanamide with an acid or alkali.

Preparation of tertiary amines

☐ By heating an alcoholic solution of NH_3 with excess of *RX*.

☐ By reduction of *N,N*-disubstituted amides with $LiAlH_4$.

☐ By decomposition of tetra ammonium hydroxide on heating.

☐ By heating ketone with secondary amines on reduction in presence of Ni catalyst **(Reductive amination).**

Methods yielding a mixture of pri., sec. and tert. amines

☐ **Hofmann's ammonolysis method :** A mixture of amines (1°, 2° and 3°) along with quaternary compound is formed when an alkyl halide is heated with alcoholic ammonia in a sealed tube at 100°C.

☐ **Ammonolysis of alcohols :** A mixture of amines is also obtained when the mixture containing vapours of alcohol and ammonia are passed over heated alumina (Al_2O_3) or thoria (ThO_2) at 350°C.

Separation of mixture of amines (1°, 2° and 3°)

When the mixture having amine salts and Quaternary ammonium compounds is distilled with KOH solution, the mixture of three amines distill over leaving behind non-volatile quaternary salt in the distillation flask.

The amine mixture may be separated by the following methods.

☐ **Fractional distillation :** The boiling points of 1°, 2° and 3° amines are quite different and thus these can be separated by fractional distillation. This method is used satisfactorily in industry.

☐ **Hofmann's method :** The mixture of three amines is treated with diethyl oxalate. The 1° amine forms a solid dialkyl oxamide, 2° amine gives a liquid oxamic ester and 3° amine does not react. The reaction mixture is subjected to fractional distillation. The 3° amine distills over and forms the first fraction. This is followed by oxamic ester which forms the second fraction. The solid oxamide remains behind in the distillation flask which on hydrolysis with KOH and then distilled to get pure amine. The oxamic ester is hydrolysed by boiling with KOH solution and distilled when pure 2° amine is obtained.

☐ **Hinsberg's method :** It involves the treatment of the mixture with benzene sulphonyl chloride, *i.e.*, Hinsberg's reagent ($C_6H_5SO_2Cl$). The solution is then made alkaline with aqueous KOH solution where 1° amine forms *N*-alkyl benzene sulphonamide (soluble in KOH). The 2° amine forms *N,N*-dialkyl benzene sulphonamide (insoluble in KOH) and 3° amine does not react. The above alkaline mixture of amines is extracted with ether. The 3° amine and dialkyl sulphonamide passes in etheral layer while salt of alkyl benzene sulphonamide remains in aqueous layer. The etheral and aqueous layers are separated.

The aqueous layer is acidified with dil. HCl and hydrolysed by heating with conc. HCl. The hydrochloride formed is then distilled with KOH when 1° amine distills over and collected.

The etheral layer is fractionally distilled when first ether distills and the other fraction is hydrolysed with conc. HCl followed by distillation with KOH solution gives pure 2° amine.

☐ **Physical Properties :** Amines are polar compounds like NH_3 and have comparatively higher boiling points than non-polar compounds of similar molecular masses. This is due to the presence of intermolecular H-bonding. The boiling points rise gradually with increase of molecular mass.

☐ Lower members are soluble in water. This is because the amines are capable of forming H-bonding with water but the solubility decreases with increase of molecular mass.

☐ **Chemical properties :** The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom.

☐ **Basic nature :** Amines form salts with mineral acids (HCl or H_2SO_4) which on treatment with NaOH liberates parent amine.

☐ Amines combine with water to form alkyl ammonium hydroxides which dissociate into ions.

☐ **Alkylation :** When amines are treated with alkyl halides, the H atoms of amino group are successively replaced by alkyl groups.

☐ **Acylation :** Primary (1°) and secondary (2°) amines react with acid chlorides or acid anhydrides to give acyl derivatives (*N*-substituted amides). Tertiary amines do not react since they do not have replacable H atom.

☐ **Reaction with sodium :** 1° and 2° amines form sodium salts when heated with sodium.

☐ **Action of halogens :** 1° and 2° amines react with halogens on heating in the presence of alkali to form mono and di halogeno-amines.

☐ **Reaction with Grignard reagents :** Primary and secondary amines form alkanes with Grignard reagents by providing H-atom of amines to alkyl (*R*) group of GR.

☐ **Carbylamine reaction :** Primary amines on heating with $CHCl_3$ in presence of alcoholic KOH produce isocyanides (carbylamines) which possess pungent (unpleasant) odour. It is a test of primary amines only and is used to distinguish 1° amines from 2° and 3° amines.

☐ **Reaction with nitrous acid ($NaNO_2$ + dil. HCl) :** Primary amines form alcohols with nitrous acid, HNO_2 ($NaNO_2$ + HCl) and N_2 gas is eliminated. (A distinction between 1°, 2° and 3° amines).

☐ **Reaction with carbon disulphide :** Primary amines on warming with CS_2 to form alkyl derivative of dithiocarbamic acid which is decomposed by $HgCl_2$ to give alkyl isothiocyanate ($RNC{=}S$) having pungent smell of mustard oil. This is known as **Hofmann's mustard oil reaction.**

☐ **Oxidation :** Amines undergo oxidation forming different products depending upon the nature of oxidising agents, types of amine and the nature of alkyl group present.

☐ (a) Primary amines are oxidised with $KMnO_4$ into aldimine or ketimine which on hydrolysis form aldehydes and ketones respectively.

☐ (b) Secondary amines on oxidation with $KMnO_4$ form tetra-alkyl hydrazine ($R_2N{-}NR_2$) and with Caro's acid (H_2SO_5) give dialkyl hydroxylamine (R_2NOH).

☐ (c) Tertiary amines are not oxidised by $KMnO_4$ but are oxidised by Caro's acid or H_2O_2 or O_3 or Fenton's reagent to amine oxides.

☐ **Condensation with aldehyde :** Primary amines condense with aldehydes to produce aldimine (Schiff's base).

☐ **Reaction with carbonyl chloride (Phosgene) :** Primary amines on heating with carbonyl chloride ($COCl_2$) form *N*, *N'*-dialkyl urea. Secondary amine forms *N,N,N',N'*-tetra alkyl urea.

☐ **Reaction with alkyl isocyanate :** Primary and secondary amines on heating with alkyl isocyanate form corresponding substituted urea.

QUESTIONS

❖ Very Short Answer Type

1. Fill in the blanks:
   (a) $(CH_3)_3CNH_2$ is a...........amine.
   (b) A secondary amine consists...........group.
   (c) Nitrogen in amines is...........hybridized.
   (d) The IUPAC name of $CH_3CH_2NHCH_3$ is...........
   (e) $CH_3CH_2CH_2NH_2$ has...........functional isomers.
   (f) Ethylamine is...........basic than ammonia.
   (g) Acetamide on treatment with...........and........... forms methylamine.
   (h) Methyl cyanide on reaction with sodium and C_2H_5OH forms...........
   (i) Hydrolysis of *N*-alkyl phthalimide gives...........
   (j) Carbylamine reaction is used for the test of........... amines.
   (k) Primary amines on reaction with nitrous acid form........
   (l) Ethylamine and acetamide both contain amino group but acetamide does not show basic nature because lone pair of electrons on .... is delocalised by .... with the carbonyl group.
   (m) Acetamide on treatment with...........forms ethylamine.
   (n) *N*-Methyl acetamide on reduction with $LiAlH_4$ forms ....
   (o) Primary nitroso-dimethyl aniline when heated with NaOH or KOH solution forms...........
   (p) Separation of primary, secondary and tertiary amines can be made with the help of...........in Hinsberg's method.
   (q) Lower amines are soluble in water due to...........
   (r) Tertiary amines do not react with acetyl chloride since they do not have...........on nitrogen.
   (s) ....is formed when ethylamine is heated with CS_2 in presence of $HgCl_2$.
   (t) The reaction,
   $$RCN \xrightarrow{SnCl_2/HCl} (A) \xrightarrow{H_2O} RCHO + NH_4Cl,$$
   is known as...........
   (u) Isocyanides form...........on reduction with nascent hydrogen.
   (v) Nitroalkanes when reduced with zinc dust and ammonium chloride form...........
   (w) Primary amines on heating with...........and .... form alkyl isocyanides.
   (x) In Hofmann's bromamide reaction of amide, carbonyl carbon is lost as...........
   (y) Out of isomeric amines.........amines are most volatile.
   (z) Basic nature of amine is due to the presence of .... on nitrogen atom.
2. State whether the following statements are **True or False:**
   (a) Aliphatic amines are insoluble in water.
   (b) Secondary amines show carbylamine reaction.
   (c) $(CH_3)_2NH$ is a stronger base than $(CH_3)_3N$.
   (d) The hydrolysis of alkyl cyanide always yields formic acid.
   (e) The aqueous solution of ethylamine precipitates iron as ferric hydroxide when added to ferric chloride solution.
   (f) Nitrogen is evolved when ethylamine is treated with nitrous acid.
   (g) Acetic acid forms ethylamine when treated with hydrazoic acid and concentrated sulphuric acid.
   (h) Primary, secondary and tertiary amines can be separated from their mixture by using ethyl oxalate.
   (i) There are two position isomers (amines) of molecular formula, C_3H_9N.
   (j) $C_2H_5NH_2$ is neutral to litmus.
   (k) Amides on reduction with $LiAlH_4$ form primary amines.
   (l) Ethylamine undergoes acetylation with acetyl chloride.
   (m) Amides are the oxidation products of nitriles (cyanides).
   (n) Nitroalkanes are less polar than isomeric alkyl nitrites.
   (o) Tertiary aliphatic amines do not react with acetyl chloride.
   (p) Both cyanides and nitrites are ambident nucleophiles.
   (q) The cyanides are also called carbylamines.
   (r) Tertiary amines react with Grignard reagents to form hydrocarbon.
   (s) The compound, $CH_3—O—N{=}O$, is methyl nitrite.
   (t) Primary amines are less soluble than tertiary amines.
   (u) Secondary amines can show metamerism.
   (v) Amines are Lewis acids.
   (w) AgCl dissolves in aqueous solution of methylamine.
   (x) α-Amino acids on heating with $Ba(OH)_2$ shows decarboxylation to produce primary amines.
   (y) Nitriles are much more poisonous than isomeric isonitriles.
   (z) Pure nitriles are obtained by dehydration of acid amides with phosphorus pentoxide.
3. Match the following:

(A) $C_6H_5SO_2Cl$	(1) Carbylamine reaction
(B) Conversion of amide to amine	(2) Quaternary salt
(C) Conversion of primary amine to isocyanide	(3) Schmidt reaction
(D) Dimethylamine	(4) Primary amine
(E) Tetraethyl ammonium iodide	(5) Hinsberg's reagent
(F) $>C—NH_2$	(6) Tertiary amine
(G) $RCOOH + N_3H$ + Conc. H_2SO_4	(7) Hofmann's bromamide reaction
(H) R_3N	(8) Secondary amine

4. Complete the following equations:

(i) $CH_3NH_2 + CHCl_3 + KOH \xrightarrow{\text{Heat}}$

(ii) $RNH_2 + CHCl_3 + KOH \xrightarrow{\text{Heat}}$

(iii) $C_2H_5NH_2 + C_2H_5I(\text{excess}) \longrightarrow$

(iv) $C_2H_5NH_2 + NaNO_2 + HCl \longrightarrow$

(v) $CH_3CONH_2 + Br_2 + NaOH \longrightarrow$

(vi) $C_2H_5NH_2 + CH_3COCl \longrightarrow$

(vii) $CH_3CN + CH_3MgBr \xrightarrow[H_2O]{H^+}$

(viii) $C_2H_5NC + H_2O \xrightarrow{\text{Dil. HCl}}$

(ix) $C_2H_5NH_2 + AgCl \longrightarrow$

(x) $EtNH_2 + KCN + Br_2 \xrightarrow{KOH} KBr + (D)$

(xi) $C_2H_5NCO + 2KOH \longrightarrow$

(xii) $CH_3CH{=}NOH + 4H \xrightarrow{Na/C_2H_5OH}$

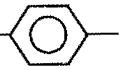
(xiii) $R_2NCN \xrightarrow{H_2O}$

(xiv) $X + 4H \xrightarrow{\text{Catalytically}} R{-}NHCH_3$

(xv) $X \xrightarrow{\text{Thermal decomposition}} (CH_3)_3N + CH_3OH$

(xvi) $X + 6H \xrightarrow{Zn/HCl} RNH_2 + 2H_2O$

(xvii) $X + RI \longrightarrow R_3N + HI$

(xviii) $X \xrightarrow[\text{(NaOH)}]{\text{Heat}}$ ON—  —OH + $(C_2H_5)_2NH$

(xix) $(CH_3)_2CH{-}NH_2 + 2HCHO + HCOOH \xrightarrow{\text{Heat}}$

(xx) $(CH_3)_3C{-}OH + HCN + H_2SO_4 \xrightarrow{\text{Heat}}$

(xxi) $CH_3CH_2NH_2 \xrightarrow[\text{Heat}]{(CH_3CO)_2O}$

5. Name (*A*), (*B*), (*C*) . . . . . . in the following equations:

(i) $CH_3CH_2COOH \xrightarrow{NH_3} (A) \xrightarrow{\text{Heat}} (B) \xrightarrow{Br_2/KOH} (C)$

(ii) $CH_3CH_2NH_2 \xrightarrow[H^+]{C_6H_5CHO} (A) \xrightarrow[\Delta]{H_2/Ni} (B)$

(iii) $C_2H_5NH_2 \xrightarrow{HNO_2} (A) \xrightarrow{[O]} (B) \xrightarrow{[O]} (C) \xrightarrow[H_2SO_4]{N_3H} (D)$

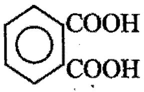
(iv) $CH_3CH_2Cl \xrightarrow{KCN} (A) \xrightarrow{H_2/Ni} (B) \xrightarrow{HNO_2} (C)$

(v) $(A) \xrightarrow[NaOH]{Br_2} (B) \xrightarrow{HNO_2} (C) \xrightarrow[I_2]{\text{Red P}} CH_3I$

(vi) $(A) \xrightarrow{AgCN} (B) \xrightarrow{Sn/HCl} (C) \xrightarrow{HNO_2} C_2H_5\underset{\displaystyle N{=}O}{\underset{|}{N}}{-}CH_3$

(vii) $PhSO_2Cl + EtNH_2 \xrightarrow{-HCl} (A) \xrightarrow{NaOH} (B) \xrightarrow{\text{Et Br}}$
$(C) \xrightarrow{H_3O^+} (D) + (E)$

(viii) $RCH_2CH_2NH_2 \xrightarrow{\text{MeI(excess)}} (A) \xrightarrow{AgOH} (B) \xrightarrow{\text{Heat}} (C)$

(ix)  $+ NH_3 \xrightarrow{\text{Heat}} (A) \xrightarrow[\text{(ii) } RI]{\text{(i) KOH}}$
$(B) \xrightarrow{H_2O} (C) + (D)$

(x) $C_2H_5CN + H_2O \xrightarrow{H_2O_2} (A) \xrightarrow{NaOBr}$
$(B) \xrightarrow{CH_3COCl} (C)$

(xi) $(A) \xrightarrow{Br_2/KOH} (B) \xrightarrow[\text{Heat}]{CHCl_3/KOH(\text{alc.})} (C) \xrightarrow{H_2/Pt} CH_3NHCH(CH_3)_2$

(xii) $(A) \xrightarrow{SOCl_2} (B) \xrightarrow{NH_3} (C) \xrightarrow{LiAlH_4} H_2NCH_2CH_2CH_2NH_2$

6. What happens when?

(i) Acetamide is heated with bromine and potassium hydroxide.

(ii) Methylamine is treated with chloroform and alcoholic solution of potassium hydroxide.

(iii) Ethylamine is treated with acetic anhydride.

(iv) Ethylamine reacts with carbon disulphide in presence of $HgCl_2$.

(v) Ethylamine is treated with nitrous acid.

(vi) Ethyl cyanide is treated with methyl magnesium bromide followed by hydrolysis.

(vii) Nitroethane is reduced with zinc and ammonium chloride.

(viii) Nitropropane is treated with nitrous acid.

(ix) Ethyl nitrite is reduced with $LiAlH_4$.

(x) Alkyl cyanide is reduced with sodium metal in ethanol.

7. (i) Name the reaction that is used to convert an amide into primary amine containing one carbon atom less than the parent.

(ii) Name the product obtained when ethyl cyanide is treated with (a) alkaline hydrogen peroxide and (b) dilute hydrochloric acid.

(iii) Write the position isomers of $C_3H_7NO_2$.

(iv) Name the compounds that are formed by heating $[(CH_3)_3NC_2H_5]^+OH^-$.

(v) Name the compounds that are formed by heating $[(CH_3)_4N]^+OH^-$.

(vi) Name the reaction used to convert primary amine into isocyanide.

(vii) Write three isomers of molecular formula C_3H_9N (amines).

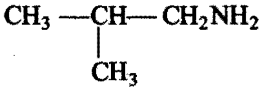
(viii) Name the type of amine if it reacts with benzene sulphonyl chloride to form a solid soluble in alkali.

(ix) Give the structure of *A* (C_3H_9N) if it reacts with benzene sulphonyl chloride to form a solid insoluble in alkali.

(x) Primary amines are formed by the use of phthalimide. What is the name of the reaction?

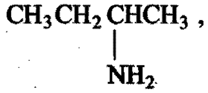
❖ Short Answer Type

8. How will you prepare ethylamine from the following?
   (a) Methyl cyanide; (b) Propionamide; (c) Propionic acid; (d) Ethyl alcohol; (e) Acetic acid; (f) Acetamide.
9. How will you obtain the following from ethylamine?
   (a) Ethyl alcohol; (b) *N*-Ethyl acetamide; (c) Ethyl isocyanide; (d) Ethyl isothiocyanate; (e) Acetaldehyde.
10. Write short notes on:
    (a) Carbylamine test
    (b) Hofmann's bromamide reaction
    (c) Gabriel phthalimide synthesis
    (d) Mustard oil reaction
    (e) Basic nature of amines
11. How would you distinguish between?
    (a) Ethylamine and diethylamine or primary amine and secondary amine.
    (b) Ethylamine and acetamide.
    (c) Diethylamine and triethylamine.
    (d) Nitro ethane and ethyl nitrite.
12. How would you bring the following conversions?
    (i) Ethylamine to ethyl alcohol.
    (ii) Acetic acid to methylamine.
    (iii) Propionamide to ethylamine.
    (iv) Ethyl chloride to *n*-propylamine (in 2 steps).
    (v) Ethyl amine to ethyl isocyanide.
    (vi) Ethyl alcohol to methylamine.
    (vii) Acetic acid to ethylamine.
    (viii) Ethylamine to methylamine.
    (ix) Methylamine to ethylamine.
    (x) Ethylamine from CH_3OH (3 steps).
    (xi) *n*-Butylamine from propene (3 steps).
    (xii) Isopropylamine from acetone.
13. (a) Give the reactions of nitrous acid with primary, secondary and tertiary amines.
    (b) Name the products with chemical reactions when the following compounds are hydrolysed:
    (i) CH_3CH_2CN with dil. HCl
    (ii) CH_3CN with alkaline H_2O_2
    (iii) C_2H_5NC with dil. HCl
    (iv) $C_2H_5NO_2$ with dil. HCl
14. Explain the following:
    (i) Alkyl cyanides have a higher boiling point than the corresponding alkyl halides.
    (ii) Cyanides are soluble in water but isocyanides are insoluble.
    (iii) Why are amines basic in nature?
    (iv) Ethylamine is more basic than aniline.
    (v) Why amines are more basic than amides?
    (vi) Tertiary amine has lowest boiling point of a group of isomeric amines.
    (vii) Silver chloride is soluble in methylamine.
    (viii) The shape of $(CH_3)_3N$ is pyramidal.
    (ix) $Me_4\overset{+}{N}OH^-$ is more basic than Me_3N.
    (x) The boiling point of ethylamine is 17°C whereas that of diethylamine is 7.4°C.
    (xi) $(CH_3)_3CNH_2$ and $(CH_3)_3CCH_2NH_2$ cannot be prepared by ammonolysis of corresponding alkyl bromides while each can be prepared from a carboxylic acid.
    (xii) There is decreasing order in basicity of: $CH_3NH_2 > CH_3N{=}CHCH_3 > CH_3CN$.
    (xiii) Dimethylamine is a stronger base than trimethyl amine.
15. Compare the basicities of:
    (i) (a) $H_2C{=}CHCH_2NH_2$, (b) $CH_3CH_2CH_2NH_2$, (c) $HC{\equiv}CCH_2NH_2$.
    [Hint: The significant difference among these three bases is the kind of hybridization with β-carbon atom. The more *s*-character it has, the more electron withdrawing and base weakening it will be. Thus, decreasing order of basicity is,
    (b) > (a) > (c)]
    (ii) (a) $HO(CH_2)_2NH_2$, (b) $HO(CH_2)_3NH_2$, (c) $CH_3CH_2NH_2$.
    [Hint: The electron withdrawing capacity of OH decreases electron density on nitrogen atom thereby decreasing basicity. This effect decreases as the distance between OH group and N increases in the chain. Thus, decreasing order of basicity is,
    (c) > (b) > (a)]
    (iii) (a) CH_3NH_2, (b) $(CH_3)_2NH$, (c) NH_3, (d) $C_6H_5NH_2$.
    [Ans. $(CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2$]
    (iv) Methylamine, Dimethylamine, Aniline, *N*-Methylaniline.
    [Ans. Dimethylamine > Methylamine > *N*-Methylaniline > Aniline]
    (v) $C_2H_5NH_2$, $(C_3H_7)_3N$, CH_3CONH_2, $CH_3\bar{N}HNa^+$.
    [Ans. $CH_3\bar{N}HNa^+ > C_2H_5NH_2 > (C_3H_7)_3N > CH_3CONH_2$]
    (vi) $CH_3CH_2CH_2CH_2NH_2$ (I),



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2NH_2$

(II)



$CH_3CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_3$

(III)

$(CH_3)_3C{-}NH_2$. (IV)

[Ans. IV < II < III < I]

16. Suggest a convenient scheme for separating aniline, *N*-methylaniline, toluene and phenol, present together in a mixture. Distillation is not to be used.

ANSWERS

1. (a) primary; (b) imino ($>$NH); (c) sp^3; (d) *N*-Methylethanamine or *N*-Methylaminoethane; (e) two [$CH_3NHC_2H_5$ and $(CH_3)_3N$]; (f) more; (g) Br_2, KOH; (h) ethylamine; (i) primary amines; (j) primary; (k) primary alcohols; (l) nitrogen, resonance; (m) $LiAlH_4$; (n) methylaminoethane; (o) dimethylamine; (p) benzene sulphonyl chloride; (q) hydrogen bonding; (r) replaceable hydrogen; (s) Ethyl isothiocyanate; (t) Stephen's reaction; (u) secondary amines;

(v) hydroxylamines; (w) chloroform, KOH or NaOH; (x) CO_3^{2-}; (y) tertiary $(CH_3)_3N$; (z) an electron pair.

2. (a) False—Lower members are soluble in water. Solubility decreases with increase of molecular mass; (b) False—Do not show carbylamine reaction; (c) True; (d) False—Alkyl cyanide on hydrolysis yields an acid depending on the nature of *R*; (e) True; (f) True; (g) False—Acetic acid forms methylamine on treatment with N_3H and conc. H_2SO_4; (h) True; (i) True; (j) False—Basic; (k) True; (l) True; (m) False—Amides are hydrolysis products of nitriles; (n) False—Nitroalkanes are more polar than alkyl nitrites; (o) True; (p) True; (q) False—Isocyanides are also called carbylamines; (r) False—Tertiary amine does not react with Grignard reagents; (s) True; (t) False—Primary amines are more soluble than tert. amines; (u) True; (v) False—Amines are Lewis bases; (w) True; (x) True; (y) False—Nitriles are less poisonous than isomeric isonitriles; (z) True.

3. (A—5); (B—7); (C—1); (D—8); (E—2); (F—4); (G—3); (H—6).

4. (i) $CH_3NH_2 + CHCl_3 + 3KOH \rightarrow CH_3NC + 3KCl + 3H_2O$

(ii) $RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$

(iii) $C_2H_5NH_2 + C_2H_5I \longrightarrow (C_2H_5)_2NH \xrightarrow{C_2H_5I} (C_2H_5)_3N \xrightarrow{C_2H_5I} (C_2H_5)_4NI$

(iv) $C_2H_5NH_2 + NaNO_2 + HCl \rightarrow C_2H_5OH + N_2 + NaCl + H_2O$

(v) $CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$

(vi) $C_2H_5NH_2 + CH_3COCl \longrightarrow C_2H_5NHCOCH_3 + HCl$

(vii) $CH_3CN + CH_3MgBr \longrightarrow (CH_3)_2C{=}NMgBr \xrightarrow{2H_2O} (CH_3)_2CO + NH_3 + Mg(OH)Br$

(viii) $C_2H_5NC + 2H_2O \xrightarrow{\text{Dil. HCl}} C_2H_5NH_2 + HCOOH$

(ix) $2C_2H_5NH_2 + AgCl \longrightarrow [(C_2H_5NH_2)_2Ag]^+Cl^-$

(x) $KOH + Br_2 \longrightarrow KBrO + HBr$

$EtNH_2 + KBrO \longrightarrow \underset{N\text{-Bromoethylamine}}{EtNHBr} + KOH$

$EtNHBr + KCN \longrightarrow \underset{N\text{-Cyanoethylamine}}{EtNHCN} + KBr$

(*D*) May be EtNHBr or EtNHCN.

(xi) $C_2H_5NCO + 2KOH \longrightarrow C_2H_5NH_2 + K_2CO_3$

(xii) $CH_3CH{=}NOH + 4H \xrightarrow{\text{Na/alcohol}} CH_3CH_2NH_2 + H_2O$

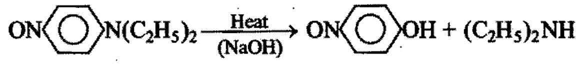
(xiii) $R_2NCN \xrightarrow{H_2O} R_2NH + CO_2 + NH_3$

(xiv) $RNC + 4H \xrightarrow{\text{Catalytically}} RNHCH_3$

(xv) $[(CH_3)_4N]^+OH \xrightarrow[\text{decomposition}]{\text{Thermal}} (CH_3)_3N + CH_3OH$

(xvi) $RNO_2 + 6H \xrightarrow{Zn/HCl} RNH_2 + 2H_2O$

(xvii) $R_2NH + RI \longrightarrow R_3N + HI$

(xviii) 

(xix) $(CH_3)_2CHNH_2 + 2HCHO + HCOOH \xrightarrow{\text{Heat}} (CH_3)_2CH{-}N(CH_3)_2 + CO_2 + H_2O$

(xx) $(CH_3)_3C{-}OH + HCN + H_2SO_4 \xrightarrow{\text{Heat}} (CH_3)_3C{-}NH_2 + HCOOH$

(xxi) $CH_3CH_2NH_2 \xrightarrow[\text{Heat}]{(CH_3CO)_2O} CH_3CH_2NHCOCH_3 + CH_3COOH$

5. (i) (*A*) $CH_3CH_2COONH_4$ (Amm. propionate);
(*B*) $CH_3CH_2CONH_2$ (Propionamide);
(*C*) $CH_3CH_2NH_2$ (Ethylamine)

(ii) (*A*) $CH_3CH_2N{=}HCC_6H_5$;
(*B*) $CH_3CH_2NH{-}H_2CC_6H_5$

(iii) (*A*) C_2H_5OH; (*B*) CH_3CHO; (*C*) CH_3COOH;
(*D*) CH_3NH_2 (Methylamine)

(iv) (*A*) CH_3CH_2CN; (*B*) $CH_3CH_2CH_2NH_2$;
(*C*) $CH_3CH_2CH_2OH$ (Propyl alcohol)

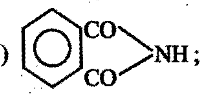
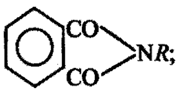
(v) (*A*) CH_3CONH_2; (*B*) CH_3NH_2; (*C*) CH_3OH

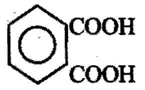
(vi) (*A*) C_2H_5Cl; (*B*) C_2H_5NC; (*C*) $C_2H_5NHCH_3$

(vii) (*A*) $PhSO_2NHEt$; (*B*) $PhSO_2N(Na)Et$; (*C*) $PhSO_2N(Et)_2$;
(*D*) $PhSO_2OH$; (*E*) $[Et_2NH_2]^+OH^-$

(viii) The amine undergoes exhaustive methylation forming $RCH_2CH_2NMe_3^+I^-$, (*A*), which is converted to (*B*), $RCH_2CH_2NMe_3^+OH^-$. When (*B*) is heated, a Hofmann elimination occurs.

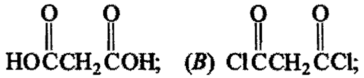
$$\underset{(B)}{RCH_2CH_2NMe_3^+OH^-} \longrightarrow \underset{(C)}{RCH{=}CH_2} + Me_3N + H_2O$$

(ix) (*A*)  ; (*B*) 

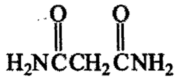
(*C*) and (*D*)  and RNH_2

(x) (*A*) $C_2H_5CONH_2$; (*B*) $C_2H_5NH_2$; (*C*) $C_2H_5NHCOCH_3$

(xi) (*A*) $(CH_3)_2CHCONH_2$; (*B*) $(CH_3)_2CHNH_2$;
(*C*) $(CH_3)_2CHNC$

(xii) 

(*A*) $HO\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}OH$; (*B*) $Cl\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}Cl$;

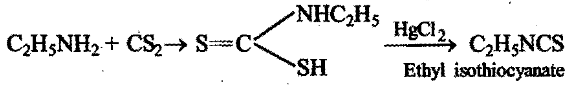


(*C*) $H_2N\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}NH_2$

6. (i) $CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$

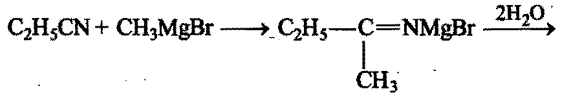
(ii) $CH_3NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3NC + 3KCl + 3H_2O$

(iii) $CH_3CH_2NH_2 + (CH_3CO)_2O \longrightarrow CH_3CH_2NHCOCH_3 + CH_3COOH$

(iv) 

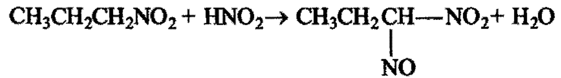
Ethyl isothiocyanate

(v) $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$

(vi) 

$C_2H_5CN + CH_3MgBr \longrightarrow C_2H_5{-}\underset{\underset{CH_3}{|}}{C}{=}NMgBr \xrightarrow{2H_2O} C_2H_5COCH_3 + NH_3 + Mg(OH)Br$

(vii) $C_2H_5NO_2 + 4[H] \xrightarrow[NH_4Cl]{Zn} \underset{\text{Ethyl hydroxylamine}}{C_2H_5NHOH} + H_2O$

(viii) 

$CH_3CH_2CH_2NO_2 + HNO_2 \rightarrow CH_3CH_2\underset{\underset{NO}{|}}{CH}{-}NO_2 + H_2O$

Nitrosonitro propane

(ix) $C_2H_5ONO + 4[H] \xrightarrow{LiAlH_4} C_2H_5OH + NH_2OH$

(x) $RCN + 4H \xrightarrow{Na/C_2H_5OH} RCH_2NH_2$

7. (i) Hofmann's bromamide reaction;
   (ii) $CH_3CH_2CONH_2$ (Propanamide); CH_3CH_2COOH (Propionic acid);
   (iii) $CH_3CH_2CH_2NO_2$, $CH_3—CH(NO_2)—CH_3$;
   (iv) $(CH_3)_3N$, C_2H_4;
   (v) $(CH_3)_3N$, CH_3OH;
   (vi) Carbylamine reaction;
   (vii) $CH_3CH_2CH_2NH_2$, $CH_3CH_2NHCH_3$, $(CH_3)_3N$;
   (viii) Primary amine;
   (ix) $CH_3CH_2NHCH_3$;
   (x) Gabriel's phthalimide reaction.
8. See the preparation of ethylamine.
9. See the properties of ethylamine.
11. (a) Ethylamine (primary amine) gives carbylamine test. It gives a foul odour when heated with chloroform and alcoholic KOH. Diethylamine (secondary amine) does not give this test.
   (b) Acetamide when heated with NaOH, gives a smell of ammonia, ethylamine does not evolve NH_3. Ethylamine gives carbylamine reaction while acetamide does not give this test.
   (c) Diethylamine reacts with nitrous acid to form *N*-nitrosoamine which is water insoluble yellow oil while triethylamine reacts with nitrous acid to form soluble nitrite salt. There is no visible sign of reaction. Diethylamine reacts with benzene sulphonyl chloride and forms a solid insoluble in alkali. Tertiary amine (triethyl amine) does not react with benzene sulphonyl chloride.
   (d) Ethyl nitrite on hydrolysis forms C_2H_5OH while nitroethane does not undergo hydrolysis.
12. (i) $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$

(ii) $CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow{Heat} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$

(iii) $CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2$

(iv) $C_2H_5Cl \xrightarrow{KCN} C_2H_5CN \xrightarrow[{[H]}]{Na/C_2H_5OH} C_2H_5CH_2NH_2$

(v) $C_2H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} C_2H_5NC + 3KCl + 3H_2O$

(vi) $C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$

[Now proceed as (ii)]

(vii) $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{SOCl_2} CH_3CH_2Cl \xrightarrow{NH_3} CH_3CH_2NH_2$

or $CH_3COOH \xrightarrow[\text{(ii) Heat}]{\text{(i) } NH_3} CH_3CONH_2 \xrightarrow{P_2O_5} CH_3CN \xrightarrow[{[H]}]{Na/C_2H_5OH} CH_3CH_2NH_2$

(viii) See conversion Sec 14.7.

(ix) See conversion Sec. 14.7.

(x) $CH_3OH \xrightarrow{SOCl_2} CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow[{[H]}]{Na/C_2H_5OH} CH_3CH_2NH_2$

(xi) $CH_3CH{=}CH_2 \xrightarrow{HBr/H_2O_2} CH_3CH_2CH_2Br \xrightarrow{KCN} CH_3CH_2CH_2CN \xrightarrow[{4[H]}]{Na/C_2H_5OH} CH_3CH_2CH_2CH_2NH_2$

(xii) $CH_3COCH_3 \xrightarrow{H_2NOH} (CH_3)_2C{=}NOH \xrightarrow{LiAlH_4} (CH_3)_2CHNH_2$

13. (a) Primary amines produce nitrogen gas.

$$RNH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O$$

Secondary amines produce a yellow oily layer.

$$R_2NH + HNO_2 \longrightarrow \underset{\substack{N\text{-Nitrosoamine}\\ \text{(Yellow oil)}}}{R_2NNO} + H_2O$$

Tertiary amines form soluble nitrite salts.

$$R_3N + HNO_2 \longrightarrow [R_3NH]^+ NO_2^-$$

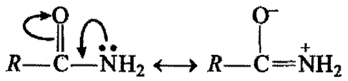
(b) (i) $CH_3CH_2CN + 2H_2O \xrightarrow{Dil.\ HCl} \underset{\text{Propanoic acid}}{CH_3CH_2COOH} + NH_3$

(ii) $CH_3CN + H_2O \xrightarrow[H_2O_2]{OH^-} \underset{\text{Ethanamide}}{CH_3CONH_2}$

(iii) $C_2H_5NC + 2H_2O \xrightarrow{Dil.\ HCl} \underset{\text{Ethanamine}}{C_2H_5NH_2} + HCOOH$

(iv) $C_2H_5NO_2 + H_2O \xrightarrow{Dil.\ HCl} CH_3COOH + NH_2OH$

14. (i) Alkyl cyanides are polar and exist as highly associated molecules, thus possess higher boiling point than alkyl halides which are less polar molecules.
   (ii) Alkyl cyanides are polar and form hydrogen bonding with water molecules while isocyanides do not form hydrogen bonding with water molecules.
   (iii) Amines contain a lone pair of electrons on its nitrogen atom which is easily available for protonation. This is the cause of basic nature. Any other group which increases the electron density on nitrogen increases the basicity.
   (iv) Ethyl group is an electron releasing group, *i.e.*, it increases electron density on nitrogen due to +*I* effect. On the other hand phenyl group is an electron withdrawing group, *i.e.*, it decreases the electron density on nitrogen due to –*I* effect. Thus, ethylamine is more basic than aniline.
   (v) In simple amines, the unshared electron pair is usually localised on the nitrogen atom, hence available for protonation. In amides, the electron pair is delocalised to the carbonyl group through resonance.



$$R—\overset{\overset{O}{\|}}{C}—\ddot{N}H_2 \longleftrightarrow R—\overset{\overset{O^-}{|}}{C}{=}\overset{+}{N}H_2$$

   (vi) Primary and secondary amines can form hydrogen bonds whereas tertiary amines fail to do so.
   (vii) Methyl amine like NH_3 forms a complex with Ag^+ ions thereby decreasing the concentration of silver ions in solution. Thus, the product of concentration of silver and chloride ions is less than solubility product of AgCl.
   (viii) Nitrogen forms three sp^3-hybridized sigma bonds to the carbon atoms of the methyl groups and has a non-bonding electron pair in the fourth sp^3-orbital. Thus, $(CH_3)_3N$ has roughly pyramidal shape.

(ix) $Me_4\overset{+}{N}OH^-$ completely ionises while Me_3N like NH_3 combines with water to produce OH^- ions.

$$Me_3N + H_2O \rightleftharpoons [Me_3\overset{+}{N}H][OH]^- \rightleftharpoons [Me_3NH]^+ + [OH^-]$$

K_b of this reaction is very small. Thus, due to high concentration of OH^- ions in $Me_4\overset{+}{N}OH^-$, it is more basic.

(x) Ethylamine possesses two hydrogen atoms that can form hydrogen bonds whereas diethylamine having only one hydrogen atom is capable of forming only one hydrogen bond.

(xi) For the preparation of $(CH_3)_3CNH_2$ (a tertiary butyl amine), a tertiary alkyl bromide is required which has the tendency to eliminate HBr.

$$(CH_3)_3CBr \xrightarrow{-HBr} \underset{\text{Alkene}}{(CH_3)_2C{=}CH_2}$$

In the case of $(CH_3)_3CCH_2NH_2$ which is actually a primary amine, a primary alkyl bromide, $(CH_3)_3CCH_2Br$ is required. This possesses a large group, $(CH_3)_3C{-}CH_2{-}$, which has large steric effect and thus S_N2 reaction is difficult to form $(CH_3)_3CCH_2NH_2$. However, rearrangement occurs to form an alkene.

$$(CH_3)_3CCH_2Br \longrightarrow (CH_3)_3C\overset{+}{C}H_2 \rightarrow (CH_3)_2\overset{+}{C}CH_2CH_3 \xrightarrow{-H^+} (CH_3)_2C{=}CHCH_3$$

These amines can be prepared easily from the corresponding acids which follow Hofmann's bromamide reaction in which there is no chance of alkene formation due to intramolecular rearrangement.

$$(CH_3)_3C{-}COOH \xrightarrow[\text{(ii) } NH_3]{\text{(i) } PCl_5} (CH_3)_3CCONH_2 \xrightarrow[KOH]{Br_2} (CH_3)_3CNH_2$$

(xii) The hybrid atomic orbitals used by nitrogen in the compounds are sp^3, sp^2 and sp respectively.

$CH_3\ddot{N}H_2(sp^3)$, $CH_3\ddot{N}{=}CHCH_3(sp^2)$, $CH_3C\ddot{N}(sp)$,

The compound with least s-character is most basic, thus, CH_3NH_2 is most basic and CH_3CN is least basic as it has more s-character.

(xiii) Two factors operate in deciding the basicity of alkyl amines, *i.e.*, inductive effect and solvation effect.

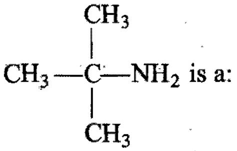
Inductive effect: Alkyl group being electron releasing, increases the charge density on nitrogen. This in turn increases the basicity of amines. Thus, the expected order of basicity is:

$$R_3N > R_2NH > RNH_2 > NH_3$$

But the steric factor in R_3N makes the availability of a lone pair of electrons on nitrogen poor than in R_2NH, predicting R_2NH a stronger base than R_3N.

OBJECTIVE QUESTIONS

SET I : This set contains the questions with single correct answer.



1. $CH_3-C(CH_3)_2-NH_2$ is a:

(a) primary amine ☐ (b) secondary amine ☐
(c) tertiary amine ☐ (d) quaternary salt ☐

2. Ethylamine reacts with nitrous acid to form: **[PMT (Haryana) 2004]**

(a) methyl alcohol ☐ (b) ethyl alcohol ☐
(c) ethane ☐ (d) ethyl nitrite ☐

3. The reaction between primary amine, chloroform and few drops of alcoholic KOH is known as: **[AFMC 2008]**

(a) Hofmann's reaction ☐
(b) Kolbe's reaction ☐
(c) Carbylamine reaction ☐
(d) Reimer-Tiemann's reaction ☐

4. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is:

(a) methylamine ☐ (b) ethylamine ☐
(c) triethylamine ☐ (d) diethylamine ☐

[**Hint** : $R_2NH + HONO \longrightarrow R_2N—NO$ (nitrosoamine) yellow oil.]

5. Gabriel phthalimide synthesis is used in the preparation of: **[AMU (Med.) 2006]**

(a) 1° amine ☐ (b) 2° amine ☐
(c) 3° amine ☐ (d) 4° amine ☐

6. Which one of the following is the weakest base?

(a) Triethylamine ☐ (b) Diethylamine ☐
(c) Ethylamine ☐ (d) Ammonia ☐

7. Methylamine can be prepared by:

(a) Wurtz reaction ☐
(b) Friedel-Crafts reaction ☐
(c) Hofmann's bromamide reaction ☐
(d) Clemmensen's reaction ☐

8. Nitroparaffins on reduction give:

(a) amides ☐ (b) alkylamines ☐
(c) ammonium salts ☐ (d) acetanilides ☐

9. Primary amines are identified by:

(a) Hofmann's reaction ☐
(b) Carbylamine reaction ☐
(c) Friedel-Crafts reaction ☐
(d) Biuret reaction ☐

10. Amines are more basic than:

(a) alcohols ☐ (b) ethers ☐
(c) esters ☐ (d) all of these ☐

11. A colourless, odourless and non-combustible gas is liberated when ethylamine reacts with:

(a) NaOH ☐ (b) CH_3COCl ☐
(c) $NaNO_2 + HCl$ ☐ (d) H_2SO_4 ☐

12. The product (*D*) in the following sequence of reactions is:

$$CH_3COOH \xrightarrow{NH_3} (A) \xrightarrow{Heat} (B) \xrightarrow{P_2O_5} (C) \xrightarrow{Na + C_2H_5OH} (D)$$

(a) ester ☐ (b) amine ☐
(c) acid ☐ (d) alcohol ☐

13. The strongest base among the following is: **[AIEEE 2007]**

(a) $C_6H_5NH_2$ ☐ (b) CH_3NH_2 ☐
(c) $(CH_3)_2NH$ ☐ (d) $(CH_3)_3N$ ☐

14. When a primary amine is warmed with carbon disulphide in the presence of mercuric chloride, the product is:

(a) carbylamine ☐ (b) alkyl isothiocyanate ☐
(c) mercaptan ☐ (d) alkyl cyanide ☐

15. The correct order of basic nature of CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ and NH_3 is: **[CET (Karnataka) 2009]**

(a) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N > NH_3$ ☐
(b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$ ☐
(c) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ ☐
(d) $NH_3 > (CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$ ☐

16. Ethylamine reacts with acetyl chloride to form:

(a) *N*-ethyl acetamide ☐ (b) ethyl chloride ☐
(c) ethyl acetate ☐ (d) ethane ☐

17. Ethylamine reacts with nitrosyl chloride (NOCl) to form:

(a) ethyl chloride ☐ (b) ethyl alcohol ☐
(c) ethyl nitrite ☐ (d) nitroethane ☐

18. Ethylamine on oxidation with acidified $KMnO_4$ gives:

(a) an acid ☐ (b) an alcohol ☐
(c) an aldehyde ☐ (d) a nitrile compound ☐

19. Which one of the following will give primary amine on hydrolysis?

(a) Nitroparaffin ☐ (b) Alkyl cyanide ☐
(c) Amide ☐ (d) Alkyl isocyanide ☐

20. When methyl iodide is treated with ammonia, the product obtained is:

(a) methylamine ☐ (b) dimethylamine ☐
(c) trimethylamine ☐ (d) all of these ☐

21. Which of the following does not react with acetyl chloride?

(a) $(CH_3)_3N$ ☐ (b) $(CH_3)_2NH$ ☐
(c) $C_2H_5NH_2$ ☐ (d) C_2H_5OH ☐

22. A solution of ethylamine:

(a) turns blue litmus red ☐
(b) turns red litmus blue ☐
(c) does not affect the litmus ☐
(d) bleaches the litmus ☐

23. Which of the following is the least basic amine ? **[PET (Kerala) 2010]**

(a) Methylamine ☐ (b) Ethylamine ☐
(c) Diethylamine ☐ (d) Aniline ☐
(e) Benzylamine ☐

24. When acetamide reacts with Br_2 and caustic soda, then we get: **[PMT (MP) 2005]**

(a) acetic acid ☐ (b) bromoacetic acid ☐
(c) ethylamine ☐ (d) CH_3NH_2 ☐

25. Butanonitrile may be prepared by:
(a) propyl alcohol + KCN ☐
(b) butyl alcohol + KCN ☐
(c) butyl chloride + KCN ☐
(d) propyl chloride + KCN ☐

26. Which compound is obtained at the end of the following reaction?

Ethylamine $\xrightarrow{HNO_2}(A)\xrightarrow{PCl_5}(B)\xrightarrow{NH_3}(C)$

(a) Ethyl cyanide ☐ (b) Ethylamine ☐
(c) Methylamine ☐ (d) Acetamide ☐

27. Mark the correct statement:
(a) methylamine is slightly acidic ☐
(b) methylamine is less basic than ammonia ☐
(c) methylamine is more basic than ammonia ☐
(d) methylamine forms salts with alkalies ☐

28. When amine is heated with chloroform and alcoholic KOH, a bad odour compound is formed. The compound is: **[AIEEE 2002; CBSE (Med.) 2003]**
(a) an alcohol ☐ (b) an aldehyde ☐
(c) a cyanide ☐ (d) an isocyanide ☐

29. Which of the following reactions does not yield an amine?
(a) $R—C{\equiv}N + H_2O \xrightarrow{H^+}$....... ☐
(b) $R—X + NH_3 \longrightarrow$....... ☐
(c) $R—CH{=}NOH + [H] \xrightarrow[C_2H_5OH]{Na}$....... ☐
(d) $RCONH_2 + 4[H] \xrightarrow{LiAlH_4}$........ ☐

30. Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine ? **[CBSE (PMT) Prelims 2010]**
(a) $NaOH\text{-}Br_2$ ☐ (b) Sodalime ☐
(c) PCl_5 ☐ (d) Hot conc. H_2SO_4 ☐

31. Nitroalkane is acidic only towards:
(a) Na_2CO_3 ☐ (b) C_2H_5OH ☐
(c) NaOH ☐ (d) liquid NH_3 ☐

32. Which of the following is not an ambident nucleophile?
(a) —ONO ☐ (b) $—OCH_3$ ☐
(c) —CN ☐ (d) —CNO ☐

33. Amines behave as: **[CET (Karnataka) 2008]**
(a) aprotic acid ☐ (b) neutral compound ☐
(c) Lewis acid ☐ (d) Lewis base ☐

34. The hybridization of nitrogen atom in amines is:
(a) sp ☐ (b) sp^2 ☐
(c) sp^3 ☐ (d) dsp^2 ☐

35. An organic compound (*A*) on reduction gave a compound (*B*). Upon treatment with HNO_2, (*B*) gave ethyl alcohol and on warming with $CHCl_3$ and alcoholic KOH, (*B*) gave offensive smell. The compound (*A*) is:
(a) CH_3CN ☐ (b) C_2H_5CN ☐
(c) CH_3NH_2 ☐ (d) CH_3NC ☐

36. Silver chloride is soluble in methylamine due to the formation of:
(a) $[Ag(CH_3NH_2)_4]Cl$ ☐ (b) $[Ag(CH_3NH_2)_2]Cl$ ☐
(c) $[Ag(CH_3NH_2)_3]Cl$ ☐ (d) $[Ag(CH_3NH_2)]Cl$ ☐

37. Hinsberg's reagent is:
(a) benzene sulphonamide ☐
(b) benzene sulphonic acid ☐
(c) benzene sulphuryl chloride ☐
(d) benzene sulphonyl chloride ☐

38. Which of the following compounds caused tragedy of Bhopal in 1984? **[EAMCET (Engg.) 2007; Punjab PMET (Med.) 2008]**
(a) Phosgene ☐ (b) Methyl isocyanate ☐
(c) Carbon monoxide ☐ (d) Methyl cyanate ☐

39. Trimethylamine has:
(a) planar geometry ☐
(b) trigonal bipyramidal geometry ☐
(c) pyramidal shape ☐
(d) octahedral geometry ☐

40. C_3H_9N represents:
(a) primary amine ☐ (b) secondary amine ☐
(c) tertiary amine ☐ (d) all of these ☐

41. The conjugate base of $[(CH_3)_3NH]^+$ is:
(a) $(CH_3)_3N$ ☐ (b) $(CH_3)_3N^-$ ☐
(c) $(CH_3)_2N^+$ ☐ (d) $(CH_3)_3N^+$ ☐

42. $CH_3CH_2NH_2$ contains a basic NH_2 group, but CH_3CONH_2 does not because:
(a) in CH_3CONH_2, the lone pair of electron on N-atom is delocalised due to resonance ☐
(b) CH_3CONH_2 is amphoteric in nature ☐
(c) in $CH_3CH_2NH_2$, the lone pair of electrons on N-atom is delocalised due to resonance ☐
(d) CH_3CONH_2 is an acidic derivative ☐

43. Acetamide and ethylamine can be distinguished by using:
(a) aqueous HCl and heat ☐
(b) aqueous NaOH and heat ☐
(c) Br_2 water ☐
(d) acidic $K_2Cr_2O_7$ ☐

44. The correct increasing order of basic strengths in, $CH_3CH_2CN, CH_3CH_2NH_2, CH_3N{=}CHCH_3$ is:
(a) $CH_3N{=}CHCH_3, CH_3CH_2NH_2, CH_3CH_2CN$ ☐
(b) $CH_3CH_2NH_2, CH_3N{=}CHCH_3, CH_3CH_2CN$ ☐
(c) $CH_3CH_2CN, CH_3N{=}CHCH_3, CH_3CH_2NH_2$ ☐
(d) $CH_3CH_2CN, CH_3CH_2NH_2, CH_3N{=}CHCH_3$ ☐

45. Which one of the following behaves both as nucleophile and as an electrophile?
(a) $CH_3C{\equiv}N$ ☐ (b) $CH_3—OH$ ☐
(c) $H_2C{=}CH—CH_3$ ☐ (d) $CH_3—NH_2$ ☐

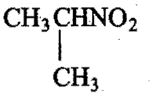
46. The boiling points of amines and their corresponding alcohols and acids vary in the order:
(a) $RCH_2NH_2 > RCOOH > RCH_2OH$ ☐
(b) $RCH_2NH_2 > RCH_2OH > RCOOH$ ☐
(c) $RCH_2NH_2 < RCOOH < RCH_2OH$ ☐
(d) $RCH_2NH_2 < RCH_2OH < RCOOH$ ☐

47. Reduction of nitroalkanes in neutral medium, (*e.g.*, $Zn + NH_4Cl$) forms mainly:
(a) R—NH_2 ☐ (b) R—NHOH ☐
(c) R—N=N—Cl ☐ (d) all of these ☐

48. Which one of the following on reduction with $LiAlH_4$ yields a secondary amine? **[CBSE (Med.) 2007]**
(a) Methyl cyanide ☐ (b) Nitroethane ☐
(c) Methyl isocyanide ☐ (d) Acetamide ☐

49. A primary nitroalkane is treated with nitrous acid, which of the following will be the main product?
(a) Pseudonitrol ☐ (b) Nitrolic acid ☐
(c) A primary amine ☐ (d) A primary alcohol ☐

50. A nitrogenous compound is treated with HNO_2 and the product so formed is further treated with NaOH solution which produces blue colouration. The nitrogenous compound is:
(a) $CH_3CH_2NH_2$ ☐ (b) $CH_3CH_2NO_2$ ☐
(c) CH_3CH_2ONO ☐ (d)



$CH_3\underset{\underset{CH_3}{|}}{C}HNO_2$ ☐

51. By heating alkyl halide with alcoholic ammonia in a sealed tube, a mixture of three amines are formed and this reaction is known as:
(a) Hofmann's bromamide reaction ☐
(b) Hinsberg's method ☐
(c) Hofmann's method ☐
(d) ammonolysis of alcohol ☐

52. By distilling glycine with barium hydroxide, it gives:
(a) ethylamine ☐ (b) methylamine ☐
(c) amino acid ☐ (d) acetic acid ☐

53. Ethylamine is obtained by the action of sodium hypobromite on the following amide:
(a) formamide ☐ (b) acetamide ☐
(c) propanamide ☐ (d) butanamide ☐

54. Primary amines on oxidation with acidified $KMnO_4$, followed by hydrolysis gives:
(a) aldehydes only ☐ (b) ketones only ☐
(c) aldehydes or ketones ☐ (d) carboxylic acids ☐

55. Secondary amines on oxidation with $KMnO_4$ gives:
(a) dialkyl hydroxylamine ☐
(b) tetraalkyl hydrazine ☐
(c) ketones ☐
(d) amine oxide ☐

56. Secondary amines on oxidation with Caro's acid gives:
(a) dialkyl hydroxylamine ☐
(b) tetraalkyl hydrazine ☐
(c) ketones ☐
(d) amine oxide ☐

57. Carbylamine reaction is shown by: **[JEE (Orissa) 2010]**
(a) Quaternary salt ☐ (b) 3°-amine ☐
(c) 2°-amine ☐ (d) 1°-amine ☐

58. Which of the following is hydrolysed to give secondary amine?
(a) Alkyl cyanide ☐ (b) Nitroalkanes ☐
(c) Acid amide ☐ (d) Dimethyl formamide ☐

59. Which of the following methods is generally not employed for the separation of primary, secondary and tertiary amines?
(a) Fractional distillation ☐
(b) Hinsberg's method ☐
(c) Hofmann's method ☐
(d) Filtration ☐

60. How many primary amines are possible for the formula $C_4H_{11}N$? **[MGIMS (Wardha) 2006; JEE (WB) 2008]**
(a) 5 ☐ (b) 6 ☐
(c) 3 ☐ (d) 4 ☐

61. Primary, secondary and tertiary amines can be distinguished by: **[AFMC 2010]**
(a) Schiff's test ☐ (b) Fehling's test ☐
(c) Hinsberg test ☐ (d) Tollen's test ☐

62. When methyl cyanide is hydrolysed in presence of alkali, it forms:
(a) acetamide ☐ (b) methane ☐
(c) $CO_2 + H_2O$ ☐ (d) acetic acid ☐

63. By passing the mixture of the vapours of alcohol and excess of ammonia over heated alumina at 350°C, the main product obtained is:
(a) primary amine ☐
(b) secondary amine ☐
(c) tertiary amine ☐
(d) a mixture of pri., sec. and tert. amines ☐

64. What is the decreasing order of basicity of pri., sec., tert., ethyl amines and NH_3?
(a) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$ ☐
(b) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$ ☐
(c) $(C_2H_5)_2NH > C_2H_5NH_2 > (C_2H_5)_3N > NH_3$ ☐
(d) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > (C_2H_5)_3N$ ☐

65. Alkylation is possible in:
(a) primary amines only ☐
(b) secondary amines only ☐
(c) tertiary amines only ☐
(d) primary and secondary amines both ☐

66. Secondary amine forms yellow oily liquid with nitrous acid, which on warming with phenol and conc. H_2SO_4 gives a brown or red colour and which at once changes into blue-green. This reaction is called as:
(a) Carbylamine reaction ☐
(b) Liebermann's nitroso reaction ☐
(c) Gabriel phthalimide reaction ☐
(d) Hofmann's mustard oil reaction ☐

67. Tertiary amines dissolve in cold nitrous acid to form salt, which on warming decomposes to give:
(a) $R_3N{\cdot}HNO_2$ ☐ (b) $R_2N{\cdot}NO$ ☐
(c) ROH ☐ (d) $R_2N{\cdot}NO + ROH$ ☐

68. Acetamide reacts with NaOBr in alkaline medium to form:
(a) NH_3 ☐ (b) CH_3NH_2 ☐
(c) CH_3CN ☐ (d) $CH_3CH_2NH_2$ ☐

69. Hofmann's hypobromite reaction affords a method of:
(a) preparing a tertiary amine ☐
(b) preparing a mixture of amines ☐

(c) stepping down a series ☐
(d) stepping up a series ☐

70. Treatment of ammonia with excess of ethyl chloride will yield:
(a) diethylamine ☐
(b) methylamine ☐
(c) tetraethyl ammonium chloride ☐
(d) ethane ☐

71. By heating ammonium chloride with two equivalents of formaldehyde it forms:
(a) dimethylamine ☐ (b) ethylamine ☐
(c) methylamine ☐ (d) ammonium formate ☐

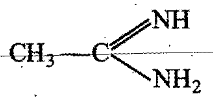
72. Comparing basic strength of NH_3, CH_3NH_2 and $C_6H_5NH_2$, it may be concluded that: **[AMU (Engg.) 2009]**
(a) basic strength remains unaffected ☐
(b) basic strength of NH_3 is highest ☐
(c) basic strength of alkylamine is lowest ☐
(d) basic strength of arylamine is lowest ☐

73. During acetylation of amines, what is replaced by acetyl group? **[CPMT 2008]**
(a) Hydrogen atom attached to nitrogen atom ☐
(b) One or more hydrogen atoms attached to nitrogen atom ☐
(c) One or more hydrogen atoms attached to carbon atom ☐
(d) Hydrogen atoms attached to either carbon atom or nitrogen atom ☐

74. Which one of the following is called a carbylamine?: **[JEE (WB) 2009]**
(a) *R*NC ☐ (b) $RCONH_2$ ☐
(c) *R*CN ☐ (d) $RCH=NH$ ☐

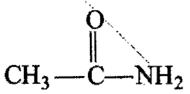
75. Which is most basic? **[AFMC 2009]**
(a) Aniline ☐ (b) *p*-nitroaniline ☐
(c) Benzylamine ☐ (d) *p*-methylaniline ☐

76. The correct order of basicities of the following compounds is: **[IIT (S) 2001]**


(1)

$CH_3-CH_2-NH_2$
(2)

$(CH_3)_2NH$
(3)


$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$
(4)

(a) 2 >1 > 3 > 4 ☐ (b) 1 > 3 > 2 > 4 ☐
(c) 3 > 1 > 2 > 4 ☐ (d) 1 > 2 > 3 > 4 ☐

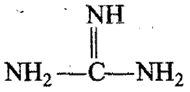
77. The compound that will react most readily with NaOH to form methanol is: **[IIT (S) 2001]**
(a) $(CH_3)_4\overset{+}{N}I^-$ ☐ (b) CH_3OCH_3 ☐
(c) $(CH_3)_3\overset{+}{S}I^-$ ☐ (d) $(CH_3)_3CCl$ ☐

78. $CH_3CH_2Cl \xrightarrow{NaCN} (X) \xrightarrow{Ni/H_2} (Y) \xrightarrow{\text{Acetic anhydride}} (Z)$
(*Z*) in the above reaction sequence is: **[CBSE (Med.) 2002]**
(a) $CH_3CH_2CH_2NHCOCH_3$ ☐
(b) $CH_3CH_2CH_2NH_2$ ☐
(c) $CH_3CH_2CH_2CONHCH_3$ ☐
(d) $CH_3CH_2CH_2CONHCOCH_3$ ☐

79. Which is most basic? **[UGET (Med.) 2002; PET (Kerala) 2007]**
(a) $C_6H_5NH_2$ ☐ (b) $(C_6H_5)_2NH$ ☐
(c) $C_2H_5NH_2$ ☐ (d) $(C_2H_5)_2NH$ ☐

80. Among following the weakest base is: **[AIIMS 2003]**
(a) $C_6H_5CH_2NH_2$ ☐ (b) $C_6H_5CH_2NHCH_3$ ☐
(c) $O_2N-CH_2NH_2$ ☐ (d) CH_3NHCHO ☐

81. The correct order of the basic strength of following compounds is: **[SCRA 2009]**


(1)

$C_6H_5NH_2$
(2)


(3)


(4)

(a) 4 > 2 > 3 > 1 ☐ (b) 4 > 2 > 1 >3 ☐
(c) 1 > 3 > 2 > 4 ☐ (d) 1 > 3 > 4 > 2 ☐

82. Ethyl isocyanide on hydrolysis in acidic medium gives: **[AIEEE 2003]**
(a) ethanoic acid and ammonium salt ☐
(b) propanoic acid and ammonium salt ☐
(c) ethylamine salt and methanoic acid ☐
(d) methylamine salt and ethanoic acid ☐

83. In the reaction,

$$CH_3CN + 2H \xrightarrow[Ether]{HCl} (X) \xrightarrow{\text{Boiling } H_2O} (Y);$$

the term *Y* is: **[BHU 2004; BVP (Med.) 2007]**
(a) acetaldehyde ☐ (b) ethylamine ☐
(c) acetone ☐ (d) dimethylamine ☐

84. A primary amine is formed from an amide, by the treatment of bromine and alkali. The primary amine has: **[BHU 2004]**
(a) 1 carbon atom less than amide ☐
(b) 1 carbon atom more than amide ☐
(c) 1 hydrogen atom less than amide ☐
(d) 1 hydrogen atom more than amide ☐

85. $C_6H_5C\equiv N + 2[H] \xrightarrow{SnCl_2/HCl} C_6H_5CHO + NH_3$
The above reaction is: **[DPMT 2004]**
(a) Mendius reaction ☐
(b) Schmidt reaction ☐
(c) Rosenmund reaction ☐
(d) Stephen's reaction ☐

86. $HCONHR \xrightarrow[Pyridine]{POCl_3} (A) + H_2O$;
(*A*) in the above reaction is: **[BHU 2005]**

(a) $RCH{=}NOH$ ☐ (b) $R{-}N{=}C{=}O$ ☐
(c) $R{-}C{\equiv}N$ ☐ (d) $R{-}\overset{+}{N}{\equiv}\overset{-}{C}$ ☐

87. Which of the following is obtained in carbylamine reaction? **[EAMCET (Med.) 2005]**
(a) $C_2H_5NH_2$ ☐ (b) $COCl_2$ ☐
(c) C_6H_5CN ☐ (d) C_6H_5NC ☐

88. Acetonitrile on reduction gives: **[MHCET (Med.) 2005]**
(a) propanamine ☐ (b) methanamine ☐
(c) ethanamine ☐ (d) none of these ☐

89. An isonitrile on reduction gives: **[JIPMER 2005]**
(a) 3° amine ☐
(b) 2° amine ☐
(c) 1° amine ☐
(d) quaternary ammonium salts ☐

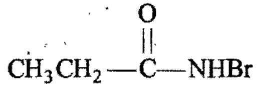
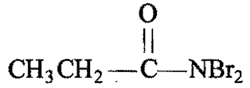
90. Which one of the following methods is neither meant for the synthesis nor for separation of amines? **[AIEEE 2005]**
(a) Hinsberg's method ☐ (b) Hofmann's method ☐
(c) Wurtz reaction ☐ (d) Curtius reaction ☐

91. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as: **[AIEEE 2005; UPSEE (Engg.) 2007]**
(a) a Schiff's base ☐ (b) an enamine ☐
(c) an imine ☐ (d) an amine ☐

92. Which of the following chemicals are used to manufacture methyl isocyanate that caused "Bhopal Tragedy"? **[AIIMS 2005]**
(i) Methylamine (ii) Phosgene
(iii) Phosphine (iv) Dimethylamine
(a) (i) and (ii) ☐ (b) (iii) and (iv) ☐
(c) (i) and (iii) ☐ (d) (ii) and (iv) ☐

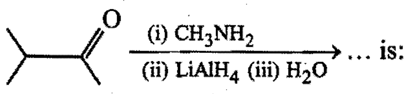
93. In the following sequence of reaction, the major product (c) is:

$$CH_3CH_2I \xrightarrow{NaCN} (A) \xrightarrow[\text{Partial hydrolysis}]{OH^-} (B) \xrightarrow{Br_2/NaOH} (C)$$

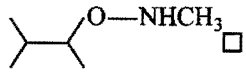
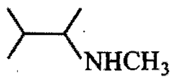
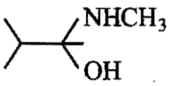
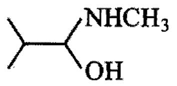
[DCE 2009]
(a) $CH_3CH_2NH_2$ ☐
(b)  $CH_3CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}NHBr$ ☐
(c) $CH_3CH_2COONH_4$ ☐
(d)  $CH_3CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}NBr_2$ ☐

94. Ethyl chloride on heating with AgCN forms a compound (X). The functional isomer of (X) is: **[KCET 2005]**
(a) C_2H_5NC ☐ (b) $C_2H_5NH_2$ ☐
(c) C_2H_5CN ☐ (d) none of these ☐

95. The major organic product formed from the following reaction,

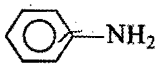


[JIPMER (Med.) 2007; AFMC 2010]

(a)  ☐ (b)  ☐
(c)  ☐ (d)  ☐

96. Which one of the following statements about CH_3CN is not true? **[PMT (Kerala) 2006]**
(a) Its IUPAC name is ethane nitrile ☐
(b) The bond between C and N is a triple bond ☐
(c) The C—C—N bond angle is 180° ☐
(d) The carbon-carbon bond is longer than the carbon-nitrogen bond ☐
(e) It has a relatively high boiling point due to hydrogen bonding ☐

97. Match the **List I** with **List II** and pick the correct matching from the codes given below:

List I	**List II**
(Reactants)	(Products)
A. $RX + KCN \xrightarrow{\text{ethanol}}$	1. 
B. $RX + CH_3COOAg \longrightarrow$	2. RCN
C. $CH_3C{\equiv}N \xrightarrow{LiAlH_4}$	3. CH_3COOR
D.  $\xrightarrow[\text{degradation}]{\text{Hofmann's}}$	4. $CH_3CH_2NH_2$
E. $R{-}NH_2 \xrightarrow[\substack{\text{reaction}\\ CHCl_3/KOH}]{\text{Carbylamine}}$	5. RNC

Codes: **[PMT (Kerala) 2006]**
(a) A—3, B—1, C—2, D—5, E—4 ☐
(b) A—2, B—3, C—4, D—1, E—5 ☐
(c) A—3, B—2, C—1, D—5, E—4 ☐
(d) A—5, B—3, C—2, D—4, E—1 ☐
(e) A—4, B—2, C—3, D—5, E—1 ☐

98. Which of the following is not a usual method for the preparation of primary amines? **[UPSEE (Engg.) 2010]**
(a) Curtius method ☐
(b) Gabriel phthalamide reaction ☐
(c) Hofmann's method ☐
(d) Reductive amination of $>C{=}O$ ☐

99. Choose the correct order for the boiling points of amines: **[CET (Gujarat) 2006]**
(a) $CH_3\ddot{N}H_2 > (CH_3)_2\ddot{N}H > (CH_3)_3\ddot{N}$ ☐
(b) $(CH_3)_2\ddot{N}H > (CH_3)_3\ddot{N} > CH_3\ddot{N}H_2$ ☐

(c) $(CH_3)_3\ddot{N} < CH_3\ddot{N}H_2 < (CH_3)_2\ddot{N}H$ ☐

(d) $CH_3\ddot{N}H_2 < (CH_3)_2\ddot{N}H < (CH_3)_3\ddot{N}$ ☐

100. State the product available by the following reaction:

$$CH_3CH_2CN + \text{ethanol} + H_2O \xrightarrow[\Delta]{\text{Conc. } H_2SO_4}$$

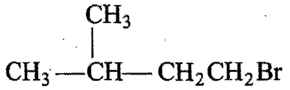
[CET (Gujarat) 2006]

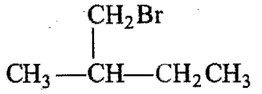
(a) ethyl formate + NH_3 ☐
(b) ethyl propanoate + NH_3 ☐
(c) ethyl butanoate + NH_3 ☐
(d) ethyl acetate + NH_3 ☐

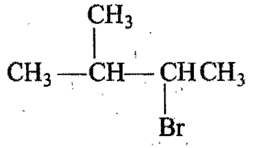
101. Which of the following reacts with Hinsberg's reagent (Benzene sulphonyl chloride) to form the product soluble in KOH? **[BHU 2006]**

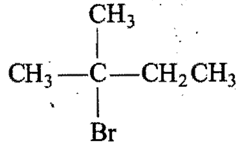
(a) Primary amine ☐ (b) Secondary amine ☐
(c) Tertiary amine ☐ (d) Quaternary amine ☐

102. Potassium phthalimide reacts with '*A*' which on hydrolysis gives isopentylamine, what is '*A*'? **[DPMT 2006]**

(a) 
$CH_3-CH(CH_3)-CH_2CH_2Br$ ☐

(b) 
$CH_3-CH(CH_2Br)-CH_2CH_3$ ☐

(c) 
$CH_3-CH(CH_3)-CHBrCH_3$ ☐

(d) 
$CH_3-C(CH_3)(Br)-CH_2CH_3$ ☐

103. Which has the highest pK_b value? **[DCE 2006]**

(a) R_3C-NH_2 ☐ (b) R_2NH ☐
(c) RNH_2 ☐ (d) NH_3 ☐

104. Amine that can not be prepared by Gabriel phthalimide synthesis is: **[PET (Kerala) 2010]**

(a) benzylamine ☐ (b) aniline ☐
(c) methyl amine ☐ (d) *iso*-butyl amine ☐
(e) *tertiary*-butyl amine ☐

105. $CH_3NH_2 + CHCl_3 + KOH \longrightarrow$ nitrogen containing compound $+ KCl + H_2O$. Nitrogen containing compound is: **[IIT 2006]**

(a) $CH_3-C{\equiv}N$ ☐ (b) $CH_3-NH-CH_3$ ☐
(c) $CH_3-\overset{-}{N}{\equiv}\overset{+}{C}$ ☐ (d) $CH_3-\overset{+}{N}{\equiv}\overset{-}{C}$ ☐

106. The molecular formula C_3H_9N cannot represent: **[BCECE (Med.) 2007]**

(a) 1° amine ☐ (b) 2° amine ☐
(c) 3° amine ☐ (d) quaternary salt ☐

107. The correct order of basic nature in aqueous solution is: **[DCE (Engg.) 2007]**

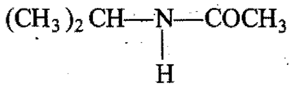
(a) $C_6H_5NH_2 > NH_3 > CH_3NH_2 > (CH_3)_2NH$ ☐
(b) $NH_3 > C_6H_5NH_2 > CH_3NH_2 > (CH_3)_2NH$ ☐
(c) $(CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2$ ☐
(d) $CH_3NH_2 > (CH_3)_2NH > NH_3 > C_6H_5NH_2$ ☐

108. Which one of the following is most basic? **[DCE (Engg.) 2007]**

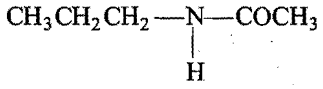
(a) FCH_2NH_2 ☐ (b) $FCH_2CH_2NH_2$ ☐
(c) $C_6H_5NH_2$ ☐ (d) $C_6H_5CH_2NH_2$ ☐

109. Isopropylamine with excess of acetyl chloride will give: **[MHCET (Med.) 2007]**

(a) $(CH_3CO)_2N-CH-(CH_3)_2$ ☐

(b) 
$(CH_3)_2CH-N(H)-COCH_3$ ☐

(c) $(CH_3)_2CHN(COCH_3)_2$ ☐

(d) 
$CH_3CH_2CH_2-N(H)-COCH_3$ ☐

110. Reduction of alkyl nitrile produces: **[CET (J & K) 2007]**

(a) secondary amine ☐ (b) primary amine ☐
(c) tertiary amine ☐ (d) amide ☐

111. Which of the following amines can be directly oxidised to the corresponding nitro compound by potassium permanganate? **[PMT (Kerala) 2007]**

(a) CH_3NH_2 ☐ (b) $(CH_3)_2CH-NH_2$ ☐
(c) $(CH_3)_2NH$ ☐ (d) $C_6H_5NH_2$ ☐
(e) $(CH_3)_3C-NH_2$ ☐

112. An aliphatic amine on treatment with alcoholic carbon disulphide and mercuric chloride forms ethyl isothiocyanate, the reaction is known as: **[AIIMS 2007]**

(a) Hofmann's reaction ☐
(b) Hofmann's rearrangement ☐
(c) Hofmann's mustard oil reaction ☐
(d) Hofmann's bromamide degradation reaction ☐

113. In order to distinguish between $C_2H_5NH_2$ and $C_6H_5NH_2$, which of the following reagents is useful? **[BHU(Mains) 2007]**

(a) Hinsberg reagent ☐ (b) β-naphthol ☐
(c) $CHCl_3/KOH$ ☐ (d) NaOH ☐

SET II: This set contains the questions with two or more correct answers.

114. Primary, secondary and tertiary amines can be distinguished by the action of:

(a) $CS_2/HgCl_2$ ☐ (b) $NaNO_2/HCl$ ☐
(c) $CHCl_3/KOH$ ☐ (d) $X_2/NaOH$ ☐

115. Nitroalkane and alkyl nitrite can be distinguished by the action of:

(a) alkali ☐ (b) nitrous acid ☐
(c) mineral acids ☐
(d) reduction with Sn/HCl ☐

116. A mixture of three amines (pri., sec. and tert.) can be prepared by:

(a) Hofmann's bromamide reaction ☐
(b) the reduction of nitroalkanes, cyanides and oximes ☐
(c) ammonolysis of alkylhalides ☐
(d) ammonolysis of alcohols ☐

117. Primary amines may be obtained by:
(a) the reduction of nitroalkanes ☐
(b) the reduction of alkyl isocyanide ☐
(c) the decarboxylation of amino acids ☐
(d) the hydrolysis of alkyl isocyanate ☐

118. Tertiary amines may be obtained by:
(a) Gabriel phthalimide synthesis ☐
(b) heating an alcoholic solution of ammonia with excess of *RX* ☐
(c) the hydrolysis of dialkyl cyanamide ☐
(d) thermal decomposition of quaternary ammonium hydroxide ☐

119. All the three amines (*pri.*, *sec.* and *tert.*) react with:
(a) HOH ☐ (b) *RX* ☐
(c) HCl ☐ (d) CH_3COCl ☐

120. A mixture of three amines can be separated into individual one by:
(a) Carbylamine reaction ☐
(b) Hinsberg's method ☐
(c) Fractional distillation method ☐
(d) Hofmann's method ☐

121. $C_4H_{11}N(X) + HNO_2 \longrightarrow C_4H_{10}O$ (3° alcohol) hence, (X) will give:
(a) Carbylamine reaction ☐
(b) Hofmann's mustard oil reaction ☐
(c) Diazonium salt (as the intermediate) ☐
(d) Hofmann's bromamide reaction ☐

122. When methyl iodide is treated with ammonia, the product obtained is/are:
(a) methylamine ☐
(b) dimethylamine ☐
(c) trimethylamine ☐
(d) quaternary ammonium salt ☐

123. The name $CH_3—C{\equiv}N$ is:
(a) methyl cyanide ☐ (b) methyl carbylamine ☐
(c) ethanenitrile ☐ (d) acetonitrile ☐

124. The positive carbylamine test is given by: [BHU (Mains) 2007]
(a) *N,N*-dimethyl aniline ☐
(b) 2,4-dimethyl aniline ☐
(c) *N*-methyl-*o*-methyl aniline ☐
(d) *p*-methyl benzylamine ☐

125. In the reaction,

$$2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+[BH_4]^-$$

the amine(s) X is (are): [IIT 2009]
(a) NH_3 ☐ (b) CH_3NH_2 ☐
(c) $(CH_3)_2NH$ ☐ (d) $(CH_3)_3N$ ☐

ASSERTION-REASON TYPE QUESTIONS

These questions given below consist of an Assertion (A) and the Reason (R). Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) Ammonolysis of alkyl halides is not a suitable method for the preparation of pure primary amines.
(R) Ammonolysis of alkyl halides yields mainly secondary amines.

2. (A) Carbylamine reaction involves chemical reaction between 1° amine and chloroform in basic medium.
(R) In carbylamine reaction, $—NH_2$ group changes into —NC group.

3. (A) The main product of reaction of alcoholic silver nitrite and ethyl bromide is nitroethane.
(R) Silver nitrite is predominantly covalent compound.

4. (A) In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.
(R) The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. [IIT (S) 2001]

5. (A) $CuCl_2$ gives a deep blue coloured solution with ethylamine.
(R) Ethylamine molecules co-ordinate with cupric ions forming a blue coloured complex.

6. (A) Amines are more basic than esters and ethers.
(R) Nitrogen is less electronegative than oxygen. It is better position to accommodate the positive charge on the proton. [AIIMS 2007]

ANSWERS

OBJECTIVE QUESTIONS

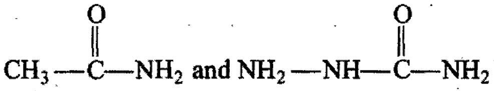
1. (a)	2. (b)	3. (c)	4. (d)	5. (a)	6. (a)	7. (c)	8. (b)	9. (b)	10. (d)
11. (c)	12. (b)	13. (c)	14. (b)	15. (c)	16. (a)	17. (a)	18. (c)	19. (d)	20. (d)
21. (a)	22. (b)	23. (d)	24. (d)	25. (d)	26. (b)	27. (c)	28. (d)	29. (a)	30. (a)
31. (c)	32. (b)	33. (d)	34. (c)	35. (a)	36. (b)	37. (d)	38. (b)	39. (c)	40. (d)
41. (a)	42. (a)	43. (b)	44. (c)	45. (a)	46. (d)	47. (b)	48. (c)	49. (b)	50. (d)
51. (c)	52. (b)	53. (c)	54. (c)	55. (b)	56. (a)	57. (d)	58. (d)	59. (d)	60. (d)
61. (c)	62. (d)	63. (a)	64. (d)	65. (d)	66. (b)	67. (d)	68. (b)	69. (c)	70. (c)
71. (c)	72. (d)	73. (b)	74. (a)	75. (c)	76. (b)	77. (a)	78. (a)	79. (d)	80. (c)
81. (c)	82. (c)	83. (a)	84. (a)	85. (d)	86. (d)	87. (d)	88. (c)	89. (b)	90. (c)
91. (b)	92. (a)	93. (a)	94. (c)	95. (b)	96. (e)	97. (b)	98. (c)	99. (a)	100. (b)
101. (a)	102. (a)	103. (d)	104. (b)	105. (d)	106. (d)	107. (c)	108. (d)	109. (c)	110. (b)
111. (e)	112. (c)	113. (b)	114. (a,b,c)	115. (a,b,d)	116. (c,d)	117. (a,c,d)	118. (b,d)	119. (a,b,c)	120. (b,c,d)
121. (a,b,c)	122. (a,b,c,d)	123. (a,c,d)	124. (b,d)	125. (a,b,c)					

ASSERTION-REASON TYPE QUESTIONS

1. (c)	2. (a)	3. (a)	4. (d)	5. (a)	6. (a)

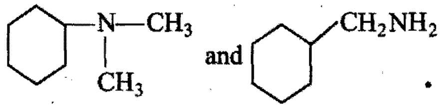
BRAIN STORMING PROBLEMS

1. Give the separation test between the following:
   - (i) CH_3NH_2 and $(CH_3)_2NH$
   - (ii) NH_3 and PH_3
   - (iii) CH_3NH_2 and CH_3NH_3OH
   - (iv) CH_3NH_2 and $C_6H_5NH_2$
   - (v) $(CH_3)_2NH$ and CH_3NH_3Cl
   - (vi)



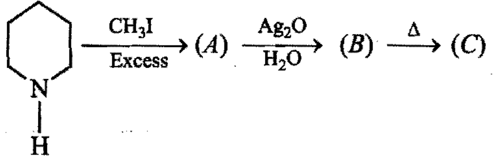
$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ and $NH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2$

   - (vii)

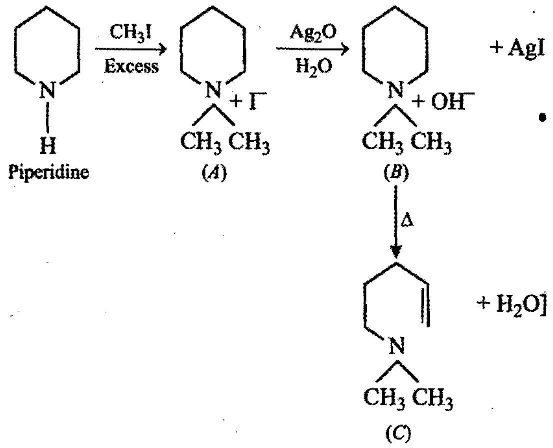


[Hint : See text]

2. Complete the following reaction:



[Ans.



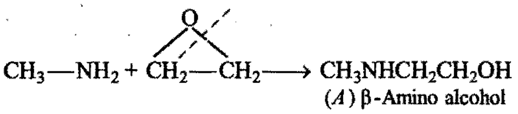
3. Explain the following reactions:
   - (i) Cope reaction
   - (ii) Schmidt reaction
   - (iii) Curtius reaction
   - (iv) Ritter reaction
   - (v) Leuckart reaction
   - (vi) Lossen reaction
   - (vii) Wagner rearrangement

[Hint : See text]

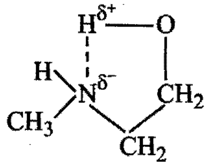
4. $CH_3NH_2 \xrightarrow[(CH_2)_2O]{} (A)$

What is (A)? Explain why (A) is less reactive than methylamine?

[Ans.



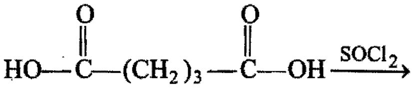
β-amino alcohol is less reactive because it is stabilized by intramolecular hydrogen bonding.



H-bonding also lowers nucleophilicity of nitrogen.]

5. Complete the following reactions:

(a)

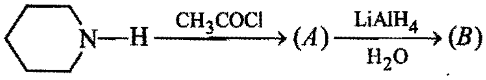


$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SOCl_2}$

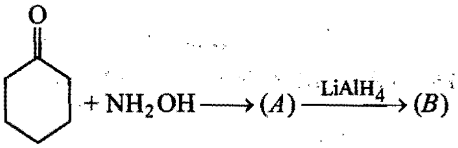
$(A) \xrightarrow{NH_3} (B) \xrightarrow[H_2O]{LiAlH_4} (C)$

(b) $CH_3(CH_2)_2CH_2OH \xrightarrow[{[O]}]{P.C.C.} (A) \xrightarrow[NaBH_3CN]{CH_3NH_2} (B)$

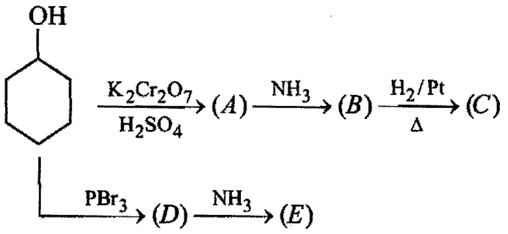
(c)



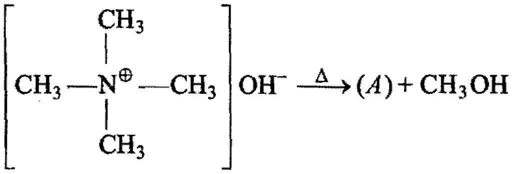
(d)



(e)



(f)



$\left[CH_3-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}-CH_3\right]OH^- \xrightarrow{\Delta} (A) + CH_3OH$

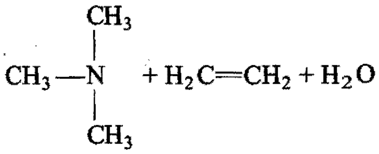
(g) $CH_3CH_2OH \xrightarrow{PBr_3} (A) \xrightarrow{NaCN} (B) \xrightarrow[300°C]{H_2/Ni} (C)$

(h) $CH_3CH_2OH \xrightarrow{KMnO_4} (A) \xrightarrow{SOCl_2} (B) \xrightarrow{NH_3}$

$(C) \xrightarrow[\Delta]{NaOH/Br_2} (D)$

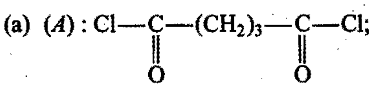
(i) $CH_3CH_2OH \xrightarrow[300°C]{Cu} (A) \xrightarrow[\text{(ii) } H_2/Ni,\ 300°C]{\text{(i) } NH_3} (B)$

(j) $\underset{1°\ \text{Amine}}{(A)} \xrightarrow[Excess]{CH_3I} (B) \xrightarrow[H_2O]{Ag_2O} (C) \xrightarrow{\Delta}$



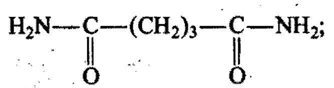
$CH_3-\underset{CH_3}{\overset{CH_3}{N}} + H_2C{=}CH_2 + H_2O$

[Ans. (a) (A) :



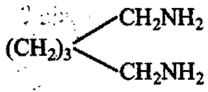
$Cl—\overset{O}{\overset{\|}{C}}—(CH_2)_3—\overset{O}{\overset{\|}{C}}—Cl$;

(B) :



$H_2N—\overset{O}{\overset{\|}{C}}—(CH_2)_3—\overset{O}{\overset{\|}{C}}—NH_2$;

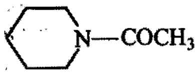
(C) :



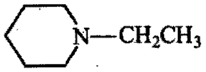
(b) (A) : $CH_3—(CH_2)_2—CHO$;

(B) : $CH_3—(CH_2)_2—CH_2—NH—CH_3$

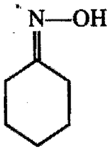
(c) (A) :



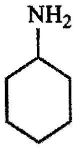
; (B) :



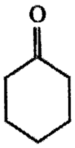
(d) (A) :



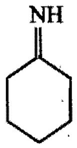
; (B) :



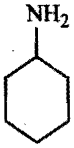
(e) (A) :



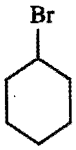
; (B) :



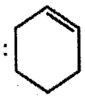
; (C) :



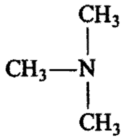
(D) :



; (E) :



(f) (A) :



$CH_3—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{N}}}}$

(g) (A) CH_3CH_2Br; (B) CH_3CH_2CN;
(C) $CH_3CH_2CH_2NH_2$

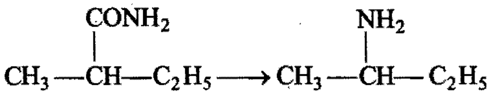
(h) (A) CH_3COOH; (B) CH_3COCl; (C) CH_3CONH_2;
(D) CH_3NH_2

(i) (A) CH_3CHO; (B) $CH_3—CH_2NH_2$

(j) (A) $C_2H_5NH_2$; (B) $[C_2H_5N(CH_3)_3]^+I^-$;
(C) $[C_2H_5N(CH_3)_3]^+OH^-$]

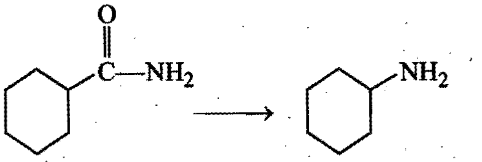
6. How will you bring out following conversions involving three steps at most?

(a)



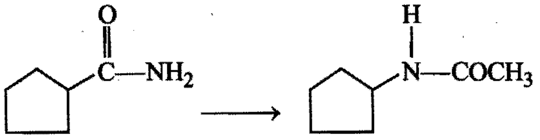
$CH_3—\overset{CONH_2}{\overset{|}{CH}}—C_2H_5 \longrightarrow CH_3—\overset{NH_2}{\overset{|}{CH}}—C_2H_5$

(b)



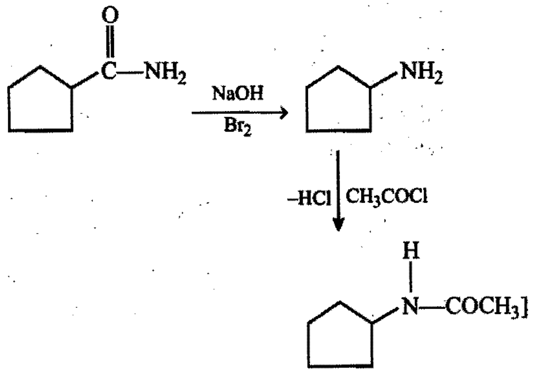
(c) $CH_3—CH_2—CN \longrightarrow CH_3—CH_2—CH_2—NH_2$

(d)



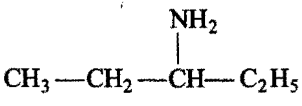
[Hint : (a) and (b) are simply Hofmann bromamide reaction.
(c) is simple reduction with Na/alcohol or with $LiAlH_4$.

(d)



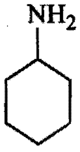
7. Select the starting substance and reagent for synthesis of following amines:

(a)



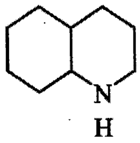
$CH_3—CH_2—\overset{NH_2}{\overset{|}{CH}}—C_2H_5$

(b)

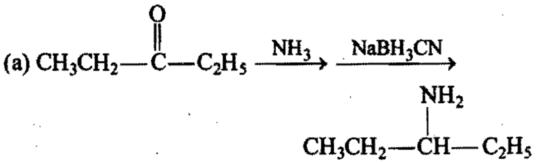


(c) $(CH_3)_3C—NH_2$

(d)

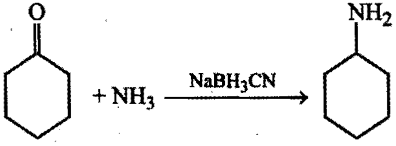


[Hint : (a)



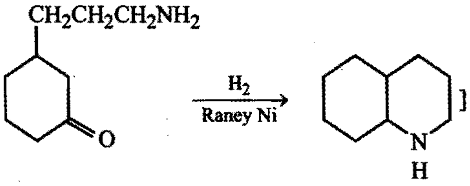
$CH_3CH_2—\overset{O}{\overset{\|}{C}}—C_2H_5 \xrightarrow{NH_3} \xrightarrow{NaBH_3CN} CH_3CH_2—\overset{NH_2}{\overset{|}{CH}}—C_2H_5$

(b)



(c) $(CH_3)_3C—NO_2 \xrightarrow{LiAlH_4} (CH_3)_3C—NH_2$

(d)



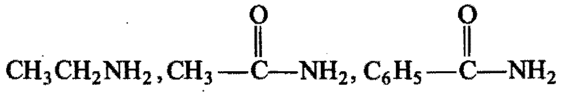
]

8. Arrange the following in decreasing order of basicity:

(a) $R—CN, R—CH{=}NR, R—NH_2$

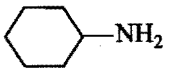
(b) $CH_2{=}CHCH_2NH_2, CH_3CH_2CH_2NH_2,$
$HC{\equiv}C—CH_2NH_2$

(c)



$CH_3CH_2NH_2, CH_3—\overset{O}{\overset{\|}{C}}—NH_2, C_6H_5—\overset{O}{\overset{\|}{C}}—NH_2$

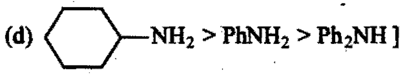
(d) $PhNH_2$, Ph_2NH,



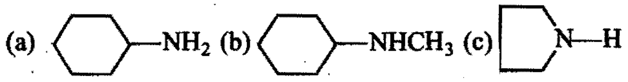
[Ans. (a) $R—NH_2 > R—CH{=}NR > R—CN$

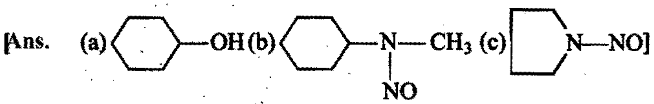
(b) $CH_3CH_2CH_2NH_2 > CH_2{=}CHCH_2NH_2 > HC{\equiv}CCH_2NH_2$

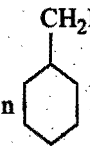

(c) $CH_3CH_2NH_2 > CH_3CONH_2 > C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2$

(d) 
$-NH_2 > PhNH_2 > Ph_2NH$]

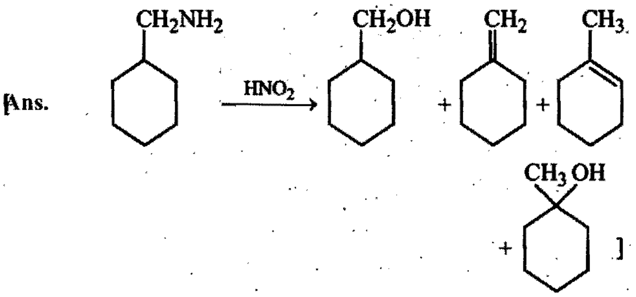
9. Give the products when following compounds are treated with nitrous acid:

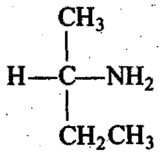


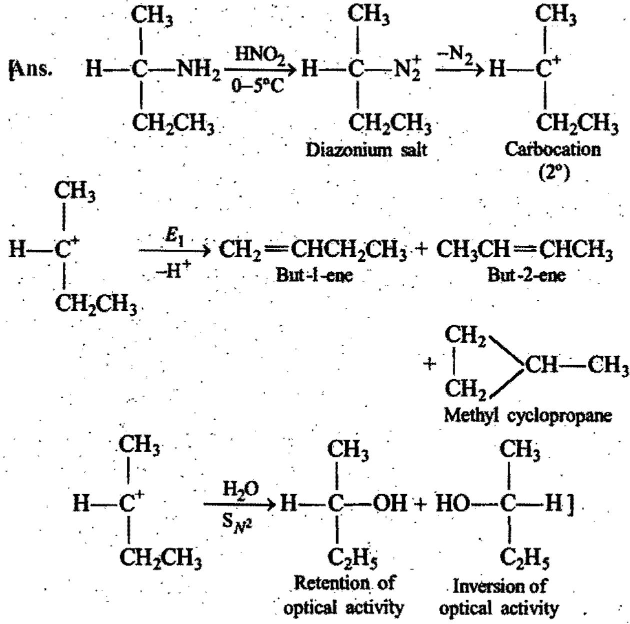
[Ans. 

10. Write down all possible products when 

is treated with nitrous acid.

[Ans. 

11. 
$H-\overset{CH_3}{\underset{CH_2CH_3}{C}}-NH_2$ is an optically active amine. Give the possible products when it is treated with nitrous acid. Discuss optical activity of the products.

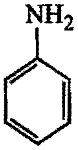
[Ans. 

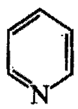
12. Give (a) conjugate acid (b) conjugate base of $HO(CH_2)_3NH_2$.

[Ans. (a) $HO(CH_2)_3NH_2 \xrightarrow{H^+} HO(CH_2)_3\overset{+}{N}H_3$
Conjugate acid

(b) $HO(CH_2)_3NH_2 \xrightarrow{-H^+} O^-—(CH_2)_3NH_2]$
Conjugate base

13. Which of the following is most basic ?

(a) 

☐
(b) 

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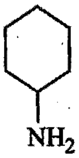
(c) 

☐
(d) 

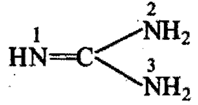
☐

14. Which of the following is the correct order of basic character?

I. 1-Amino propane
II. Ethanamide
III. Guanidine $[HN{=}C(NH_2)_2]$
IV. Aniline

(a) I > II > III > IV ☐ (b) III > I > IV > II ☐
(c) IV > III > I > II ☐ (d) III > II > I > IV ☐

15. Which nitrogen is protonated readily in guanidine ?



(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) All of these ☐

16. Which of the following has the highest pK_b value ?

(a) 

☐
(b) 

☐

(c) 

☐
(d) 

☐

17. Which of the following is insoluble in dil. HCl ?

(a) Aniline ☐ (b) Triphenylamine ☐
(c) Ethylamine ☐ (d) Dimethylamine ☐

18. Which of the following may be prepared by Gabriel phthalimide synthesis ?

(a) Aliphatic amines ☐ (b) Aromatic amines ☐
(c) Aliphatic amides ☐ (d) Aromatic amides ☐

19. When an organic compound was treated with sodium nitrite and HCl in the ice-cold condition, nitrogen gas was evolved. The compound is :

(a) a nitro compound ☐ (b) a primary amine ☐
(c) a secondary amine ☐ (d) a tertiary amine ☐

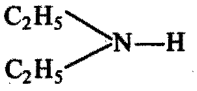
20. In carbylamine reaction :

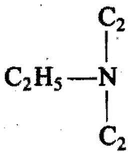
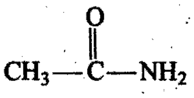
(a) the nucleophile is RNH_2 and electrophile is $:CCl_2$ ☐

(b) the nucleophile is primary amine and electrophile is CCl_3^- ☐

(c) the nucleophile is CCl_3^- and the electrophile is primary amine ☐
(d) the attacking reagent is electrophile ☐

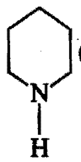
21. Which one of the following will not react with the Grignard reagent (C_2H_5MgBr)?

(a) $C_2H_5—NH_2$ ☐ (b)

☐

(c)

$(C_2H_5)_3N$ ☐ (d)

$CH_3—\overset{O}{\overset{\|}{C}}—NH_2$ ☐

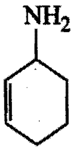
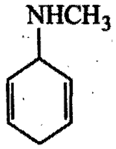
22. One mole of an amine (A) consumes two moles of methyl bromide to give a quaternary ammonium salt. The amine (A) is:

(a) $(CH_3)_3CCH_2NH_2$ ☐ (b) $(CH_3)_2NCH_2CH_3$ ☐

(c)

(Piperidine) ☐ (d)

(Pyridine) ☐

23. An optically active compound (A) decolourises Br_2/CCl_4 and releases N_2 with nitrous acid. The compound (A) is:

(a)

☐ (b)

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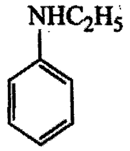
(c)

☐ (d)

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24. $(A) \xrightarrow{H_2/Pt}$ 1° Amine

$(B) \xrightarrow{H_2/Pt}$ 2° Amine

(A) and (B) respectively are:

(a) RNC, RNC ☐ (b) RCN, RCN ☐
(c) RCN, RNC ☐ (d) RNC, RCN ☐

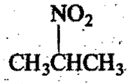
25. $(A) \xrightarrow[\text{[H]}]{\text{Reduction}}$ Primary amine

The compound (A) may be:

(a) alkyl isocyanide ☐ (b) alkyl cyanide ☐
(c) acidamide ☐ (d) 1° nitroalkane ☐

26. How many products will be obtained when propane is subjected to vapour phase nitration?

(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 5 ☐

[Hint: $CH_3CH_2CH_3 \xrightarrow[700\text{-}900°C]{\text{Fuming } HNO_3} CH_3CH_2CH_2NO_2 +$

$CH_3\underset{}{\overset{NO_2}{\overset{|}{C}}}HCH_3 + CH_3CH_2NO_2 + CH_3NO_2$]

27. $R—Cl + NH_3$ (excess) $\longrightarrow$ (X) (major product),

the major product (X) is a:

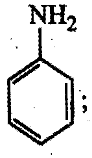
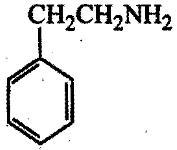
(a) 1° amine ☐ (b) 2° amine ☐
(c) 3° amine ☐ (d) 4° ammonium salt ☐

[Hint: $R—Cl + NH_3\text{(excess)} \longrightarrow R—NH_2 + HCl$
when ammonia is taken in excess, 1° amine is formed as the major product.]

28. Mixture of 1°, 2° and 3° amines can be separated by:

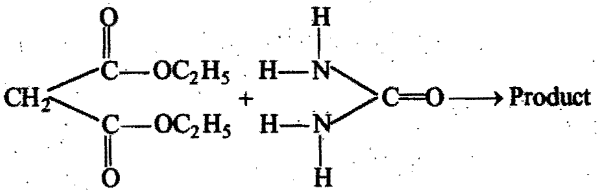
(a) Hinsberg's method ☐ (b) fractional distillation ☐
(c) Hofmann's method ☐ (d) Victor Meyer's method ☐

29. Arrange following amines in the decreasing order of their basicity:

$CH_3CH_2CH_2NH_2$; (I)

(II) ;

(III)

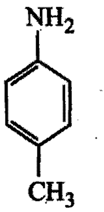
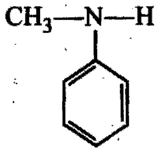
(a) I > III > II ☐ (b) I > II > III ☐
(c) III > II > I ☐ (d) II > III > I ☐

30. The product obtained in the following reaction is:



(a) hypnotic agent ☐ (b) barbituric acid ☐
(c) cyclic amide ☐ (d) cyclic ketone ☐

31. Which of the following amines will show carbylamine reaction?

(a)

☐ (b)

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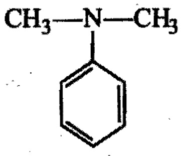
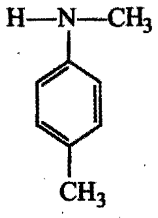
(c)

☐ (d)

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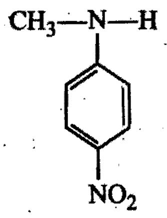
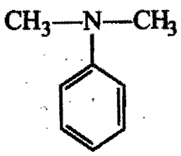
32. Which of the following amines will show positive Liebermann's nitroso test?

(a)

☐ (b)

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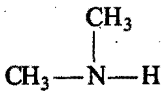
(c) 

$CH_3-\overset{\overset{CH_3}{|}}{N}-H$ ☐ (d) None of these ☐

33. Which among the following is amphoteric ?
(a) CH_3-NH_2 ☐ (b) $(CH_3)_2NH$ ☐
(c) $(CH_3)_3N$ ☐ (d) CH_3CONH_2 ☐

34. Which of the following is the most basic amine ?
(a) CH_3-NH_2 ☐ (b) $ClCH_2NH_2$ ☐
(c) Cl_2CH-NH_2 ☐ (d) CCl_3-NH_2 ☐

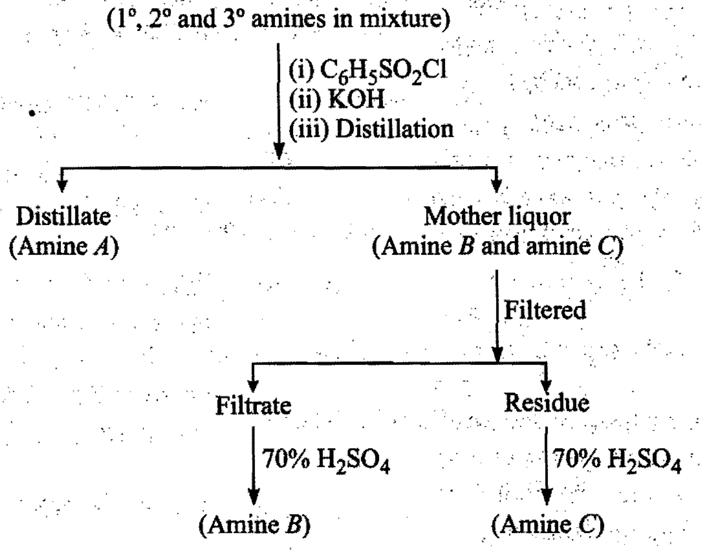
ANSWERS : BRAIN STORMING PROBLEMS

13. (c)	**14.** (b)	**15.** (a)	**16.** (a)	**17.** (b)	**18.** (a)	**19.** (b)	**20.** (a)	**21.** (c)	**22.** (c)
23. (a)	**24.** (c)	**25.** (b,c,d)	**26.** (c)	**27.** (a)	**28.** (a,b,c)	**29.** (a)	**30.** (a,b,c)	**31.** (a)	**32.** (a,c)
33. (d)	**34.** (d)								

LINKED COMPREHENSION TYPE QUESTIONS

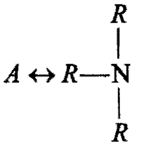
Passage 1

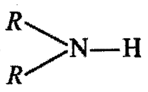
Benzene sulphonyl chloride ($C_6H_5SO_2Cl$) is called Hinsberg's reagent. It is used for the distinction between primary, secondary and tertiary amines. It is also used for separation of primary, secondary and tertiary amines from their mixture.



Answer the following questions :

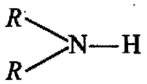
1. Which of the following is correctly matched?

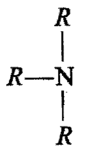
(a) $A \leftrightarrow$  R_3N

(b) $B \leftrightarrow$  R_2N-H

(c) $C \leftrightarrow R-NH_2$ (d) $A \leftrightarrow R-NH_2$

2. Which of the following amines does not react with benzene sulphonyl chloride ?

(a) $R-NH_2$ (b)  R_2N-H

(c)  R_3N (d) Both (a) and (b)

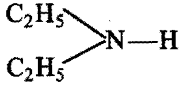
3. Which of the following is primary amine $R-NH_2$?

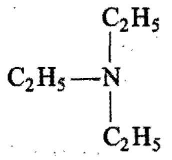
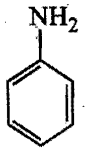
(a) A (b) B
(c) C (d) Cannot be predicted

4. The residue insoluble in KOH obtained in the Hinsberg's test, corresponds to :

(a) primary amine (b) secondary amine
(c) tertiary amine (d) aromatic primary amine

5. Which of the following amines represent C ?

(a) $C_2H_5-NH_2$ (b)  $(C_2H_5)_2N-H$

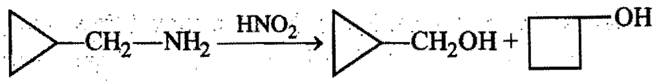
(c)  $(C_2H_5)_3N$ (d) 

Passage 2

Nitrous acid reacts with all classes of amines. The products obtained from these reactions depend on whether the amine is primary, secondary or tertiary and whether the amine is aliphatic or aromatic.

Aliphatic primary amines react with nitrous acid ($NaNO_2$ + HCl) to form alcohol as major product. In addition to alcohol, alkene and alkyl halides are also formed as minor product.

Certain cyclic primary amines can undergo either ring expansion or ring contraction reactions on treatment with nitrous acid. This reaction is called Demjanov ring expansion or contraction.

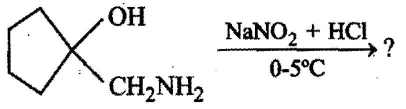


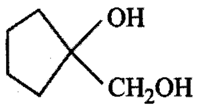
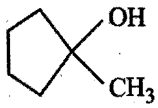
Answer the following questions:

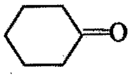
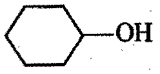
1. What will be the major product when 2-amino propane is treated with nitrous acid?

(a) 1-Propanol (b) 2-Propanol
(c) Propene (d) Cyclopropane

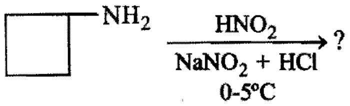
2. The product(s) obtained in the following reaction will be :

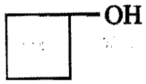
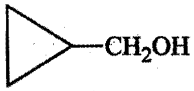


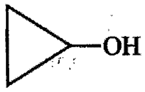
(a)  (b) 

(c)  (d) 

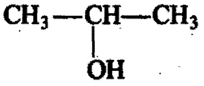
3. Which of the following product(s) will be obtained in the following reaction?



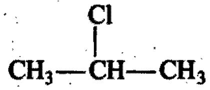
(a)  (b) 

(c)  (d) $CH_3CH_2CH_2CH_2OH$

4. Which of the following product(s) will be obtained when isopropylamine is treated with sodium nitrite and hydrochloric acid?

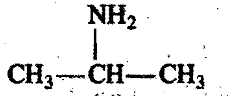
(a) 
$CH_3-\underset{OH}{CH}-CH_3$

(b) $CH_3-CH=CH_2$

(c) 
$CH_3-\overset{Cl}{CH}-CH_3$

(d) All of these

5. Two compounds (A) and (B) are treated with nitrous acid,


$CH_3-\overset{NH_2}{CH}-CH_3$; $CH_3CH_2CH_2NH_2$

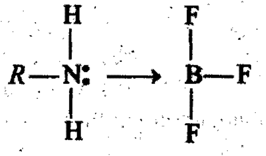
(A) (B)

The corresponding stable carbocation intermediates are:

	(From A)	(From B)
(a)	$CH_3-CH_2-\overset{+}{C}H_2$	$CH_3-CH_2-\overset{+}{C}H_2$
(b)	$CH_3-\overset{+}{C}H-CH_3$	$CH_3-CH_2-\overset{+}{C}H_2$
(c)	$CH_3-\overset{+}{C}H-CH_3$	$CH_3-\overset{+}{C}H-CH_3$
(d)	none of these	

Passage 3

Amines are basic compounds. They act as Lewis base due to the presence of lone pair of electrons at nitrogen.



Amines also behave as Arrhenius base as well as Bronsted base

$$CH_3-NH_2 + HOH \rightleftharpoons CH_3-NH_3^+ + OH^-$$

$$CH_3-NH_2 + H^+Cl^- \rightleftharpoons CH_3-NH_3^+ + Cl^-$$

Basic character of amines depends on the factors like inductive effect, steric hindrance and resonance.

Alkyl groups and electron releasing groups hence these groups increase the electron density at nitrogen as well as the basic character of amines. Basic character of tertiary amines is reduced due to the steric hindrance of three alkyl groups. Experimentally it is observed that stronger bases have smaller values of pK_b (greater values of K_b).

Answer the following questions:

1. Which among the following is the most basic in gas phase?

(a) NH_3 (b) CH_3-NH_2

(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

2. Which among the following is the most basic in aqueous medium ?

(a) NH_3 (b) CH_3-NH_2

(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

3. Which among the following factors influence the basicity of amines?

I—the inductive effect of alkyl group

II—the polar effect

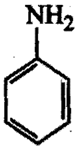
III—the resonance

(a) I, II (b) I, III

(c) II, III (d) I, II, III

4. Which of the following is the most basic?

(a) CH_3-NH_2 (b) $C_2H_5-NH_2$

(c) $C_3H_7-NH_2$ (d) 

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	1. (a)	2. (c)	3. (b)	4. (b)	5. (b)
Passage 2	1. (b)	2. (a,c)	3. (a,b)	4. (d)	5. (b)
Passage 3	1. (d)	2. (c)	3. (d)	4. (c)	

15

BIOMOLECULES

15.1 INTRODUCTION

Biomolecules are the organic compounds present as essential constituent of living organisms in different cells. They build up all the living systems and are responsible for their growth, maintenance and their ability to reproduce.

Nearly, all the compounds found in cells are composed of carbon, hydrogen, oxygen, nitrogen, phosphorus and sulphur. The most abundant substance in living cells is water which amounts to approximately 70% mass of the cells. Next come the compounds of carbon which can be put into two types. The first are the small molecules containing upto 30 carbon atoms and these are the raw materials from which the second type of molecules having very high molecular masses are synthesised. The molecules of the second type are termed as **macromolecules.** Nearly, all the carbon compounds found in living cells can be placed into one or another of four classes:

(i) Carbohydrates,
(ii) Amino acids and proteins,
(iii) Nucleic acids,
(iv) Lipids.

15.2 CARBOHYDRATES—DEFINITION, NOMENCLATURE AND CLASSIFICATION

The carbohydrates are naturally occurring organic substances and are present in both plants and animals. The dry mass of plants is composed of 50 to 80% of the polymeric carbohydrate cellulose. Carbohydrates are formed in the plants by a process known as **photosynthesis** from carbon dioxide and water. Photosynthesis is catalysed by the green pigment, chlorophyll, in presence of sunlight.

$$nCO_2 + nH_2O \xrightarrow[\text{Chlorophyll}]{\text{Light}} (CH_2O)_n + nO_2$$

Animals do not synthesise carbohydrates but rely on plants for their supply.

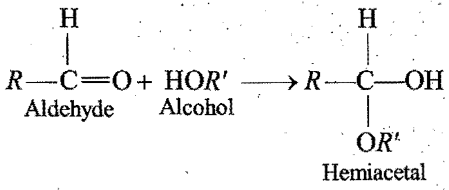
Definition : Carbohydrates are mainly compounds of carbon, hydrogen and oxygen. The name 'carbohydrate' arose from the mistaken belief that the substances of this kind were hydrates of carbon, since their molecular formulae could be expressed in the form of $C_x(H_2O)_y$, *i.e.*, hydrogen and oxygen existed in the ratio of 2 : 1 as in water molecule. For example,

Glucose : $C_6H_{12}O_6$ or $C_6(H_2O)_6$
Sucrose : $C_{12}H_{22}O_{11}$ or $C_{12}(H_2O)_{11}$
Starch, cellulose : $(C_6H_{10}O_5)_n$ or $[C_6(H_2O)_5]_n$

However, a number of compounds have been discovered which are carbohydrates by chemical behaviour but do not possess the formula $C_x(H_2O)_y$, *e.g.*, rhamnose ($C_6H_{12}O_5$) or 2-deoxyribose ($C_5H_{10}O_4$). It is also important to note that all compounds possessing the formula $C_x(H_2O)_y$ are not necessarily carbohydrates, *e.g.*, formaldehyde, $HCHO[C(H_2O)]$, acetic acid, $CH_3COOH[C_2(H_2O)_2]$, lactic acid $CH_3CHOH{\cdot}COOH[C_3(H_2O)_3]$, etc. Certain carbohydrates are also known which contain nitrogen or sulphur in addition to carbon, hydrogen and oxygen. However, the term carbohydrate has been retained.

Carbohydrates are now defined as a class of compounds that include polyhydroxy aldehydes or polyhydroxy ketones and large polymeric compounds that can be broken down (hydrolysed) into polyhydroxy aldehydes or ketones.

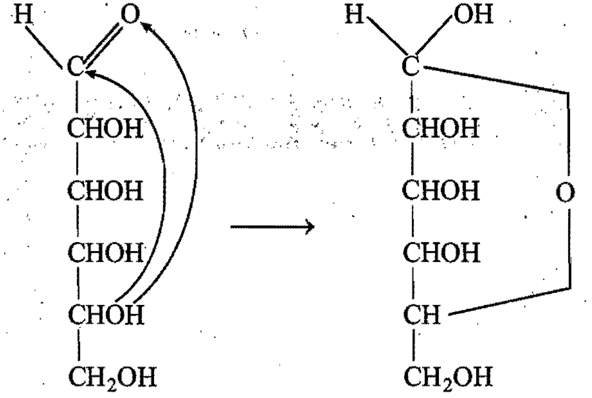
This definition is not entirely satisfactory. Carbohydrates contain $>C{=}O$ and —OH groups. A carbonyl compound reacts with an alcohol to form a hemiacetal,



$$\underset{\text{Aldehyde}}{R{-}\overset{\overset{\displaystyle H}{|}}{C}{=}O} + \underset{\text{Alcohol}}{HOR'} \longrightarrow \underset{\text{Hemiacetal}}{R{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OR'}{|}}{C}}{-}OH}$$

In carbohydrates, the carbonyl group combines with an alcoholic group of the same molecule to form an internal hemiacetal. Thus, the correct definition of a carbohydrate is as follows:

"A polyhydroxy compound that has an aldehydic or a ketonic functional group either free or as hemiacetal or acetal".



Glucose ($C_6H_{12}O_6$) An internal hemiacetal

In general, carbohydrates are white solids, sparingly soluble in organic solvents and (except certain polysaccharides) are soluble in water. Many carbohydrates of low molecular masses have a sweet taste. Carbohydrates are often referred to as **saccharides** (Latin, *saccharum* = sugar) because of sweet taste of the simpler members of the class.

Nomenclature : The names of the simpler carbohydrates end in -ose. Carbohydrates with an aldehydic structure are known as *aldoses* and those with ketonic structure as *ketoses*. The number of carbon atoms in the molecule is indicated by a Greek prefix.

Number of Carbon atoms in the molecule	Aldose	Ketose
3	Aldotriose	Ketotriose
4	Aldotetrose	Ketotetrose
5	Aldopentose	Ketopentose
6	Aldohexose	Ketohexose
7	Aldoheptose	Ketoheptose

Classification : The carbohydrates are divided into three major classes depending upon whether or not they undergo hydrolysis, and if undergo hydrolysis, how many products are formed.

(i) Monosaccharides (Simple sugars) : These are single unit carbohydrates (polyhydroxy aldehydes or polyhydroxy ketones) which cannot be broken into lower sugars upon hydrolysis. With a few exceptions, they have general formula, $C_nH_{2n}O_n$. Glucose is the most important member of this class. These are crystalline in nature, readily dissolve in water and are sweet in taste (sugars). Monosaccharides with 3 to 9 carbon atoms are known.

(ii) Oligosaccharides : These include those carbohydrates which are formed by interaction of definite number of monosaccharide units with the elimination of definite number of water molecules. They are made of 2 to 10 units of monosaccharides (simple sugars). These carbohydrates on hydrolysis give 2 to 10 molecules of monosaccharides. These are called **oligosaccharides.** The oligosaccharides containing two monosaccharide units are called **disaccharides** and those containing three or four or five units and so on, are termed **trisaccharides, tetrasaccharides, pentasaccharides** respectively. For example,

Disaccharides ($C_{12}H_{22}O_{11}$) on hydrolysis give two molecules of same or different monosaccharides. For example,

Sucrose ($C_{12}H_{22}O_{11}$) is a disaccharide as on hydrolysis it gives two different monosaccharide units, *i.e.*, one molecule of glucose and one molecule of fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Other examples of disaccharides are maltose and lactose, etc.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{(Enzyme maltase)}]{H^+} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

Trisaccharides ($C_{18}H_{32}O_{16}$) on hydrolysis give three molecules of the same or different monosaccharides. For example,

Raffinose ($C_{18}H_{32}O_{16}$) is a trisaccharide as on hydrolysis, it gives three different monosaccharide units.

$$\underset{\text{Raffinose}}{C_{18}H_{32}O_{16}} + 2H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

Tetrasaccharides ($C_{24}H_{42}O_{21}$) on hydrolysis give four molecules of the same or different monosaccharides. For example,

Stachyose ($C_{24}H_{42}O_{21}$) is a tetrasaccharide as on hydrolysis, it gives one molecule each of glucose and fructose and two molecules of galactose units.

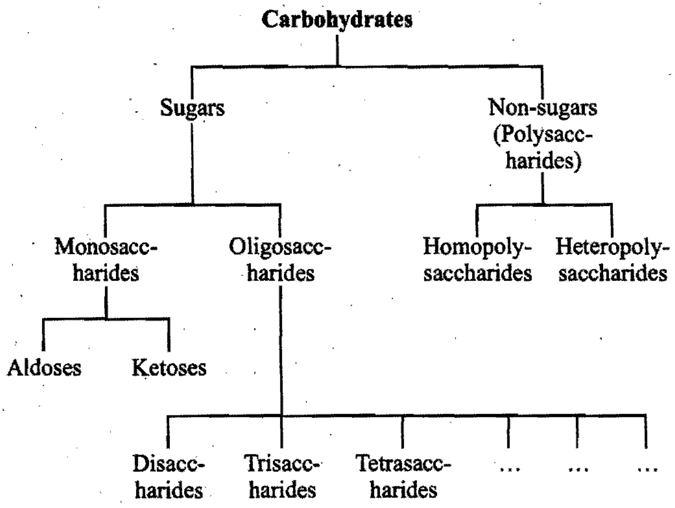
$$\underset{\text{Stachyose}}{C_{24}H_{42}O_{21}} + 3H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{2C_6H_{12}O_6}$$

(iii) Polysaccharides (Non-sugars) : Like oligosaccharides, these are also formed from monosaccharides but the exact number of monosaccharide molecules taking part in their formation is not known. They are regarded to have been formed by union of '*n*' molecules of monosaccharides with elimination of '*n*' molecules of water. These carbohydrates yield a large number of molecules of monosaccharides on hydrolysis. The general formula of polysaccharides is $(C_6H_{10}O_5)_n$, where $n = 100 - 3000$. Starch, cellulose, inulin and glycogen are the examples of polysaccharides.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Polysaccharides are colourless, amorphous solids having no taste and insoluble in cold water. These have very long chains or are polymers of monosaccharides that may be either linear or branched in structure. If the polymer is made up from a single monosaccharide, the polysaccharide is called a **homopolysaccharide** and if two or more different monosaccharides are found in a polymer, it is called a **heteropolysaccharide**. They are also called **non-sugars.**

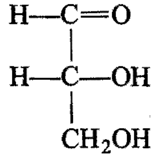
The complete classification of carbohydrates may be depicted in short in the following chart:



15.3 MONOSACCHARIDES

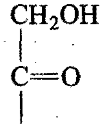
These are the simplest one unit non-hydrolysable sugars. They have the general formula $C_nH_{2n}O_n$ where n varies from 3 to 9 carbon atoms. About 20 monosaccharides occur in nature. The simplest are trioses (n = 3).

$C_3H_6O_3$;
Triose



Glyceraldehyde
(An aldotriose)

;



Dihydroxyacetone
(A ketotriose)

The most important naturally occurring monosaccharides are pentoses and hexoses. A common pentose is **ribose** and two common hexoses are **glucose** and **fructose.**

Except ketotriose (dihydroxy acetone), all aldoses and ketoses (monosaccharides) contain asymmetric carbon atoms and are optically active. Number of isomers depend on the number of asymmetric carbon atoms in the molecule of monosaccharide and is derived by the formula 2^n, where n is the number of asymmetric carbon atoms in the molecule.

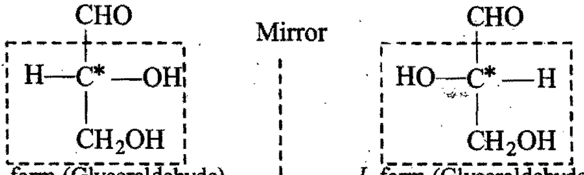
No. of carbon atoms		No. of asymmetric carbon atoms	No. of isomers
Trioses (3)	$CH_2OHCHOHCHO$	1	2
	$CH_2OHCOCH_2OH$	—	—
Tetroses (4)	$CH_2OH(CHOH)_2CHO$	2	4
	$CH_2OHCHOHCOCH_2OH$	1	2
Pentoses (5)	$CH_2OH(CHOH)_3CHO$	3	8
	$CH_2OH(CHOH)_2COCH_2OH$	2	4
Hexoses (6)	$CH_2OH(CHOH)_4CHO$	4	16
	$CH_2OH(CHOH)_3COCH_2OH$	3	8

Examples are:

Aldotriose	—	Glyceraldehyde
Ketotriose	—	Dihydroxy acetone
Aldotetroses	—	Erythrose, Threose
Ketotetrose	—	Erythrulose
Aldopentoses	—	Arabinose, Ribose, Xylose, Lyxose
Ketopentoses	—	Ribulose, Xylulose
Aldohexoses	—	Glucose, Mannose, Allose,Altrose, Gulose, Idose, Galactose, Talose
Ketohexoses	—	Fructose, Sorbose, Tagalose, etc.

Aldohexoses exist in sixteen optically active forms, *e.g.*, glucose, mannose, galactose, allose, altrose, idose, gulose and talose each existing in two forms. The enantiomer which rotates the plane of polarized light to the right is written as (+). The other enantiomer that rotates the plane to the left is written as (–). The (+) and (–) signs only specify the direction of rotation of the plane polarized light by a particular enantiomer but it does not give any indication of the arrangement of OH and H around the asymmetric carbon atom.

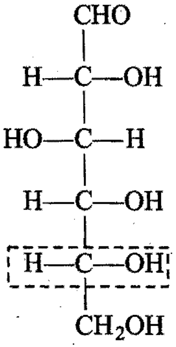
The sugars are divided into two families, the *D*-family and *L*-family. In 1906, Rosanoff decided arbitrarily these two families on the basis of configuration of the simplest sugar, glyceraldehyde which he took as standard exists in two enantiomeric forms as shown below:



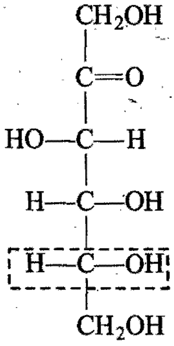
D-form (Glyceraldehyde)
(—OH group on the right side of lowest asymmetric carbon)

L-form (Glyceraldehyde)
(—OH group on the left side of lowest asymmetric carbon)

The sugars having the same configuration as of *D*-glyceraldehyde at the asymmetric carbon (adjacent to primary alcoholic group) most distant from the carbonyl group are designated as ***D*-sugars** and those having configuration as *L*-glyceraldehyde are designated as ***L*-sugars.** Glucose from aldoses and fructose from ketoses are most important. The natural glucose and fructose are *D*-forms.



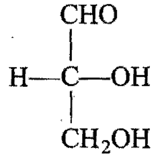
D(+)Glucose



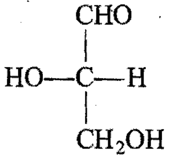
D(–) Fructose

CONFIGURATION OF MONOSACCHARIDES

(i) Aldotriose: $CHOCHOHCH_2OH$, isomers $(2)^1 = \mathbf{2}$

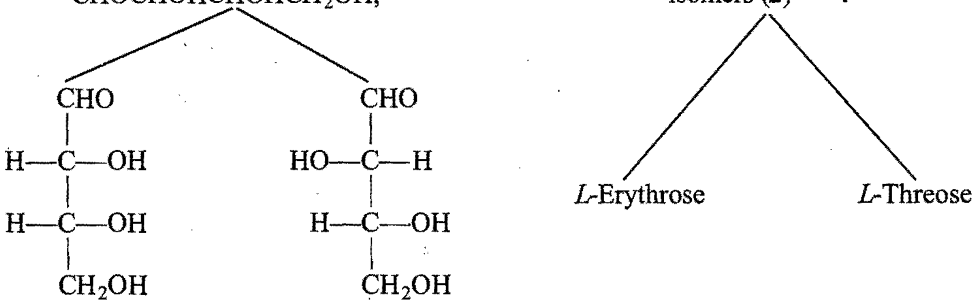


D-Glyceraldehyde



L-Glyceraldehyde

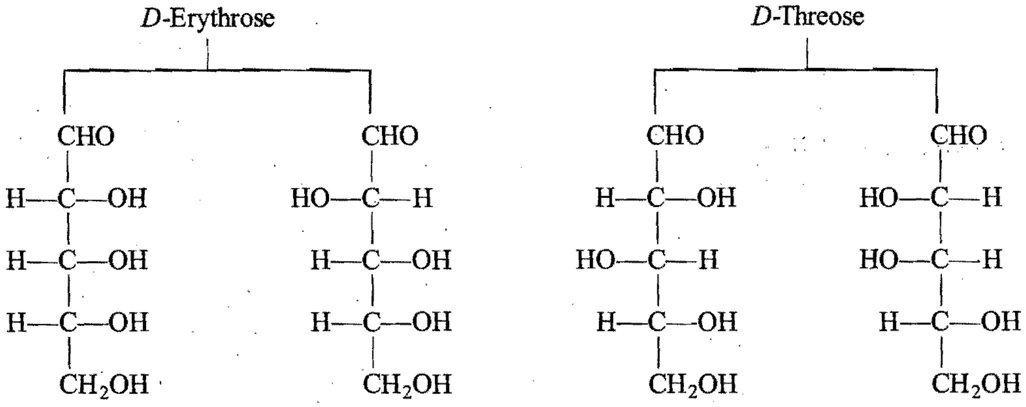
(ii) Aldotetrose: $CHOCHOHCHOHCH_2OH$, isomers $(2)^2 = \mathbf{4}$



D-Erythrose *D*-Threose

So it has four isomers, *i.e.*, *D*, *L*-Erythrose, and *D*, *L*-Threose.

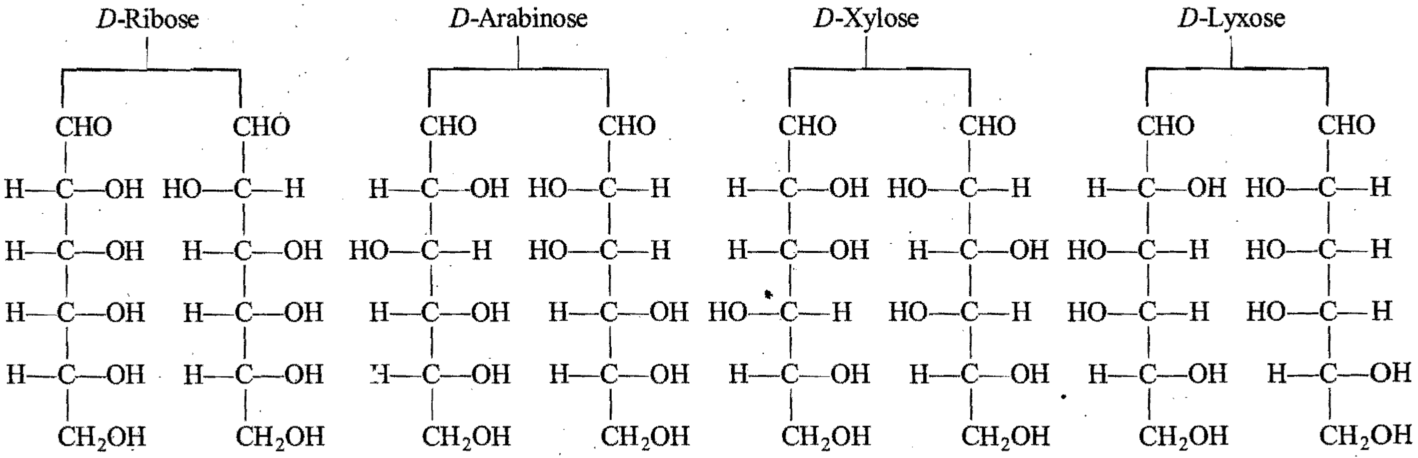
(iii) Aldopentose: $CHOCHOHCHOHCHOHCH_2OH$, isomers $(2)^3 = \mathbf{8}$



D-Ribose *D*-Arabinose *D*-Xylose *D*-Lyxose

So aldopentoses has eight isomers, *i.e.*, *D*- and *L*-Ribose, *D*- and *L*-Arabinose, *D*- and *L*-Xylose and *D*, *L*-Lyxose.

(iv) Aldohexose: $CHO(CHOH)_4CH_2OH$, isomers $(2)^4 = \mathbf{16}$



D-Allose *D*-Altrose *D*-Glucose *D*-Mannose *D*-Gulose *D*-Idose *D*-Galactose *D*-Talose

1. GLUCOSE, $C_6H_{12}O_6$, (ALDO-HEXOSE)

Glucose is known as **dextrose** because it occurs in nature as the optically active dextrorotatory isomer. It is also called **grape sugar** as it is found in most sweet fruits such as grapes, mangoes, apples and pears etc. It is present in honey also and is essential constituent of human blood. The blood normally contains 65 to 110 mg of glucose per 100 mL (hence named **Blood sugar**). The level may be much higher in diabetic persons. The urine of diabetic persons also contain considerable amount of glucose. In combined form, it occurs in disaccharides and polysaccharides such as starch and cellulose. It is also present in various glycosides like **amygdalin** and **salicin.**

Preparation (Laboratory method) : It is prepared in laboratory by acid hydrolysis of cane-sugar in alcoholic solution.

$$\underset{\substack{\text{Cane-sugar}\\ \text{(Sucrose)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

HCl(dil.) is used for hydrolysis. Glucose being much less soluble in alcohol than fructose separates out by crystallising on cooling leaving behind more soluble fructose in solution. The two are separated by filtration.

Manufacture : It is obtained on a large scale by the hydrolysis of starch (corn starch or potato starch) on boiling with hot dilute H_2SO_4 or HCl at 393 K under 2-3 atm. pressure.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\Delta]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

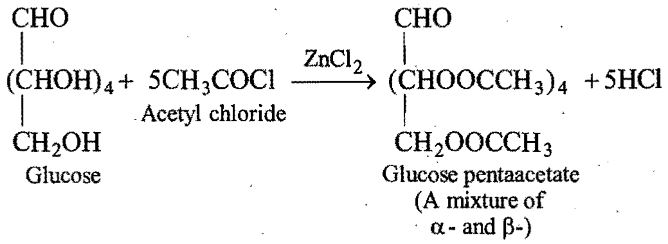
A thin paste of starch is boiled with dilute acid till the hydrolysis is complete. The excess of acid is neutralized with chalk (calcium carbonate) and the filtrate containing glucose is decolourised with animal charcoal. The solution is concentrated and evaporated under reduced pressure. Glucose is obtained in crystalline form.

Physical properties : It is a colourless crystalline solid, melts at 146°C. It is readily soluble in water. From aqueous solution, it separates as a crystalline monohydrate ($C_6H_{12}O_6 \cdot H_2O$) which melts at 86°C. It is sparingly soluble in alcohol but insoluble in ether. It is less sweet (three-fourth) than cane-sugar. It is optically active and the ordinary naturally occurring form is (+) glucose or dextro form. It shows **mutarotation.**

Chemical properties : Glucose is a polyhydroxy aldehyde, *i.e.*, aldohexose. It has five —OH groups (one 1° alcoholic group and four 2° alcoholic groups) and one aldehydic group. It shows characteristics of hydroxyl and aldehydic groups. The important chemical reactions of the glucose are the following:

1. Alcoholic Reactions (Reactions Due to —OH Group)

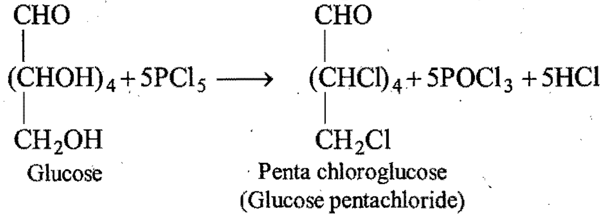
(a) Reaction with acid chlorides and acid anhydrides : Glucose forms penta acetyl derivatives with acid chlorides or acid anhydrides in presence of anhydrous zinc chloride, $ZnCl_2$.



$$\begin{array}{l}\text{CHO}\\ |\\ (\text{CHOH})_4\\ |\\ \text{CH}_2\text{OH}\\ \text{Glucose}\end{array} + \underset{\text{Acetyl chloride}}{5CH_3COCl} \xrightarrow{ZnCl_2} \begin{array}{l}\text{CHO}\\ |\\ (\text{CHOOCCH}_3)_4\\ |\\ \text{CH}_2\text{OOCCH}_3\\ \text{Glucose pentaacetate}\\ \text{(A mixture of}\\ \alpha\text{- and }\beta\text{-)}\end{array} + 5HCl$$

This shows that a molecule of glucose contains 5 —OH groups and has cyclic structure.

(b) Reaction with PCl_5 : Glucose reacts with phosphorus pentachloride to form pentachloroglucose.



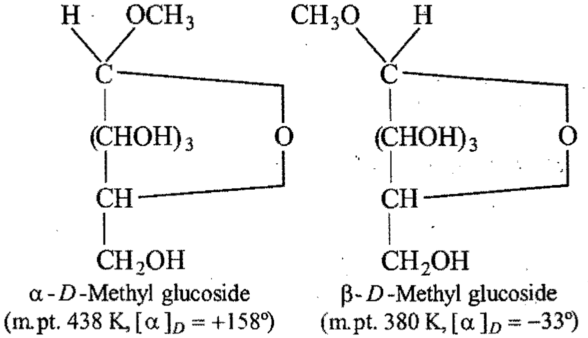
$$\begin{array}{l}\text{CHO}\\ |\\ (\text{CHOH})_4\\ |\\ \text{CH}_2\text{OH}\\ \text{Glucose}\end{array} + 5PCl_5 \longrightarrow \begin{array}{l}\text{CHO}\\ |\\ (\text{CHCl})_4\\ |\\ \text{CH}_2\text{Cl}\\ \text{Penta chloroglucose}\\ \text{(Glucose pentachloride)}\end{array} + 5POCl_3 + 5HCl$$

(c) Reaction with metallic hydroxides : Glucose behaves as a weak acid. It reacts with certain metallic hydroxides like $Ca(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$, $Cu(OH)_2$, etc., to form metallic glucosates, *i.e.*, $C_6H_{12}O_6 \cdot CaO$ (calcium glucosate) which is soluble in water.

$$\underset{\text{Glucose}}{C_6H_{11}O_5}\text{—}OH + \underset{\text{Calcium hydroxide}}{H\text{—}O\text{—}Ca\text{—}OH} \longrightarrow \underset{\text{Calcium glucosate}}{C_6H_{11}O_5\text{—}O\text{—}Ca\text{—}OH} + H_2O$$

(d) Formation of glycosides : When treated with methyl alcohol in presence of dry HCl gas, glucose yields monomethyl ether which is actually a mixture of α- and β-forms indicating that one of the —OH group is different from others (supports that glucose has a cyclic structure).

$$\underset{\text{Glucose}}{C_6H_{11}O_5\text{—}OH} + H\text{—}OCH_3 \xrightarrow{HCl} \underset{\substack{\alpha\text{- and }\beta\text{-Methyl}\\ \text{glucoside}}}{C_6H_{11}O_5OCH_3} + H_2O$$



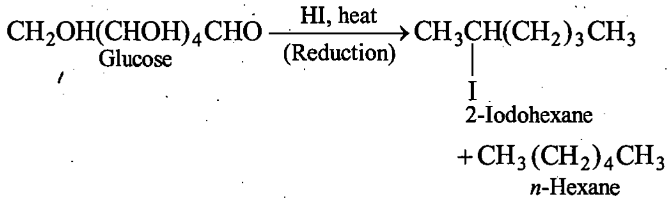
α-*D*-Methyl glucoside (m.pt. 438 K, $[\alpha]_D = +158°$)   β-*D*-Methyl glucoside (m.pt. 380 K, $[\alpha]_D = -33°$)

2. Reactions of Carbonyl Group (Aldehydic Group)

(a) Reduction : Glucose undergoes reduction with sodium amalgam in aqueous solution or $NaBH_4$ forming *D*-sorbitol, a hexahydric alcohol.

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + 2H \xrightarrow[H_2O]{Na-Hg} \underset{D\text{-Sorbitol}}{CH_2OH(CHOH)_4CH_2OH}$$

On prolonged heating with concentrated HI and red phosphorus at 110°C, glucose forms a mixture of 2-iodohexane and *n*-hexane.



$$\underset{\text{Glucose}}{\mathrm{CH_2OH(CHOH)_4CHO}} \xrightarrow[\text{(Reduction)}]{\text{HI, heat}} \underset{\text{2-Iodohexane}}{\mathrm{CH_3\underset{\substack{|\\ I}}{C}H(CH_2)_3CH_3}} + \underset{n\text{-Hexane}}{\mathrm{CH_3(CH_2)_4CH_3}}$$

(b) Oxidation : Glucose undergoes readily oxidation with various oxidising agents, *i.e.*, glucose acts as a powerful reducing agent. As such it reduces Fehling's solution and Tollens' reagent.

(i) Reaction with Fehling's solution : Fehling's solution is reduced to a red precipitate of cuprous oxide.

$$\underset{\text{Glucose}}{\mathrm{CH_2OH(CHOH)_4CHO}} + 2\mathrm{CuO} \longrightarrow \underset{\text{Gluconic acid}}{\mathrm{CH_2OH(CHOH)_4COOH}} + \underset{\text{(red ppt.)}}{\mathrm{Cu_2O}}$$

(ii) Reaction with Tollens' reagent : With ammoniacal silver nitrate solution (Tollens' reagent), a silver mirror or black precipitate is formed.

$$\underset{\text{Glucose}}{\mathrm{CH_2OH(CHOH)_4CHO}} + \mathrm{Ag_2O} \longrightarrow \underset{\text{Gluconic acid}}{\mathrm{CH_2OH(CHOH)_4COOH}} + \underset{\text{(Mirror)}}{2\mathrm{Ag}}$$

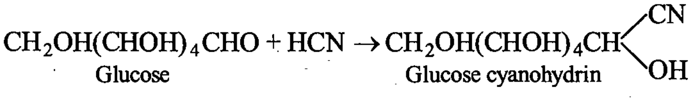
(iii) Reaction with bromine water : Glucose is oxidised to gluconic acid (a monocarboxylic acid) with bromine water or alkaline iodine solution or any mild oxidising agent.

$$\underset{\text{Glucose}}{\mathrm{CH_2OH(CHOH)_4CHO}} + [\mathrm{O}] \xrightarrow{\mathrm{Br_2/H_2O}} \underset{\text{Gluconic acid}}{\mathrm{CH_2OH(CHOH)_4COOH}}$$

(iv) Reaction with nitric acid : Nitric acid or any other strong oxidising agent converts glucose to saccharic acid or glucaric acid (a dicarboxylic acid) containing same number of carbon atoms.

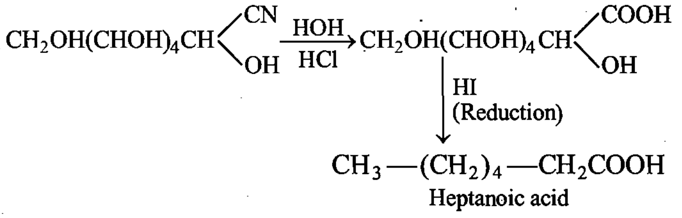
$$\underset{\text{Glucose }(\mathrm{C_6})}{\mathrm{CH_2OH(CHOH)_4CHO}} + 3[\mathrm{O}] \xrightarrow{\mathrm{HNO_3}} \underset{\text{Saccharic acid }(\mathrm{C_6})}{\mathrm{COOH(CHOH)_4COOH}} + \mathrm{H_2O}$$

(c) Reaction with HCN : An addition product, glucose cyanohydrin is formed.



$$\underset{\text{Glucose}}{\mathrm{CH_2OH(CHOH)_4CHO}} + \mathrm{HCN} \rightarrow \underset{\text{Glucose cyanohydrin}}{\mathrm{CH_2OH(CHOH)_4CH}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{OH}\end{smallmatrix}}$$

Hydrolysis of glucose cyanohydrin gives hydroxy acid. Reduction of the corresponding acid formed gives a clue regarding the nature of the monosaccharide carbon chain.

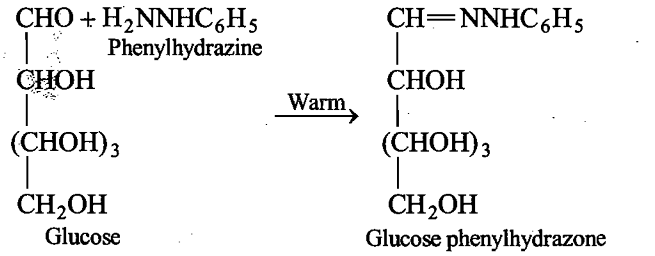


$$\mathrm{CH_2OH(CHOH)_4CH}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{OH}\end{smallmatrix} \xrightarrow[\mathrm{HCl}]{\mathrm{HOH}} \mathrm{CH_2OH(CHOH)_4CH}\begin{smallmatrix}\mathrm{COOH}\\ \mathrm{OH}\end{smallmatrix} \xrightarrow[\text{(Reduction)}]{\mathrm{HI}} \underset{\text{Heptanoic acid}}{\mathrm{CH_3{-}(CH_2)_4{-}CH_2COOH}}$$

(d) Reaction with hydroxylamine : Glucose forms an oxime with hydroxylamine.

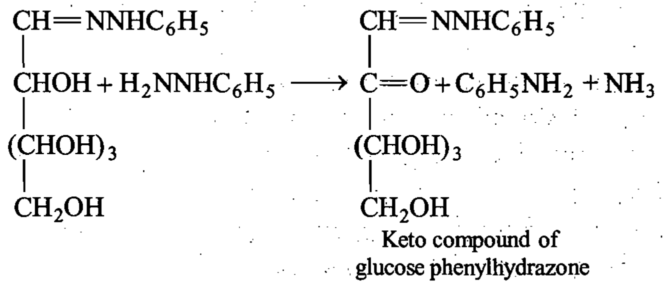
$$\underset{\text{Glucose}}{\mathrm{CH_2OH(CHOH)_4CHO}} + \mathrm{NH_2OH} \longrightarrow \underset{\text{Glucose oxime}}{\mathrm{CH_2OH(CHOH)_4CH{=}NOH}} + \mathrm{H_2O}$$

(e) Reaction with phenylhydrazine (Fischer's mechanism) : When warmed with excess of phenylhydrazine, glucose first forms phenylhydrazone by condensation with —CHO group.



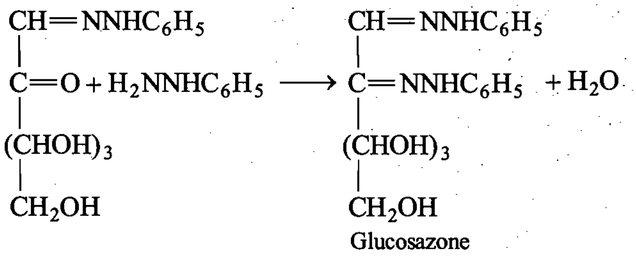
$$\begin{array}{l}\mathrm{CHO + H_2NNHC_6H_5}\\ |\quad \text{Phenylhydrazine}\\ \mathrm{CHOH}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\\ \text{Glucose}\end{array} \xrightarrow{\text{Warm}} \begin{array}{l}\mathrm{CH{=}NNHC_6H_5}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\\ \text{Glucose phenylhydrazone}\end{array}$$

The adjacent —CHOH group is then oxidised by a second molecule of phenylhydrazine.



$$\begin{array}{l}\mathrm{CH{=}NNHC_6H_5}\\ |\\ \mathrm{CHOH + H_2NNHC_6H_5}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH{=}NNHC_6H_5}\\ |\\ \mathrm{C{=}O + C_6H_5NH_2 + NH_3}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\\ \text{Keto compound of}\\ \text{glucose phenylhydrazone}\end{array}$$

The resulting carbonyl compound reacts with a third molecule of phenylhydrazine to yield glucosazone.



$$\begin{array}{l}\mathrm{CH{=}NNHC_6H_5}\\ |\\ \mathrm{C{=}O + H_2NNHC_6H_5}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH{=}NNHC_6H_5}\\ |\\ \mathrm{C{=}NNHC_6H_5 + H_2O}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\\ \text{Glucosazone}\end{array}$$

3. Miscellaneous Reactions

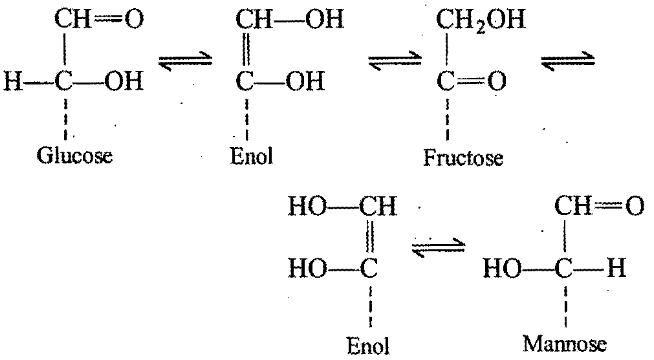
(a) Fermentation : A solution of glucose is readily fermented by the enzyme, zymase, present in yeast to form ethanol and carbon dioxide.

$$\underset{\text{Glucose}}{\mathrm{C_6H_{12}O_6}} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2\mathrm{C_2H_5OH}} + 2\mathrm{CO_2}$$

(b) Dehydration : When heated strongly or when treated with warm concentrated sulphuric acid, glucose is dehydrated to give a black mass (sugar carbon).

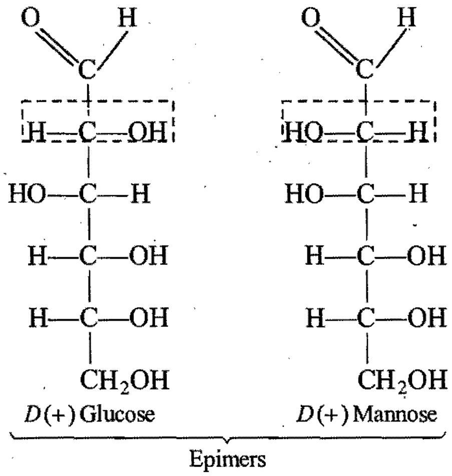
(c) Reaction with alkalies : When warmed with concentrated alkali, glucose first turns yellow, then brown and finally gives a resinous mass.

A dilute solution of glucose, when warmed with dilute solution of alkali, some glucose is converted into fructose and mannose. ***D*-glucose** and ***D*-mannose** are **epimers.** [Epimers are a pair of diastereomers that differ only in the configuration about a single carbon atom *i.e.*, at C-2 position.] *e.g.*,



This reaction is called **Lobry de Bruyn Van Ekenstein rearrangement** and is believed to occur *via* 1,2-enolization.

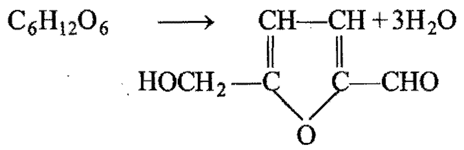
The same equilibrium mixture is obtained even if one starts with *D*(+) mannose or *D*(–) fructose.



(d) Action of concentrated hydrochloric acid : When heated with conc. HCl, glucose forms laevulic acid.

$$C_6H_{12}O_6 \xrightarrow{\text{Conc. HCl}} \underbrace{CH_3COCH_2CH_2COOH}_{\text{Laevulic acid}} + HCOOH + H_2O$$

On treatment with conc. HCl, glucose can also form 5-hydroxymethyl furfural.



5-Hydroxymethyl furfural

This 5-hydroxymethyl furfural gives violet colouration with an alcoholic solution of α-naphthol (**Molisch test** for carbohydrates).

This on acid treatment with conc. HCl gives laevulic acid.

Uses : Glucose is used:

(i) in the preservation of fruits and preparation of jams and jellies.

(ii) in the preparation of confectionery and as a sweetening agent.

(iii) as a food for patients, invalids and children.

(iv) in the form of calcium glucosate as medicine in treatment of calcium deficiency.

(v) as a reducing agent in silvering of mirrors.

(vi) as a raw material for alcoholic preparations.

(vii) in industrial preparation of vitamin-C.

(viii) in the processing of tobacco.

(ix) as an intravenous injection to the patients with lower glucose content in blood.

Tests of glucose : (i) When heated in a dry test tube, it melts, turns brown and finally black, giving a characteristic smell of burnt sugar.

(ii) When warmed with a little conc. H_2SO_4, it leaves a charred residue of carbon.

(iii) When it is boiled with dilute NaOH solution, it first turns yellow and then brown.

(iv) Molisch's test : This is a general test for carbohydrates. A drop or two of alcoholic solution of α-naphthol is added to 2 mL of glucose solution. 1 mL of concentrated H_2SO_4 is added carefully along the sides of the test tube. The formation of a violet ring, at the junction of two liquids confirms the presence of a carbohydrate.

(v) Silver mirror test : A mixture of glucose and ammoniacal silver nitrate is warmed in a test tube. Appearance of silver mirror on the inner walls confirms glucose.

(vi) Fehling's solution test : A little glucose is warmed with Fehling's solution. A red precipitate of cuprous oxide is formed.

(vii) Osazone formation : Glucose on heating with excess of phenylhydrazine in acetic acid gives a yellow crystalline compound, m.pt. 205°C.

Structure of Glucose : The structure of glucose has been established as follows:

(A) Open chain structure : It is based on the following points :

(i) Elemental analysis and molecular mass determination show that the molecular formula of glucose is $C_6H_{12}O_6$.

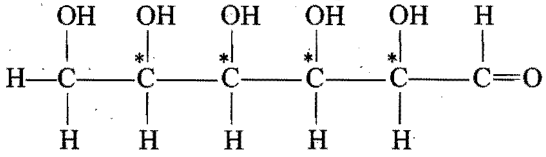
(ii) Glucose, on complete reduction with HI and red phosphorus, finally gives *n*-hexane. This indicates that it contains a straight chain of six carbon atoms.

(iii) It reacts with acetic anhydride and forms penta- acetate derivative. This shows the presence of five hydroxyl groups each linked to a separate carbon atom as the molecule is stable.

(iv) Glucose combines with hydroxylamine to form a monoxime. It also combines with one mole of HCN to form a cyanohydrin. These reactions indicate the presence of a carbonyl group, $>C{=}O$, in the glucose molecule.

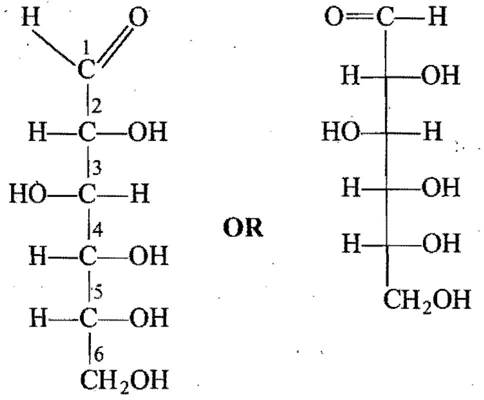
(v) Mild oxidation of glucose with bromine water gives gluconic acid. Further, glucose also reduces Tollens' reagent and Fehling's solution. These reactions show the presence of an aldehyde group.

On the basis of these observations, the following open chain structure can be written for glucose.



$$H-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{\overset{*}{C}}}-\underset{H}{\overset{OH}{\overset{*}{C}}}-\underset{H}{\overset{OH}{\overset{*}{C}}}-\underset{H}{\overset{OH}{\overset{*}{C}}}-\overset{H}{C}=O$$

There are four asymmetric carbon atoms marked by asterisks (*) in the molecule. This representation is incomplete, because a definite configuration to these asymmetric centres has not been assigned. The configuration of *D*-glucose was proved by **Emil Fischer.** The structure of *D*-glucose as elucidated by Emil Fischer is:



D-Glucose

Evidence against open-chain structure : The open-chain formula of glucose accounts for most of the reactions satisfactorily but fails to explain the following:

(i) Even though an aldehyde group is present, the glucose does not react with $NaHSO_3$ and NH_3.

(ii) Glucose does not give the Schiff's test and 2,4-DNP test for aldehydes.

(iii) Glucose does not react with Grignard reagents.

(iv) Glucose penta-acetate does not react with hydroxylamine.

(v) Two isomeric methyl glucosides (α and β) are obtained by heating glucose with methyl alcohol in presence of dry HCl gas.

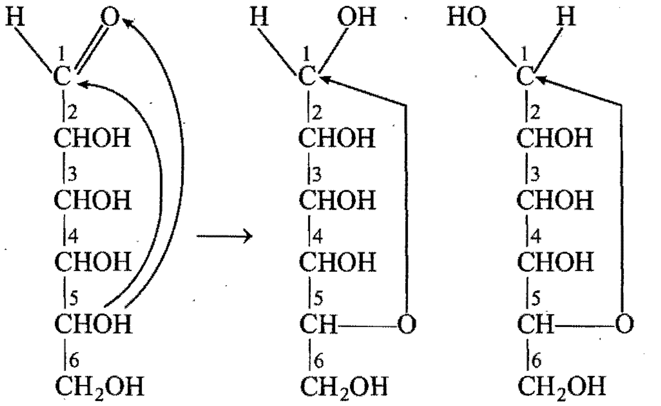
(vi) Glucose exists in two stereoisomeric forms (α and β). α-*D* (+)-glucose m.p. 419K with specific rotation +110° is obtained by crystallizing glucose from concentrated aqueous or alcoholic or acetic acid solution at 303K, whereas β-*D* (+)-glucose m.p. 423K with specific rotation +19.7° is obtained by crystallizing glucose from hot and saturated aqueous solution or pyridine solution at 371K.

(vii) An aqueous solution of glucose shows **mutarotation**, *i.e.*, its specific rotation gradually decreases from +110° to +52.5° in case of α-glucose and increases from +19.7° to +52.5° in case of β-glucose.

All these observations indicate that free aldehydic group is not present in the molecule.

(B) Cyclic structure of glucose : *D*-glucose exists in two optically active forms known as α-*D*-glucose and β-*D*-glucose.

α-*D*-glucose has specific rotation of +110° and β-*D*-glucose has specific rotation of +19.7°. The two isomers are interconvertible in aqueous solution. The equilibrium rotation is +52°. The equilibrium mixture has 36% α-glucose, 64% β-glucose. Glucose forms a stable cyclic hemiacetal (according to Fischer) between —CHO group and the —OH group of the fifth carbon atom in pyranose structure. In this process first carbon atom becomes asymmetric giving two isomers (I) and (II) which differ only in the configuration of the first asymmetric carbon.



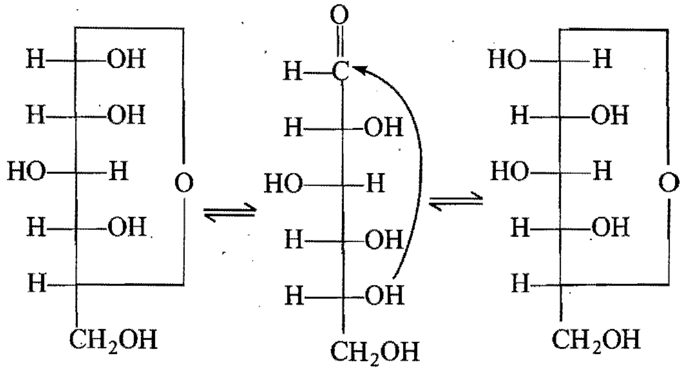
D-Glucose α-*D*-Glucose (I) β-*D*-Glucose (II)

$[\alpha]_D = +52.5°$ $[\alpha]_D = +110°$ $[\alpha]_D = +19.7°$

$$\underset{36\%}{\alpha\text{-Glucose}} \rightleftharpoons \underset{0.02\%}{\text{Open chain form}} \rightleftharpoons \underset{64\%}{\beta\text{-Glucose}}$$

$$\alpha\text{-D-Glucose} \rightleftharpoons \text{Equilibrium mixture} \rightleftharpoons \beta\text{-D-glucose}$$

The exact spatial arrangement of different —OH groups was given by Emil Fischer after studying many other properties.



α-*D*-(+) Glucose
$[\alpha]_D = +110°$

Open chain structure
(Equilibrium mixture)
$[\alpha]_D = +52.5°$

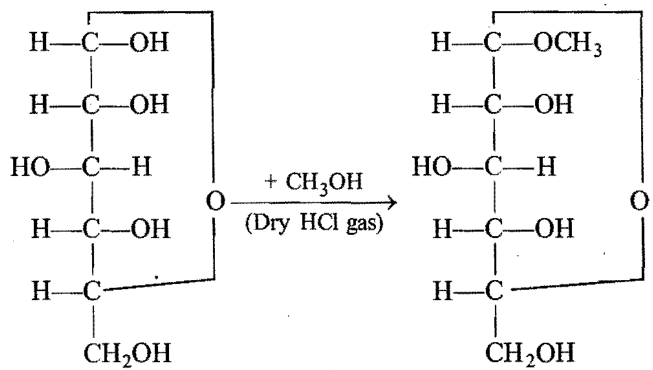
β-*D*-(+) Glucose
$[\alpha]_D = +19.7°$

All reducing carbohydrates, *i.e.*, monosaccharides (glucose, fructose, etc.) and disaccharides (maltose, lactose, etc.) undergo mutarotation in aqueous solution.

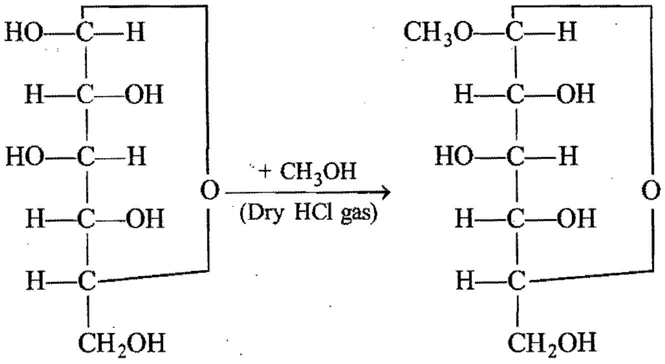
Carbon-1, in both configurations (I) and (II), is called an anomeric carbon atom. Due to anomeric carbon, glucose exists in two forms. Both the forms have different physical properties and are called **anomers.**

The ring structure explains all the reactions of glucose. The objections against the open chain structure of glucose have also been satisfactory explained, *e.g.*,

(i) α- and β-glucose on treatment with CH_3OH in presence of dry HCl gas forms **α-, and β-methyl glucosides** respectively.


α-*D*-Glucose (I)

α-*D*-Methyl glucoside


β-*D*-Glucose (II)

β-*D*-Methyl glucoside

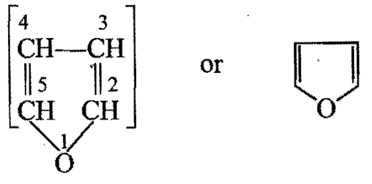
(ii) No reaction with NH_3 and $NaHSO_3$: The glucose ring is not very stable. It is easily broken up by **strong reagents** like HCN, NH_2OH and $C_6H_5NHNH_2$, etc., to give the intermediate aldehyde form, which reacts with them just like an aldehyde.

But weak reagents like NH_3 and $NaHSO_3$ are unable to open the chain and cannot react with it. This explains the inability of glucose to form aldehyde ammonia and bisulphite compound.

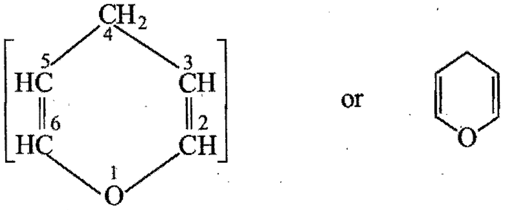
(iii) It explains mutarotation : Ordinary glucose is α-glucose, with a fresh aqueous solution has specific rotation, $[\alpha]_D$ + 110°. On keeping the solution for some time; α-glucose slowly changes into an equilibrium mixture of α-glucose (36%) and β-glucose (64%) and the mixture has specific rotation +52.5°.

Similarly a fresh aqueous solution of β-glucose having specific rotation, $[\alpha]_D$ + 19.7°, on keeping (standing) gradually changes into the same equilibrium mixture (having, specific rotation +52.7°). So an aqueous solution of glucose shows a physical property, known as **mutarotation,** *i.e.*, a change in the value of specific rotation (muta = change; rotation = specific rotation) is called **mutarotation.**

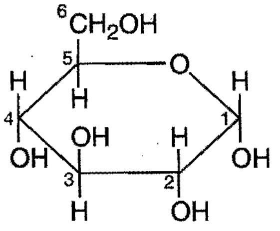
(iv) Methods for determining the size of rings : Fischer and Tollens' proposed that the ring or the internal hemiacetal is formed between C^1 and C^4. It means the ring is **Furan type** or 5-membered ring; this is called **Furanose structure;**

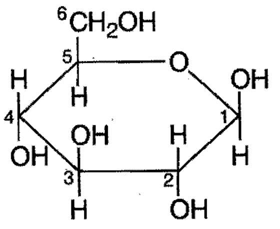

Furan

However, according to Haworth and Hirst the ring is formed between C^1 and C^5. It means the ring is **Pyran type** or 6-membered ring, this is called **Pyranose structure.**


Pyran

The two forms of *D*-glucose are also shown by **Haworth projection** formula which are given below:

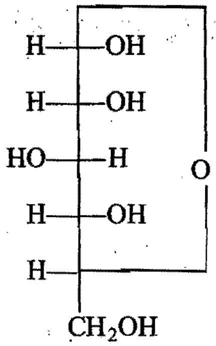

α-*D*-Glucose
(α-*D*(+) Glucopyranose)


β-*D*-Glucose
(β-*D* (+) Glucopyranose)

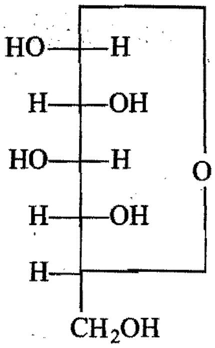
The above projection formulae show that the six membered ring is planar but actually the ring has a chain structure similar to cyclohexane.

In Haworth formula, all the OH groups on the right in Fischer's formula are directed below the plane of the ring while those on the left go above the plane. The terminal CH_2OH projects above the plane of the ring.

The **Fischer projection** formula of α- and β-glucose are given ahead:



α-*D* (+) glucopyranose



β-*D* (+) glucopyranose

2. FRUCTOSE, FRUIT SUGAR, $C_6H_{12}O_6$, (KETO-HEXOSE)

It is present in abundance in fruits and hence is called **fruit sugar.** It is also present in cane-sugar and honey along with glucose in combined form. The polysaccharide **inulin** is a polymer of fructose and gives only fructose on hydrolysis. Since, naturally occurring fructose is laevorotatory, it is also known as **laevulose.**

Fructose is a keto-hexose. It is obtained along with glucose by hydrolysis of cane-sugar with dilute H_2SO_4.

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Warm}]{H_2SO_4\ (\text{dil.})} \underset{D\text{-Glucose}}{C_6H_{12}O_6} + \underset{D\text{-Fructose}}{C_6H_{12}O_6}$$

The solution having equal molecules of *D*-glucose and *D*-fructose is termed **invert sugar** and the process is known as **inversion.**

The excess of sulphuric acid is neutralized by adding milk of lime. A little more of lime is added which converts both glucose and fructose into calcium glucosate and calcium fructosate respectively. Calcium fructosate being insoluble in water separates out. It is filtered off and suspended in water through which carbon dioxide is circulated. Carbon dioxide decomposes calcium fructosate into fructose and calcium carbonate. Calcium carbonate is removed by filtration and the filtrate is concentrated under reduced pressure.

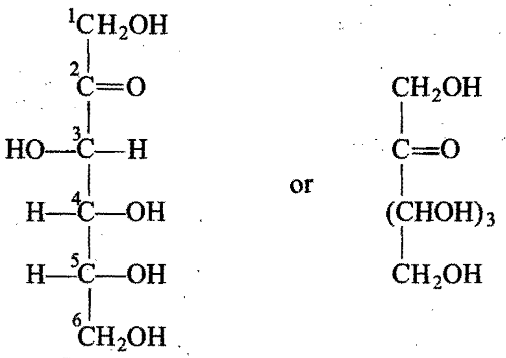
$$\underset{\text{Calcium fructosate}}{C_6H_{11}O_5\text{—O—CaOH}} + CO_2 \longrightarrow \underset{\text{Fructose}}{C_6H_{12}O_6} + CaCO_3$$

Fructose is prepared on large scale **by hydrolysis of inulin** with dilute sulphuric acid and excess of H_2SO_4 is removed as $BaSO_4$.

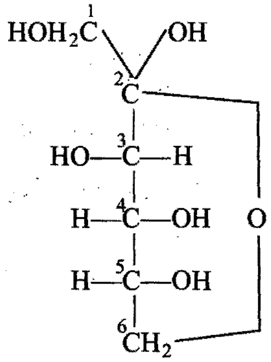
$$\underset{\text{Inulin}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H_2SO_4(\text{dil.})} \underset{\text{Fructose}}{nC_6H_{12}O_6}$$

Properties : The anhydrous fructose is a colourless crystalline compound. It melts at 102°C. It is soluble in water but insoluble in benzene and ether. It is less soluble in water than glucose. It is the sweetest of all sugars and its solution is laevorotatory. Like glucose, it also shows **mutarotation.**

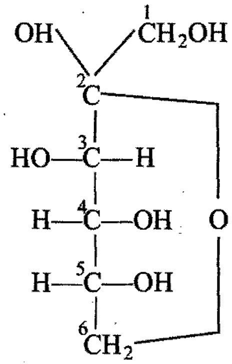
Structure of fructose : Fructose is a pentahydroxy ketone and its open chain and closed chain structures can be represented as:



D-Fructose
$[\alpha]_D = -92°$



α-*D*-Fructose
$[\alpha]_D = -21°$



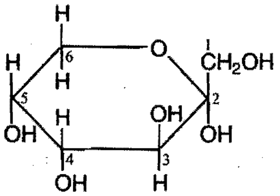
β-*D*-Fructose
$[\alpha]_D = -133°$

Fructose also undergoes **mutarotation.**

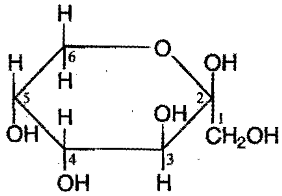
$$\underset{[\alpha]_D = -21°}{\alpha\text{-}D\text{-Fructose}} \rightleftharpoons \underset{[\alpha]_D = -92°}{\text{Equilibrium mixture}} \rightleftharpoons \underset{[\alpha]_D = -133°}{\beta\text{-}D\text{-Fructose}}$$

However, in combined state (such as in sucrose), fructose exists in furanose form (α and β). The two forms of *D*-fructose are also shown by Fischer and Haworth projection formulae, which are as follows:

Haworth projection formulae

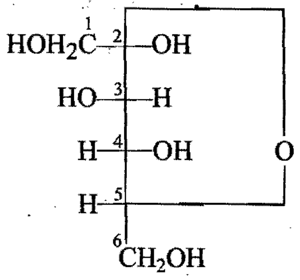


α-*D*-Fructose
or α-*D*-Fructopyranose

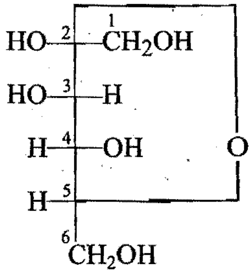


β-*D*-Fructose
or β-*D*-Fructopyranose

Fischer projection formulae

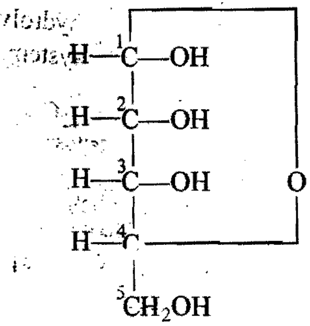


α-*D*-Fructofuranose

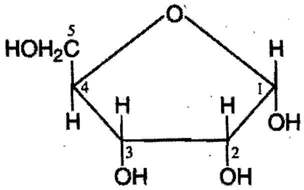


β-*D*-Fructofuranose

Similarly, ribose (and 2-deoxy ribose) also exist in furanose form.



α-*D*-Ribose
or α-*D*-Ribofuranose



Haworth projection
(α-*D*-Ribofuranose)

Fructose gives reactions similar to glucose. The difference in properties is due to the fact that it contains a ketonic group while glucose contains an aldehydic group.

Comparison of Glucose and Fructose

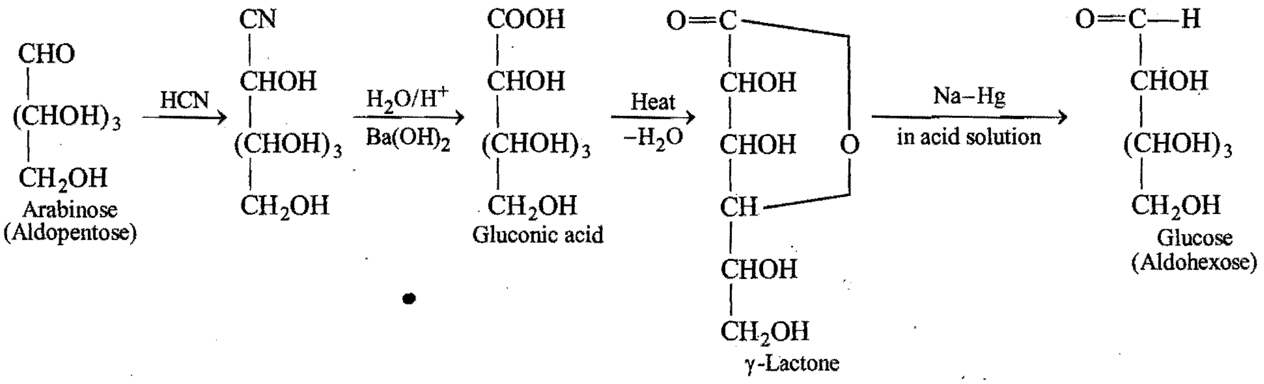
Property	Glucose	Fructose
1. Molecular formula	$C_6H_{12}O_6$.	$C_6H_{12}O_6$.
2. Nature	Polyhydroxy aldehyde.	Polyhydroxy ketone.
3. Melting point	146°C.	102°C.
4. Optical activity of natural form	Dextrorotatory.	Laevorotatory.
5. With ethyl alcohol	Almost insoluble.	More soluble.
6. Oxidation		
(a) with bromine water	Gluconic acid.	No reaction.
(b) with conc. nitric acid	Saccharic acid (Glucaric acid).	Mixture of glycollic acid, tartaric acid and trihydroxy glutaric acid.
7. Reduction with $NaBH_4$ or Na-Hg/H_2O	*D*-sorbitol.	Mixture of *D*-sorbitol and *D*-mannitol.
8. Calcium hydroxide	Forms calcium glucosate, soluble in water.	Forms calcium fructosate, insoluble in water.
9. Molisch's reagent	Forms a violet ring.	Forms a violet ring.
10. Fehling's solution	Gives red precipitate.	Gives red precipitate.
11. Tollens' reagent	Forms silver mirror.	Forms silver mirror.
12. Phenylhydrazine	Forms osazone.	Forms osazone.
13. Resorcinol + HCl(dil.) (Selivanoff's test)	No colouration.	Gives red or brown colour or precipitate.
14. Freshly prepared ammonium molybdate sol. + few drops of acetic acid **(Pinoff's test)**	Light blue colour.	Bluish green colour on heating.
15. Alcoholic α-naphthol + HCl(conc.) **(Furfural test)**	No colouration.	A purple colour (violet) on boiling.

15.4 INTERCONVERSIONS OF MONOSACCHARIDES

1. Conversion of aldopentose into aldohexose (Killiani-Fischer Synthesis)

The conversion of an aldose to the next higher member involves the following steps:

(i) Formation of a cyanohydrin.
(ii) Hydrolysis of —CN to —COOH forming aldonic acid.
(iii) Conversion of aldonic acid into lactone by heating.
(iv) The lactone is finally reduced with sodium amalgam or sodium borohydride to give the higher aldose.

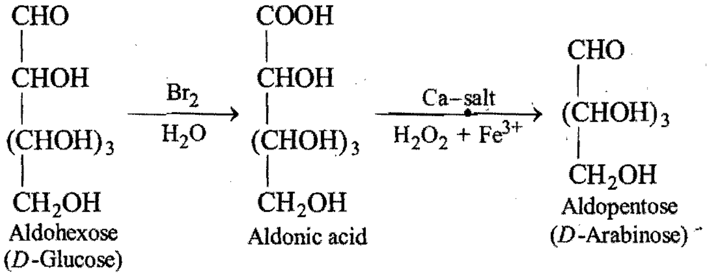


2. Conversion of aldohexose into aldopentose (Ruff Degradation)

(i) An aldose can be converted to the next lower member by **Ruff Degradation.** It involves two steps:

(a) Oxidation of the aldose to aldonic acid by using bromine water.

(b) The aldonic acid is treated with $CaCO_3$ to give the calcium salt which is then oxidised by Fenton's reagent (H_2O_2 + ferric sulphate) to form the next lower aldose.

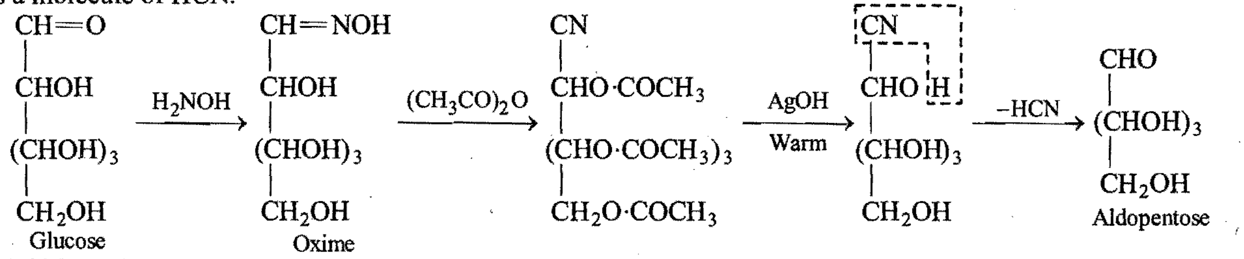


(ii) By Wohl's method : It involves the following steps:

(a) Formation of oxime with hydroxylamine.

(b) Heating of oxime with acetic anhydride undergoes dehydration into cyano compound, whereas the hydroxyl groups get acetylated.

(c) The acetyl derivative is warmed with ammoniacal silver nitrate which removes the acetyl group by hydrolysis and eliminates a molecule of HCN.



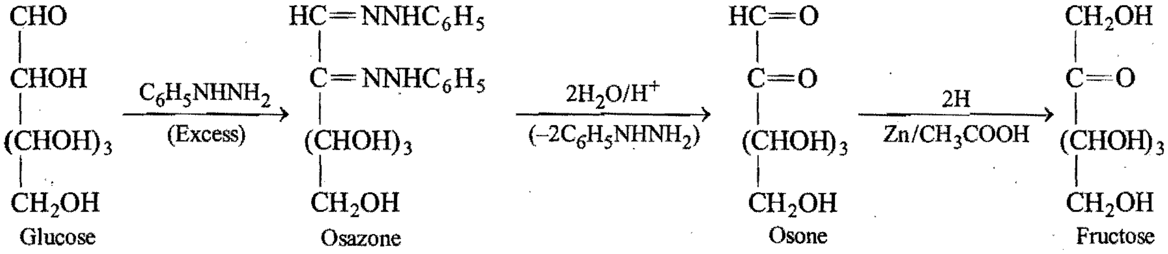
3. Conversion of Glucose into Fructose

Three steps are involved:

(i) Treatment of aldose with excess of phenylhydrazine to form osazone.

(ii) Hydrolysis of osazone with dil. HCl to form osone.

(iii) Reduction of osone with zinc and acetic acid to form ketose.

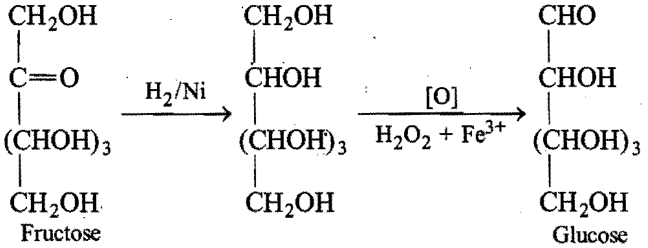


4. Conversion of Fructose into Glucose

Two steps are involved:

(i) Reduction of a ketose with H_2/Ni to form polyhydric alcohol.

(ii) Oxidation with Fenton's reagent to form aldose.



15.5 DISACCHARIDES

Carbohydrates which upon hydrolysis give two molecules of same or different monosaccharides are called **Disaccharides.** They have a general formula $C_{12}H_{22}O_{11}$. The three most important disaccharides are sucrose, maltose and lactose. The hexoses obtained on hydrolysis may be same or different.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{or Invertase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

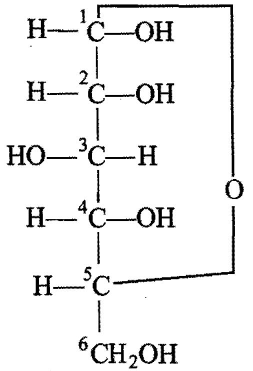
$$\text{Lactose} \xrightarrow[\text{or Lactase}]{H^+} \text{Glucose} + \text{Galactose}$$

$$\text{Maltose} \xrightarrow[\text{or Maltase}]{H^+} \text{Glucose} + \text{Glucose}$$

The hydrolysis is done by dilute acids or enzymes.

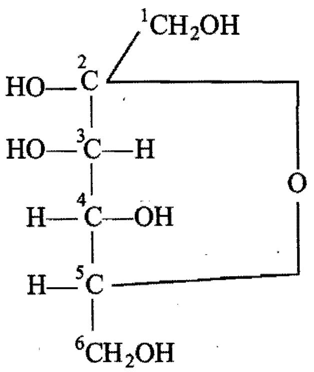
In disaccharides, the two monosaccharides are joined together by **glycosidic linkage.** A glycoside bond is formed when hydroxy group of the hemiacetal carbon of one monosaccharide condenses with a hydroxy group of another monosaccharide giving —O— bond with the elimination of a H_2O molecule.

1. Sucrose (cane-sugar), $C_{12}H_{22}O_{11}$: It is formed by the condensation of α-*D*-glucopyranose ($C_1-\alpha$) unit and β-*D*-fructofuranose ($C_2-\beta$) unit. These units are joined by α-β-glycosidic linkage between C_1 of the glucose unit and C_2 of the fructose unit.

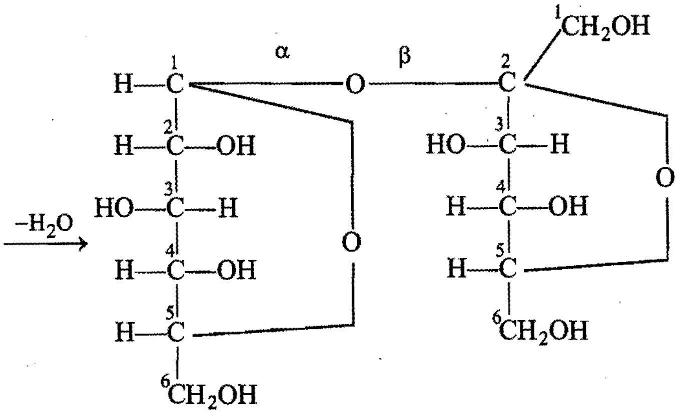


α-Glucosepyranose

+

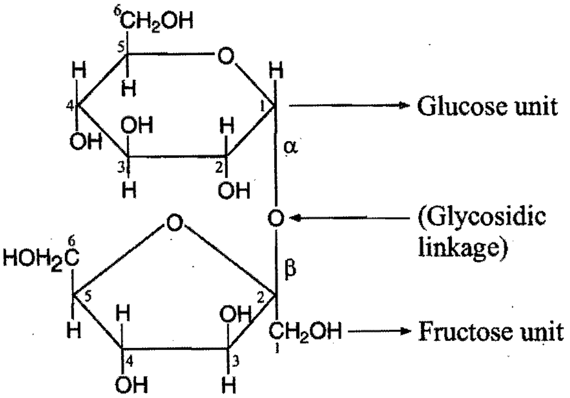


β-Fructosefuranose



Fischer Projection formulae of Sucrose
[α-*D*-Glucopyranoside, β-*D*-Fructofuranoside]

OR



Haworth Projection formulae of Sucrose

Sucrose is a **non-reducing sugar** since, both glucose ($C_1-\alpha$) and fructose ($C_2-\beta$) are connected to each other through their reducing centre and it does not contain any aldehyde or ketonic group and hence does not give the properties of monosaccharides (glucose or fructose). Also, sucrose is stable towards alkalies and does not show **mutarotation.**

Sucrose is our common table sugar which is obtained from sugar-cane and sugar beets. It is actually found in all photosynthetic plants.

It is a colourless, odourless crystalline compound and melts at 458 K. It is highly soluble in water, slightly soluble in alcohol and insoluble in ether. It is dextrorotatory but does not show **mutarotation.** It is a non-reducing sugar as it does not reduce Tollens' or Fehling's reagent. Sucrose, on heating slowly and carefully, melts and then if allowed to cool, it solidifies to pale yellow glassy mass called 'Barley sugar'. When heated to 473 K, it loses water to form brown amorphous mass called *Caramel.* On strong heating, it chars to almost pure carbon giving smell of burnt sugar.

Uses : Sucrose is used :

(i) as a sweetening agent for various food preparations, jams, syrups, sweets, etc.

(ii) in the manufacture of sucrose octa-acetate required to denature alcohol, to make paper transparent and to make anhydrous adhesives.

Inversion of cane-sugar : The hydrolysis of sucrose by boiling with a mineral acid or by enzyme invertase or sucrase, produces a mixture of equal molecules of *D*(+) glucose and *D*(–) fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Invertase}]{H^+} \underset{D\text{-Glucose}}{C_6H_{12}O_6} + \underset{D\text{-Fructose}}{C_6H_{12}O_6}$$

(This mixture is laevorotatory)

Sucrose solution is dextrorotatory. Its specific rotation is + 66.5°. But on hydrolysis, it becomes laevorotatory. The specific rotation of *D*(+) glucose is +52.7° and of *D*(–) fructose is –92.4°. Therefore, the net specific rotation of an equimolar mixture of *D*(+) glucose and *D*(–) fructose is,

$$\frac{+52.7° - 92.4°}{2} = -19.85°$$

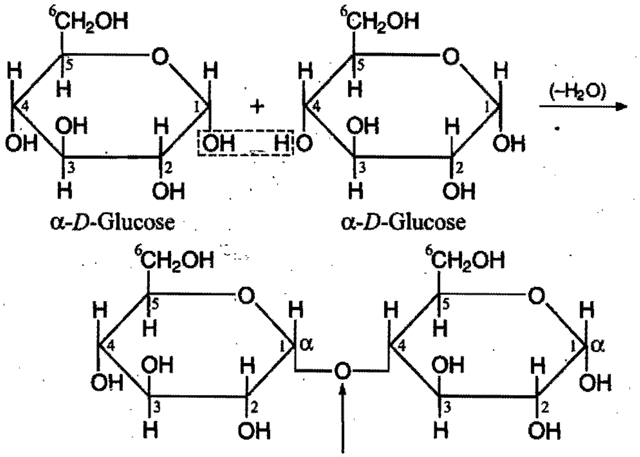
Thus, in the process of hydrolysis of sucrose, the specific rotation changes from + 66.5° to –19.85°, *i.e.*, a change in the sign of optical rotation from dextro to laevorotatory and it is said that inversion has taken place. The process of hydrolysis of sucrose is thus termed as **inversion of sugar** and the hydrolysed mixture having equal molar quantities of *D*(+) glucose and *D*(–) fructose is called **invert sugar.** The enzyme that brings the inversion is named as **invertase.** Invert sugar (130) is sweeter than sucrose (100), glucose (70), galactose (32) and lactose (10), but less sweet than fructose (170).

2. Maltose (Malt sugar), $C_{12}H_{22}O_{11}$: The partial hydrolysis of starch by the enzyme diastase (present in malt) produces maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

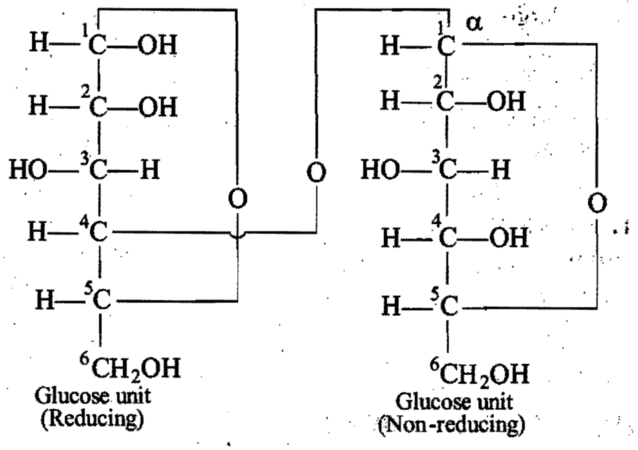
It is formed by the condensation of two molecules of α-*D*-glucopyranose in which (C_1 – α) of one glucose unit is connected to C_4 of the other glucose unit as shown below:

Haworth Projection formulae of α-*D*-Maltose



Glycosidic linkage α-*D*-Maltose

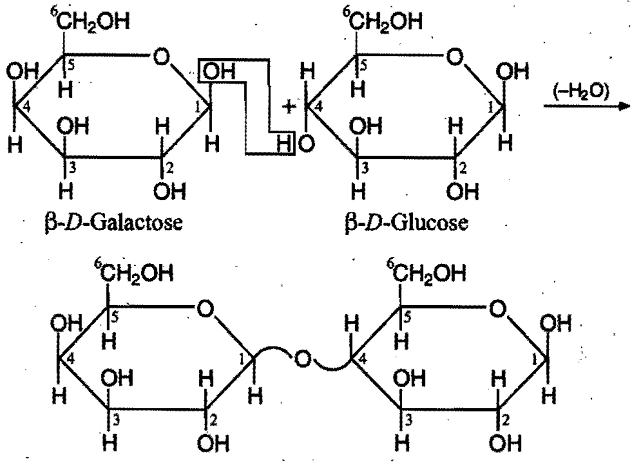
Fischer projection formulae of α-*D*- Maltose



Further, since in maltose one of the glucose unit exists in the hemiacetal form and is a **reducing sugar** which forms osazone. It also reduces Tollens' reagent, Fehling's solution and show **mutarotation.**

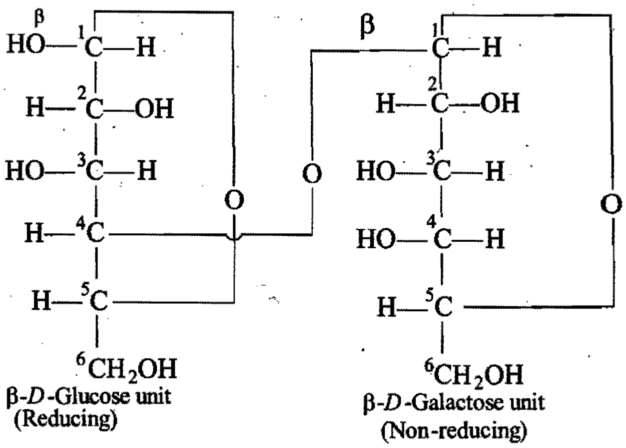
3. Lactose (milk sugar), $C_{12}H_{22}O_{11}$: It is obtained by the condensation of one molecule of β-*D*-galactopyranose (C_1 – β) unit and one molecule of β-*D*-glucopyranose (C_4 – β) unit as shown below :

Haworth Projection formulae of β-*D*-Lactose



Lactose

Fischer projection formulae of β-*D*-Lactose



Thus, lactose like maltose is a **reducing sugar** in which glucose unit is in the reducing form. It forms an osazone, undergoes **mutarotation** and also reduces Tollens' or Fehling's solution.

Reducing and non-reducing sugars : Those saccharides which reduce Fehling's solution or Tollens' reagent or Bendict's solution are called **reducing sugars** and those which do not reduce these reagents are called **non-reducing sugars.** Reducing sugars contain either α-hydroxy aldehyde or α-hydroxy ketone or they contain cyclic hemiacetal or hemiketal or structures in equilibrium with open chain forms having a free —CHO or $>C=O$ group. Non-reducing sugars do not contain free aldehyde or ketone group. They contain stable acetal or ketal structures which cannot be opened into a free carbonyl group.

Reducing sugars	**Non-reducing sugars**
D-Glucose, *D*-Fructose	Sucrose, Starch, Cellulose
Maltose, Lactose	Glycogen, Dextrin

15.6 POLYSACCHARIDES (STARCH AND CELLULOSE)

Polysaccharides are polymers of monosaccharides. The most important polysaccharides are starch and cellulose. They have a general formula $(C_6H_{10}O_5)_n$. Starch (Amylum) is most widely distributed in vegetable kingdom. It is found in the leaves, stems, fruits, roots and seeds. Concentrated form of starch is present in wheat, corn, barley, rice, potatoes, nuts, etc. It is the most important food source of carbohydrates.

Starch : Starch is the major food material and a white amorphous substance with no taste or smell. When heated to a temperature between 200–250°C, it changes into dextrin. At higher temperature charring occurs. When boiled with dilute acid or hydrolysed by the enzyme, *amylase* (present in saliva), starch ultimately yields glucose.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \longrightarrow \underset{\text{Dextrin}}{(C_6H_{10}O_5)_{n_1}} \longrightarrow \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6}$$

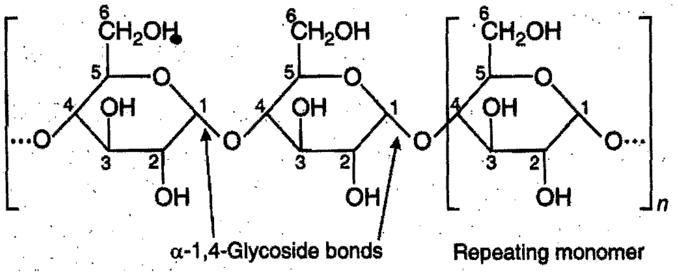
Both n and n_1, are unknown, but n is believed to be greater than n_1.

When treated with enzyme, *diastase*, it yields maltose.

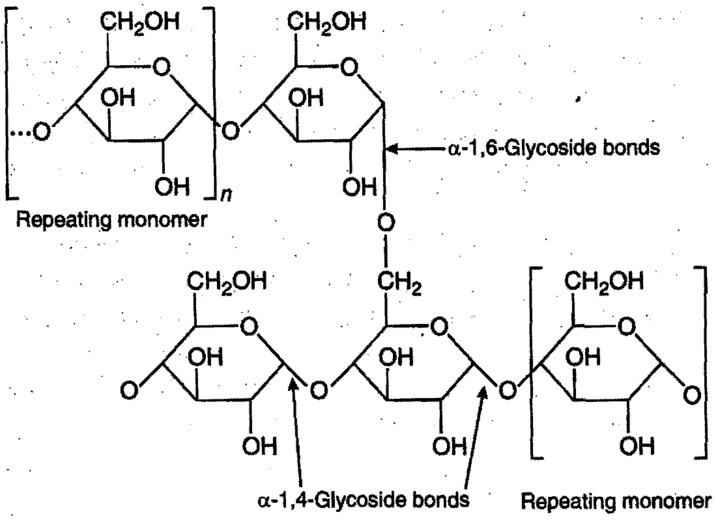
$$2(C_6H_{10}O_5)_n + nH_2O \longrightarrow \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

Starch solution gives a blue colour with a drop of iodine which disappears on heating to 75–80°C and reappears on cooling. The exact chemical nature of starch varies from source to source ($n = 200 - 1000$). Even the starch obtained from same source consists of two fractions (i) amylose (20%) and (ii) amylopectin (80%).

Amylose is a linear polymer while amylopectin is a highly branched polymer. Both are composed of α-*D*-glucose units which are linked to one another through α-linkage involving C_1 of one glucose unit with C_4 of the other by glycosidic linkages. The number of *D*-glucose units in amylose range from 60–300. It is soluble in hot water. **Amylopectin** consists of *D*-glucose units from 300–600. It is insoluble in water.



Structure of amylose



Structure of amylopectin

Uses : Starch and its derivatives are used:

(i) as the most valuable constituent of food as rice, bread, potato and corn-flour, etc.

(ii) in the manufacture of glucose, dextrin and adhesives (starch paste).

(iii) in paper and textile industry.

(iv) in calico printing as a thickening agent for colours.

(v) nitro starch is used as an explosive.

(vi) starch-acetate is a transparent gelatin like mass and is used mainly for making sweets.

Cellulose : It is found in all plants and so is the most abundant of all carbohydrates. It is the material used to form cell walls and other structural features of the plants. Wood is about 50% cellulose and the rest is lignin. Cotton (90-95% cellulose) and paper are largely composed of cellulose. Infact, more than 50% of all the living matter is cellulose.

Pure cellulose is obtained by successively treating cotton, wool, flax or paper with dilute alkali, dilute HCl or HF. This treatment removes mineral matter, water, alcohol and ether. Cellulose is left behind as a white amorphous powder.

Cellulose is insoluble in water and in most of the organic solvents. It decomposes on heating but does not melt. It dissolves in ammoniacal copper hydroxide solution (Schweitzer's reagent) but cellulose does not reduce Tollens' reagent or Fehling's solution. It does not form osazone and is not fermented by yeast. Further, cellulose also dissolves in a solution of zinc chloride in hydrochloric acid.

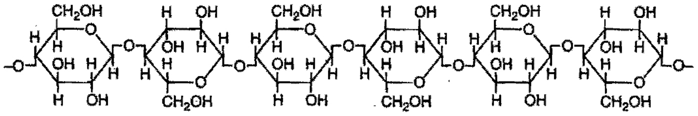
When it is treated with concentrated H_2SO_4 in cold, it slowly passes into solution. The solution when diluted with water, a starch like substance amyloid is precipitated and is called **parchment paper.** When boiled with dilute H_2SO_4, it is completely hydrolysed into *D*-glucose.

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

When cellulose is treated with concentrated NaOH solution, it forms a gelatinous semi-transparent mass which imparts lusture to cotton (mercerised) and this process is called **mercerisation.**

The cattle, goats and other ruminants can feed directly cellulose (grass, straw, etc.,) as they have digestive enzymes (celluloses) capable of hydrolysing cellulose into glucose. Man and many other mammals lack the necessary enzymes in their digestive tract and thus cannot use cellulose as food stuff.

Cellulose is a straight chain polysaccharide composed of *D*-glucose units which are joined by *B*-glycosidic linkages between C-1 of one glucose unit and C-4 of the next glucose unit. The number of *D*-glucose units in cellulose ranges from 300 to 50000.



Structure of cellulose

Uses : Cellulose is used:

(i) as such in the manufacture of cloth (cotton), canvas and gunny bags (jute) and paper (wood, bamboo, straw, etc.).

(ii) in the form of cellulose nitrates for the manufacture of explosives (gun-powder), medicines, paints and lacquers. The cellulose nitrates with camphor yield *celluloid* which is used in the manufacture of toys, decorative articles and photographic films.

(iii) in the form of cellulose acetate for the manufacture of rayon (artificial silk) and plastics.

IMPORTANCE OF CARBOHYDRATES

The carbohydrates perform two important functions in living bodies:

(i) Biofuels: Carbohydrates such as glucose, fructose, sugars, starch, glycogen, etc., act as **biofuels** and hence, **provide energy for the functioning of living organisms.**

In human system, all the carbohydrates except cellulose can serve as source of energy. Starch and various sugars (glycogen etc.), which are taken as food are first hydrolysed to glucose by the enzymes present in the digestive system.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Amylase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Glucose on slow oxidation to CO_2 and H_2O in the presence of enzymes liberates large amount of energy which is used by the body for carrying out various functions.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2 \longrightarrow 6CO_2 + 6H_2O + 2868\ \text{kJ}$$

Reserved food materials: Starch is the major food reserve material in plants and stored in seeds which is capable of making its own food by photosynthesis. Similarly, **glycogen** stored in liver and muscles acts as the reserve food material in animals. In case of emergency, the liver glycogen is readily hydrolysed to glucose which, in turn, gets oxidized in the blood to provide the much needed energy.

Both glycogen and amylopectin are branched polymers of α-*D*-glucose; rather glycogen is more highly branched than amylopectin. The molecular weight of glycogen is very high (contains 10^5 glucose units), whereas amylopectin chains consist of 20-25 glucose units and glycogen chains consist of 10-14 glucose units.

It may be noted that **cellulose cannot be hydrolysed in our body** because enzymes required for its hydrolysis are not present in our body, hence, **cellulose is not digestible.** However, grazing animals (such as cow, buffalo and deer, etc.,) can use cellulose of grass and plants as food by converting them into glucose.

(ii) They act as constituents of cell membrane.

15.7 PROTEINS AND AMINO ACIDS

Proteins : Proteins are a class of biologically important compounds. They are crucial to virtually all processes in living systems. Some of them are hormones which serve as chemical messengers that coordinate certain biochemical activities. Insulin, for example, controls the level of sugar in the blood stream. Others are enzymes that act as catalysts of biochemical reactions. Some proteins serve to transport the substances through the organism. Haemoglobin, for instance, carries oxygen in blood stream and delivers to different parts of the body. There are long fibrous proteins, such as **actin** and **myosin,** that are found in muscle. Another fibrous protein, α-**keratin,** serves as the major constituent of hair, nails and skin, while **collagen** is the prime constituent of tendons.

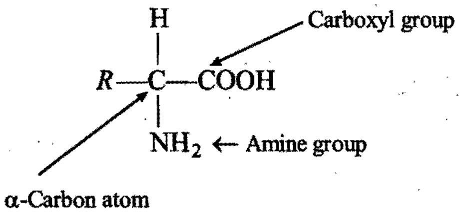
Proteins are also found in toxins (poisonous materials) as well as in antibodies.

Despite their wide range of functions, all proteins have something in common with another. **They are nitrogenous organic compounds of high molecular masses ranging from about 6000 to approximately 10,00,000. They are condensation polymers (actually polyamides) made up of linking together in various combinations, a number of different simple monomeric units called α-amino acids.** Proteins are synthesized by both plants and animals and on partial hydrolysis give peptides of varying molecular masses which upon complete hydrolysis give α-amino acids.

$$\text{Proteins} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \alpha\text{-aminoacids}$$

Amino acids : An amino acid is a bifunctional organic molecule that contains both a carboxyl group, —COOH, as well as an amine group, —NH_2. They are **classified as acidic** (containing two —COOH groups), **basic** (containing two —NH_2 groups) or **neutral** according to number of amine and carboxyl groups in a molecule. Neutral amino acids contain only one amine and one carboxyl group. They are further classified according to the position of amine group in relation to carboxyl group into α-, β-, γ- and δ-amino acids. Out of these α-amino acids are most important as they are building blocks of bio-proteins.

In an α-amino acid, the amine group is located on the carbon atom adjacent to the carboxyl group (the α-carbon atom). The general structure of the α-amino acids is represented as:

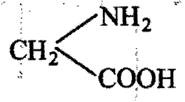
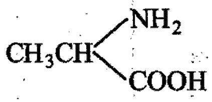
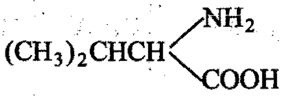
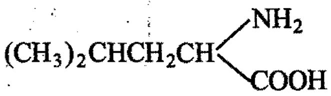
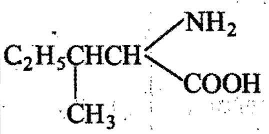
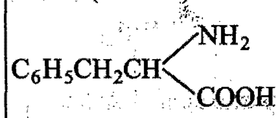
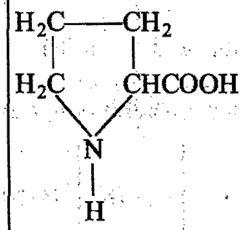


$$R\text{—}\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}\text{—}COOH$$

R may be alkyl, aryl or any other group.

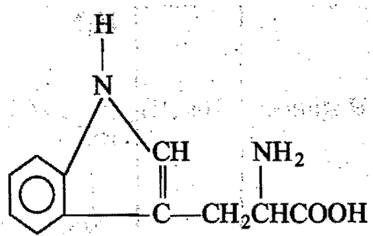
The proteins differ in the nature of *R*-group bonded to α-carbon atom. The nature of *R*-group determines the properties of proteins. There are about 20 amino acids which make up the bio-proteins. Out of these 10 amino acids **(non-essential)** are synthesised by our bodies and rest are essential in the diet **(essential amino acids)** and supplied to our bodies by food which we take for proper health and growth because they cannot be synthesised in the body. The α-amino acids are classified into the following four types:

(i) Amino acids with non-polar side chain : Examples are:

Amino acids	Abbreviation (One letter code)	Structure
1. Glycine	Gly (G)	 $CH_2(NH_2)COOH$
2. Alanine	Ala (A)	 $CH_3CH(NH_2)COOH$
3. Valine*	Val (V)	 $(CH_3)_2CHCH(NH_2)COOH$ (Essential)
4. Leucine*	Leu (L)	 $(CH_3)_2CHCH_2CH(NH_2)COOH$ (Essential)
5. Isoleucine*	Ile (I)	 $C_2H_5CH(CH_3)CH(NH_2)COOH$ (Essential)
6. Phenyl alanine *	Phe (F)	 $C_6H_5CH_2CH(NH_2)COOH$ (Essential)
7. Proline	Pro (P)	

(It does not fit the general formula)

(ii) Amino acids with polar but neutral side chain : Examples are:

1. Tryptophan*	Trp (W)	 (Essential)

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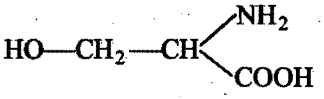
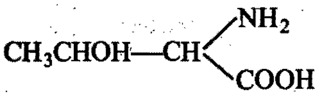
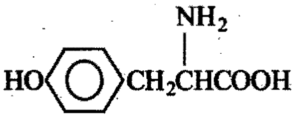
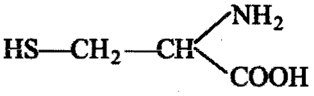
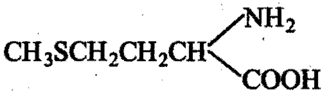
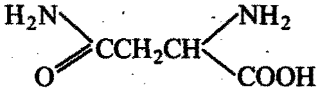
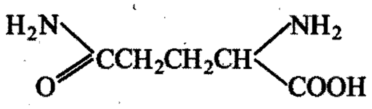
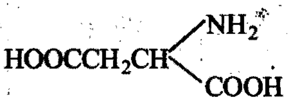
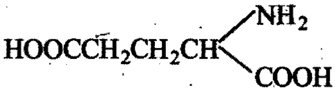
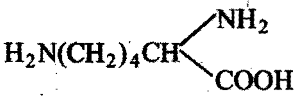
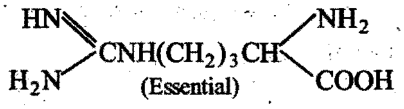
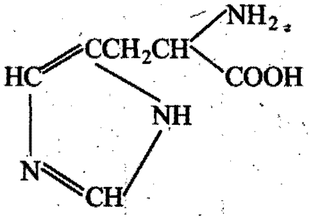
* Essential amino acids

2. Serine	Ser (S)	 $\mathrm{HO{-}CH_2{-}CH}{<}^{\mathrm{NH_2}}_{\mathrm{COOH}}$
3. **Threonine***	Thr (T)	 $\mathrm{CH_3CHOH{-}CH}{<}^{\mathrm{NH_2}}_{\mathrm{COOH}}$ (Essential)
4. Tyrosine	Tyr (Y)	
5. Cystine	Cys (C)	 $\mathrm{HS{-}CH_2{-}CH}{<}^{\mathrm{NH_2}}_{\mathrm{COOH}}$
6. Methionine*	Met (M)	 $\mathrm{CH_3SCH_2CH_2CH}{<}^{\mathrm{NH_2}}_{\mathrm{COOH}}$ (Essential)
7. Asparagine	Asn (N)	
8. Glutamine	Gln (Q)	

(iii) Amino acids with acidic side chains : Examples are:

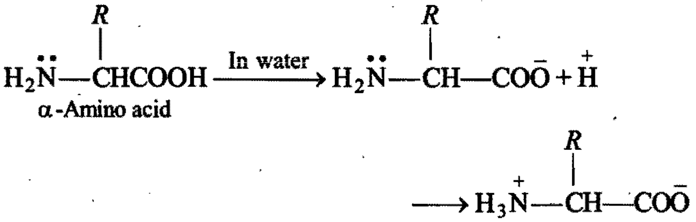
1. Aspartic acid	Asp (D)	 $\mathrm{HOOCCH_2CH}{<}^{\mathrm{NH_2}}_{\mathrm{COOH}}$
2. Glutamic acid	Glu (E)	 $\mathrm{HOOCCH_2CH_2CH}{<}^{\mathrm{NH_2}}_{\mathrm{COOH}}$

(iv) Amino acids with basic side chains : Examples are:

1. Lysine*	Lys (K)	 $\mathrm{H_2N(CH_2)_4CH}{<}^{\mathrm{NH_2}}_{\mathrm{COOH}}$ (Essential)
2. Arginine*	Arg (R)	 (Essential)
3. Histidine*	His (H)	 (Essential)

Configuration of α-amino acids : Except glycine, all the α-amino acids are optically active and have an asymmetric carbon atom (α-carbon atom). Hence, each of these amino acids can exist in two stereoisomeric forms, *i.e.*, *D* and *L*. However, all the naturally occuring amino acids belong to *L* configuration. In other words, proteins exclusively consist of *L*-amino acids. In contrast, all the sugars belong to *D*-series.

Zwitter ion and isoelectric point : Since, the —NH_2 group is basic and —COOH group is acidic, in neutral solution, it exists in an internal ionic form called a **Zwitter ion** where the proton of —COOH group is transferred to the —NH_2 group to form **inner salt,** also known as **dipolar ion.**



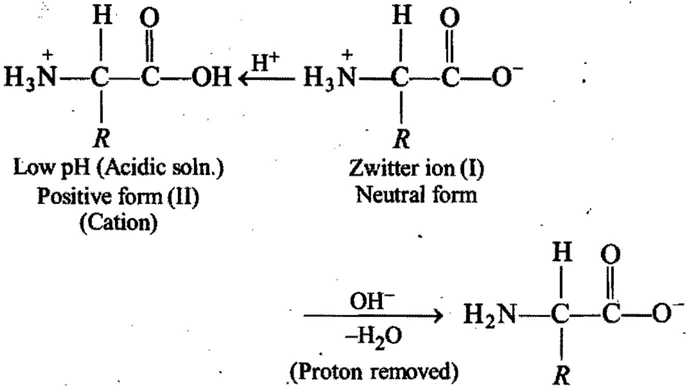
$$\underset{\alpha\text{-Amino acid}}{\mathrm{H_2\ddot{N}{-}\overset{\overset{R}{|}}{C}HCOOH}} \xrightarrow{\text{In water}} \mathrm{H_2\ddot{N}{-}\overset{\overset{R}{|}}{C}H{-}CO\bar{O}} + \overset{+}{\mathrm{H}}$$

$$\longrightarrow \mathrm{H_3\overset{+}{N}{-}\overset{\overset{R}{|}}{C}H{-}CO\bar{O}}$$

Zwitter ion
(Dipolar ion)

The Zwitter ion is dipolar, charged but overall electrically neutral and contains both a positive and negative charge.

Therefore, amino acids are high melting crystalline solids and **amphoteric in nature.** Depending on the pH of the solution, the amino acid can donate or accept proton. In the acidic medium, COO^- ion of the Zwitter ion accepts a proton to form the cation (II) while in the basic medium, $^+NH_3$ ion loses a proton to form the anion (III).



$$\mathrm{H_3\overset{+}{N}{-}\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}OH} \xleftarrow{H^+} \mathrm{H_3\overset{+}{N}{-}\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}O^-} \xrightarrow[-H_2O]{OH^-} \mathrm{H_2N{-}\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}O^-}$$

Low pH (Acidic soln.)
Positive form (II)
(Cation)

Zwitter ion (I)
Neutral form

(Proton removed)

High pH (Basic soln.)
Negative form (III)
(Anion)

Thus, $^+NH_3$ group acts as the acid while COO^- group acts as the base.

When an ionised form of amino acid is placed in an electric field, it will migrate towards the opposite electrodes. Depending on the pH of the medium, following three things may happen:

(i) In acidic solution (low pH), the positive ion moves towards cathode [exist as cation, structure (II)].

(ii) In basic solution (high pH), the negative ion moves towards anode [exist as anion, structure (III)].

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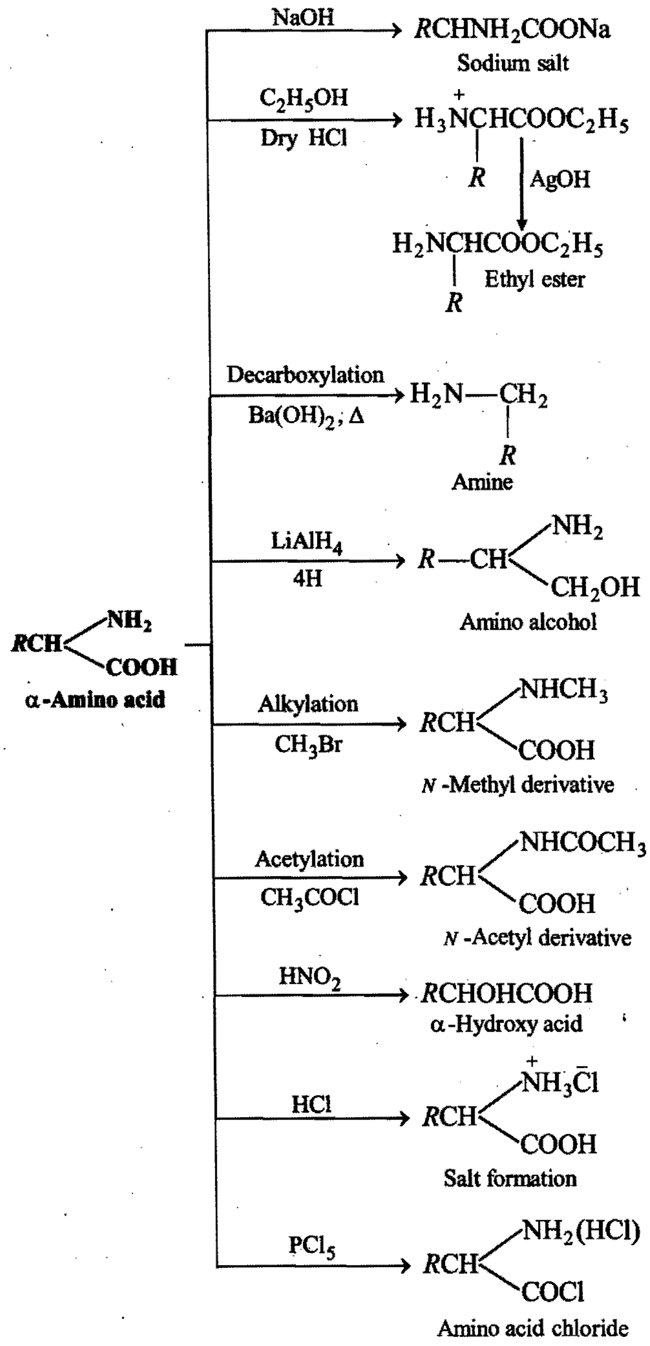
*Essential amino acids

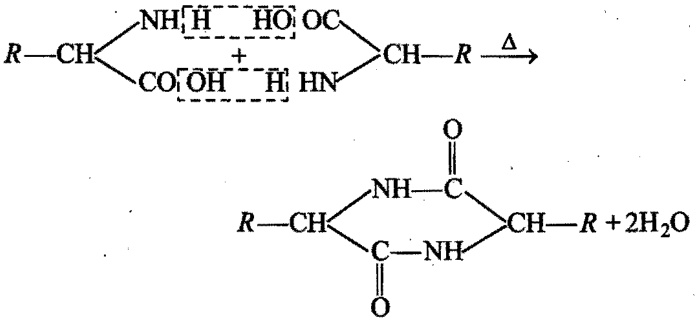
(iii) The Zwitter ion does not move towards any of the electrodes [neutral dipolar ion, structure (I)].

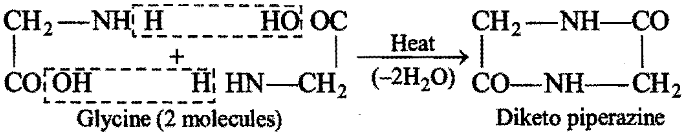
The intermediate pH at which the amino acid shows no tendency to migrate towards any of the electrodes and exists the equilibrium when placed in an electric field is known as isoelectric point. This is characteristic of a given amino acid and depends on the nature of *R*-linked to α-carbon atom.

(A) As regards the **chemical properties,** α-amino acids show the reactions of —NH_2 group, —COOH group and in which both the groups are involved. A summary of chemical properties is given below:

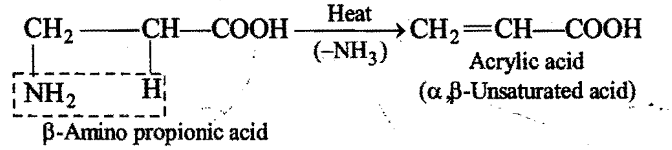


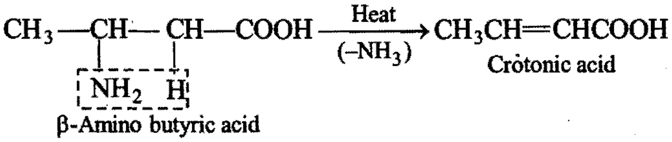
Action of heat : α-*Amino acids* lose two molecules of water and form cyclic amides.



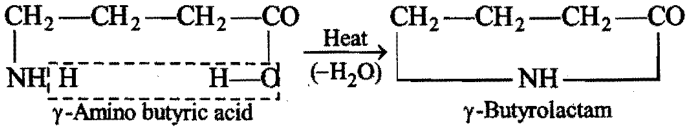


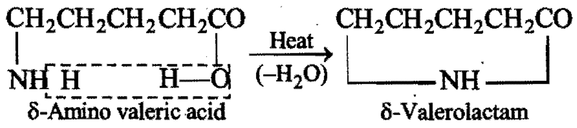
β-*Amino acids* lose a molecule of ammonia per molecule of amino acid to yield α, β-unsaturated acids.





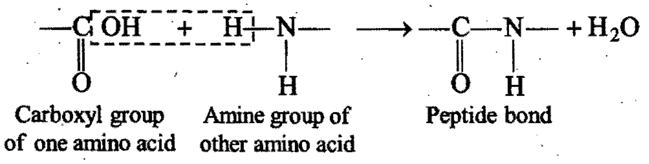
γ-*Amino acids* and δ-*amino acids* undergo intramolecular dehydration to form cyclic amides called **Lactams.**



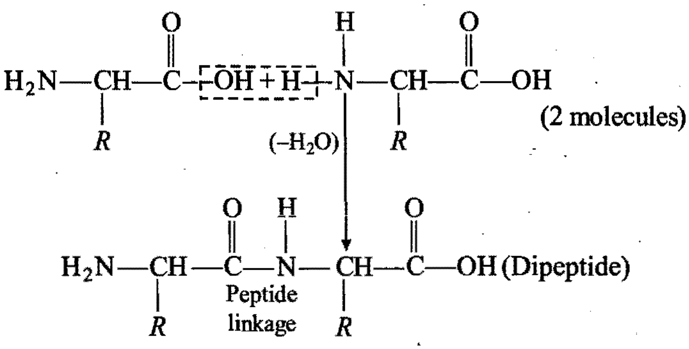


These lactams have stable five or six membered rings.

(B) Formation of proteins—Peptide bond : Proteins are formed by joining the carboxyl group of one amino acid to the α-amino group of another amino acid. **The bond formed between two amino acids by the elimination of a water molecule is called a peptide linkage or bond.** The peptide bond is simply another name for amide bond.

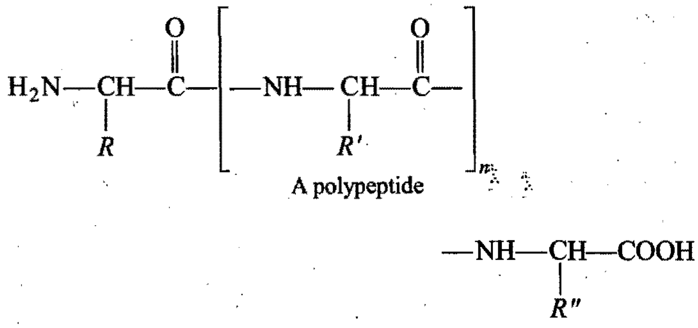


The product formed by linking amino acid molecules through peptide linkages, —CO—NH—, is called a **peptide.** Peptides are further designated as di, tri, tetra or penta peptides accordingly as they contain two, three, four or five amino acid molecules, same or different, joined together in the following fashions.



$$H_2N-\underset{R}{CH}-\overset{O}{\overset{\|}{C}}-OH+H-\overset{H}{N}-\underset{R}{CH}-\overset{O}{\overset{\|}{C}}-OH \text{ (2 molecules)} \xrightarrow{(-H_2O)} H_2N-\underset{R}{CH}-\underbrace{\overset{O}{\overset{\|}{C}}-\overset{H}{N}}_{\text{Peptide linkage}}-\underset{R}{CH}-\overset{O}{\overset{\|}{C}}-OH \text{ (Dipeptide)}$$

When the number of amino acid molecules is large, the product is termed polypeptide which may be represented as,



$$H_2N-\underset{R}{CH}-\overset{O}{\overset{\|}{C}}-\left[-NH-\underset{R'}{CH}-\overset{O}{\overset{\|}{C}}-\right]_n-NH-\underset{R''}{CH}-COOH$$

Depending upon the number of amino acids present, the peptides have been classified as:

(i) Oligopeptides — Contain 2 to 9 amino acids.

(ii) Polypeptides — Contain 10 to 100 amino acids.

(iii) Proteins — Contain more than 100 amino acids.

The formation of a protein linking together different amino acids is not a random process. Each molecule of a given protein has the same sequence of the amino acids along its polypeptide chain. Haemoglobin consists of 574 amino acid units in its molecule in a definite sequence. When only one specific amino acid in the sequence is changed, it becomes a defective haemoglobin which loses its specific property of carrying oxygen in blood stream and results in a disease called *sickle cell anaemia.*

Normal haemoglobin,

—Val—His—Leu—Thr—Pro—**Glu**—Glu—Lys—

Sickle cell haemoglobin,

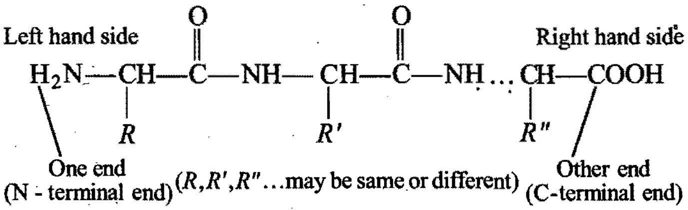
—Val—His—Leu—Thr—Pro—**Val**—Glu—Lys—

Composition of proteins : Composition of a protein varies with source. An approximate composition is as follows:

Carbon 50–53%; hydrogen 6–7%; oxygen 23–25%; nitrogen 16–17%; sulphur about 1%. Other elements may also be present, *e.g.*, phosphorus (in nucleoproteins); iodine (in thyroid proteins) and iron (in haemoglobin).

Structure of proteins : The structure of proteins is very complex. Their complete structure may be studied under three headings, *i.e.*, primary, secondary and tertiary.

1. Primary structure of proteins: The primary structure of a protein refers to the number and sequence of the amino acids in its polypeptide chains (discussed in the formation of proteins). The primary structure is represented beginning with the amino acid whose amino group is free (the N-terminal end) and it forms the one end of the chain. Free carboxyl group (C-terminal end) forms the other end of the chain.



$$H_2N-\underset{R}{CH}-\overset{O}{\overset{\|}{C}}-NH-\underset{R'}{CH}-\overset{O}{\overset{\|}{C}}-NH\ldots\underset{R''}{CH}-COOH$$

Side chains may have basic groups or acidic groups as —NH_2 in lysine and —COOH in aspartic acid. Because of these acidic and basic side chains, there are positively and negatively charged centres. Though the peptide linkage is stable, the reactivity is due to these charged centres in the side chains.

The primary structure of a protein is usually determined by its successive hydrolysis with mineral acids or enzymes into various products having decreasing molecular mass as shown below:

Proteins ⟶ Proteoses ⟶ Peptones ⟶ Polypeptides ⟶ Simple peptides ⟶ α-Amino acids

The first ever primary structure of a protein, *i.e.*, **Insulin** was determined by the British Chemist, **Frederic Sanger** (awarded Nobel Prize in 1963). Since, then, the primary structures of so many different proteins have been determined.

Primary structure tells us nothing about the shape or conformation of the molecule. Most of the bonds in protein molecules being single bonds can assume infinite number of shapes due to free rotation about single bonds. However, it has been confirmed that each protein has only a single three dimensional conformation.

2. Secondary structure of proteins: The arrangement (fixed configuration) of polypeptide chains assumed as a result of hydrogen bonding is called the secondary structure of proteins. It gives information:

(a) about the manner in which the protein chain is folded and bent;

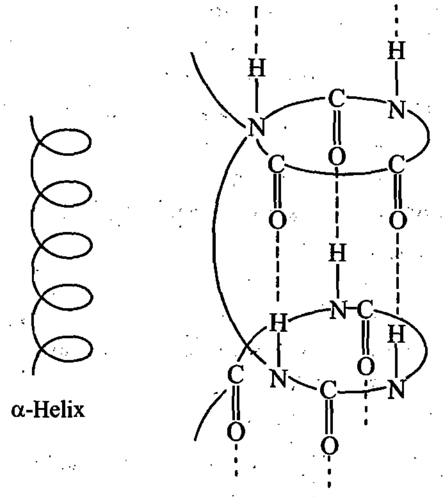
(b) about the nature of the bonds which stabilize this structure.

Secondary structure of proteins is mainly of two types depending upon the size of the R-groups.

(i) α-Helix: This structure is formed when the chain of α-amino acids coils as a right handed screw (called α-helix) because of the formation of **intramolecular hydrogen bonding** between amide groups of the same peptide chain, *i. e.*, NH group in one unit is linked to carbonyl oxygen of the fourth unit by hydrogen bonding. This hydrogen bonding between different units is responsible for holding helix in a stable position. The side chains of these units project outward from the coiled backbone.

The α-helix is also known as 3.6_{13} helix, since each turn of the helix has approximately 3.6 amino acids and a 13 membered ring is formed by H-bonding. The pitch or the distance between two successive turns is 54 pm.

Such proteins are elastic, *i.e.*, they can be stretched. On stretching weak hydrogen bonds break up and the peptide chain acts like a spring. The hydrogen bonds are reformed on releasing the tension. Proteins such as *myosin* in nucleus and *keratin* in hair, wool, nails, claws, horns, feathers and dead outer layers of skin cells have α-helix structure **(Fig. 15.1).**



H-Bonds in α-Helix

Fig. 15.1 α-Helix structure

(ii) β-pleated sheet : A different type of secondary structure is possible when polypeptide chains are arranged side by side in a zig-zag manner with alternate R-groups on the same side. The chains are held together by a very large number of hydrogen bonds between C=O and NH of different chains. Thus, the neighbouring peptides chains are bonded together by intermolecular H-bond resulting in the formation of a flat sheet. These sheets can slide over each other to form a three dimensional structure called a β-pleated (folded) sheet. The silk protein fibroin has a β-pleated structure.

The **α-helix** type structure is assumed if R-groups are larger whereas **β-pleated sheet** type structure **(Fig. 15.2)** generally exists in cases if R-groups are smaller.

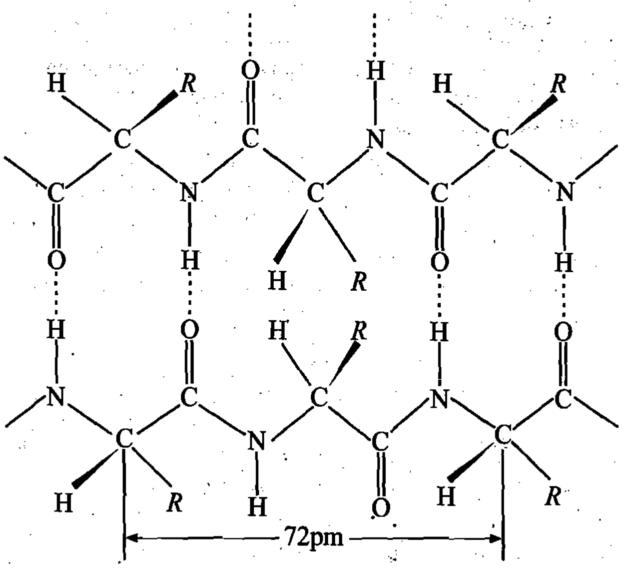


Fig. 15.2 β-Pleated sheet structure

3. Tertiary structure of proteins: The tertiary structure of proteins refers to the definite geometric pattern in which the entire protein molecule folds up in the three dimensional space to produce a specific shape (or compact form). Further folding, twisting and bending of secondary structure is called the tertiary structure of proteins. The two important **tertiary structures of proteins are fibrous structure and globular structure.** The fibrous proteins, *e.g.*, silk, collagen and keratins have large helical content and have rod like rigid shape insoluble in water. *At normal* pH *and temperature, each protein will take a shape (tertiary structure) that is energetically most stable.* This shape is specific to a given amino acid sequence and is called the **native state of the protein.** The tertiary structure of a protein is controlled by several different kinds of interactions that serve to hold the folded segments of the chain in place. These interactions may be any of the given below :

(i) Intramolecular hydrogen bonding,
(ii) Ionic interaction or salt bridge,
(iii) van der Waals' interaction or disulphide (S—S) bonds,
(iv) Hydrophobic (water hating side chains) interaction.

An example of disulphide bridge is found in **insulin** which consists of two polypeptide chains.

Perutz and Kendrew shared the 1962 Nobel Prize in Chemistry for determining the **tertiary structure of haemoglobin** and **myoglobin** through X-ray diffraction studies.

Globular proteins possess **tertiary structure.** In general, globular proteins are very tightly folded into a compact spherical form.

Characteristic differences between globular and fibrous proteins are given ahead:

Globular Proteins	Fibrous Proteins
1. These are cross-linked proteins and are condensation product of acidic and basic amino acids.	These are linear condensation polymer.
2. These are soluble in water, mineral acids and bases.	These are insoluble in water but soluble in strong acids and bases.
3. These proteins have three dimensional folded structure. These are stabilised by internal hydrogen bonding.	These are linear polymers held together by intermolecular hydrogen bonds.

Proteins can also be classified on the basis of their **functions.**

Protein	Function	Examples
1. Enzymes	Biological catalysts, vital to all living systems.	Trypsin, pepsin.
2. Structural proteins	Proteins that hold living systems together.	Collagen.
3. Hormones	Act as messengers.	Insulin.
4. Transport proteins	Carry ions or molecules from one place to another in the living system.	Haemoglobin.
5. Protective proteins (antibiotics)	Destroy any foreign substance released into the living system.	Gamma globulin.
6. Toxins	Poisonous in nature.	Snake venom.

Tests of proteins :

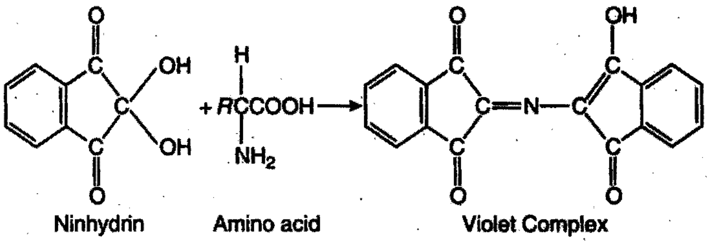
(i) Biuret test : On adding a dilute solution of copper sulphate to alkaline solution of protein, a violet colour is developed. This test is due to the presence of peptide (—CO—NH—) linkage.

(ii) Xanthoproteic test : Some proteins give yellow colour with concentrated nitric acid (formation of yellow stains on fingers while working with nitric acid in laboratory). The formation of yellow colour is due to reaction of nitric acid with benzenoid structures. Thus, when a protein solution is warmed with nitric acid a yellow colour may be developed which turns orange on addition of NH_4OH solution.

(iii) Millon's test : When millon's reagent (mercurous and mercuric nitrate in nitric acid) is added to a protein solution, a white precipitate which turns brick red on heating, may be formed. This test is given by proteins which yield tyrosine on hydrolysis. This is due to presence of phenolic group.

(iv) Ninhydrin test : **This test is given by all proteins.** When a protein is boiled with a dilute solution of ninhydrin, a violet colour is produced.

(v) Nitroprusside test : Proteins containing —SH group give this test. When sodium nitroprusside solution is added to proteins having —SH group, a violet colour is developed.



(vi) Molisch's test : This test is given by those proteins which contain carbohydrate residue. On adding a few drops of alcoholic solution of α-naphthol and concentrated sulphuric acid to the protein solution, a violet ring is formed.

(vii) Hopkins-Cole test : On adding concentrated sulphuric acid down the side containing a solution of protein and glyoxalic acid, a violet colour is developed.

Uses of proteins : (i) As food : Proteins constitute as essential part of our food. Meat, eggs, fish, cheese provide proteins to human beings.

(ii) In textile : Casein (a milk protein) is used in the manufacture of artificial wool and silk.

(iii) In the manufacture of amino acids : Amino acids, needed for medicinal use and feeding experiments, are prepared by hydrolysis of proteins.

(iv) In industry : Gelatin (protein) is used in food products, capsules and photographic plates. Glue (protein) is used as adhesive and in sizing paper. Leather is obtained by tanning the proteins of animal hides.

(v) In controlling body processes : Haemoglobin present in blood is responsible for carrying oxygen and carbon dioxide. Hormones (proteins) control various body processes.

(vi) As enzymes : Reactions in living systems always occur with the aid of substances called enzymes. **Enzymes are proteins produced by living systems and catalyse specific biological reactions.**

The important enzymes are :

Enzymes	Reaction catalysed
1. Urease	Urea $\longrightarrow CO_2 + NH_3$
2. Invertase	Sucrose $\longrightarrow$ Glucose + Fructose
3. Maltase	Maltose $\longrightarrow$ 2Glucose
4. Amylase	Starch $\longrightarrow$ n Glucose
5. Pepsin	Proteins $\rightarrow$ Polypeptides $\rightarrow$ α-Amino acids
6. Trypsin	Polypeptides $\longrightarrow$ α-Amino acids
7. Carbonic anhydrase	$H_2CO_3 \longrightarrow H_2O + CO_2$
8. Nuclease	DNA, RNA $\longrightarrow$ Nucleotides
9. Lactase	Lactose $\longrightarrow$ Glucose + Galactose
10. Emulsin	Cellulose $\longrightarrow$ nGlucose
11. RNA Polymerase	Ribo nucleotide triphosphates $\longrightarrow$ RNA
12. DNA Polymerase	Deoxy nucleotide triphosphate $\longrightarrow$ DNA

15.8 NUCLEIC ACIDS

In every living cell, there are found nucleoproteins, which are made up of proteins and natural polymers and of great biological importance, are called nucleic acids. Nucleic acids are complex compounds of carbon, hydrogen, oxygen, nitrogen and phosphorus. They play an essential role in transmission of the hereditary characteristics and biosynthesis of proteins. The genetic information coded in nucleic acids programmes the structure of all proteins including enzymes and thereby they control all metabolic activities of living organisms.

Two types of nucleic acids are found in biological systems, these are:

(i) Deoxyribonucleic acid (DNA) and

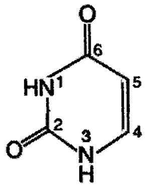
(ii) Ribonucleic acid (RNA)

Nucleic acids like proteins and carbohydrates are biopolymers. They are also called **polynucleotides** and the simple units that make up the nucleic acid are called **nucleotides.** Nucleotides are themselves composed of following three simple molecules:

1. A nitrogenous base : These are heterocyclic organic compounds having two or more nitrogen atoms in ring skeleton. They are called bases because the lone pairs of electrons on the nitrogen atoms make them as Lewis bases. Their structures are given below:

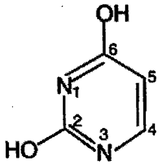
(a) Pyrimidine derivatives :

(i)

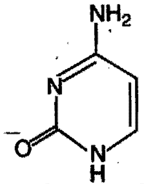


Uracil (U)
(RNA)

or

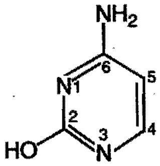


(ii)



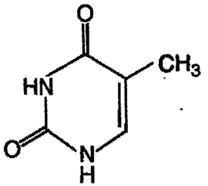
Cytosine (C)
(RNA)
(DNA)

or



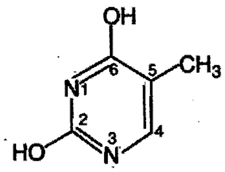
Cytosine (C)

(iii)

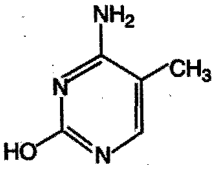


Thymine (T)
(DNA)

or

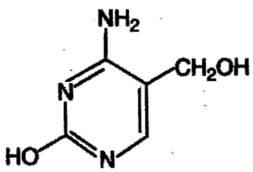


(iv)



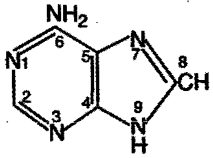
5-Methyl cytosine

;



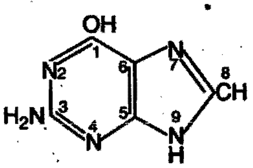
5-Hydroxy methyl cytosine

(b) Purine derivatives :



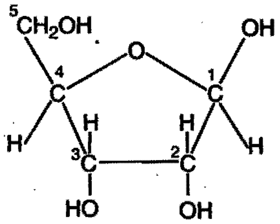
Adenine (A)
(DNA)
(RNA)

;



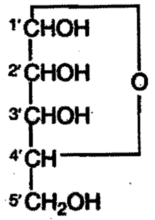
Guanine (G)
(DNA)
(RNA)

2. A five-carbon sugar (pentose) : In RNA, the sugar is β-*D*-ribose whereas in DNA, the sugar is β-*D*-2-deoxyribose.

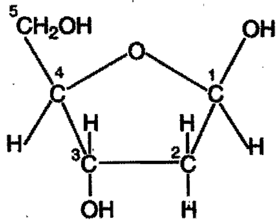


D-Ribose

or

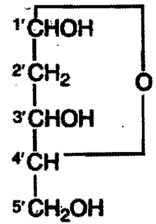


D-Ribofuranose



D-2-Deoxyribose

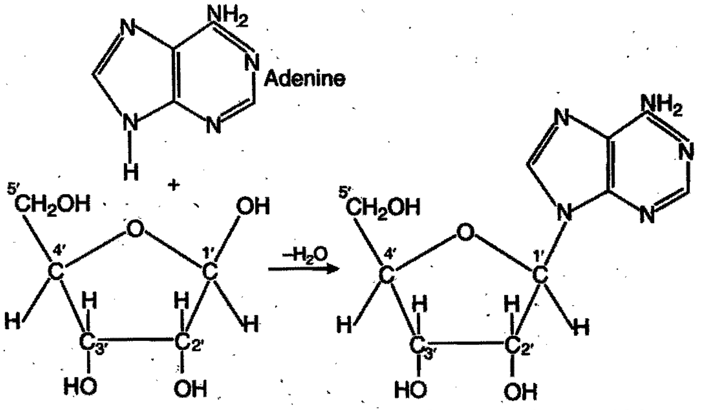
or



2-Deoxy-(*D*) ribofuranose

Both differ only at carbon atom 2′ in the ring.

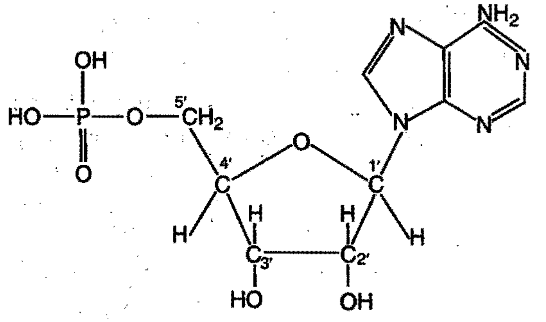
3. Phosphoric acid, H_3PO_4 : Phosphoric acid forms esters to —OH groups of the sugars to bind nucleotide segments together.



A molecule called **nucleoside** is formed by condensing a molecule of the nitrogenous base with the appropriate pentose (*i.e.*, Base + Sugar). During the formation of nucleosides, it is position-1-of pyrimidine base or position-9-of purine base which is attached to C_1' of the sugar (ribose or deoxy ribose) by a β-linkage.

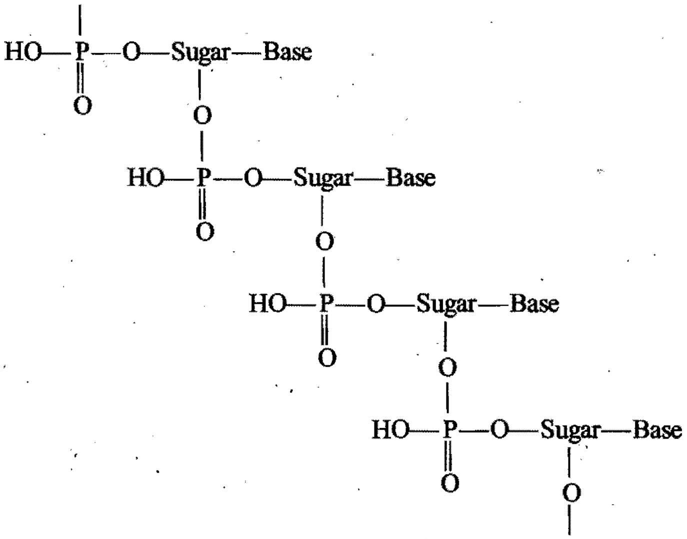
A nucleotide results when the nucleoside combined with phosphoric acid mainly at carbon 5′ of the pentose (*i.e.*, Base + Sugar + Phosphoric acid). Hence, nucleotides are nucleoside monophosphate.

It is also shown experimentally that in nucleotide structures, the point of attachment with phosphoric acid may be 2′, 3′ or 5′ in the ribose molecule and 3′ or 5′ in the deoxyribose molecule to the nucleoside structures.

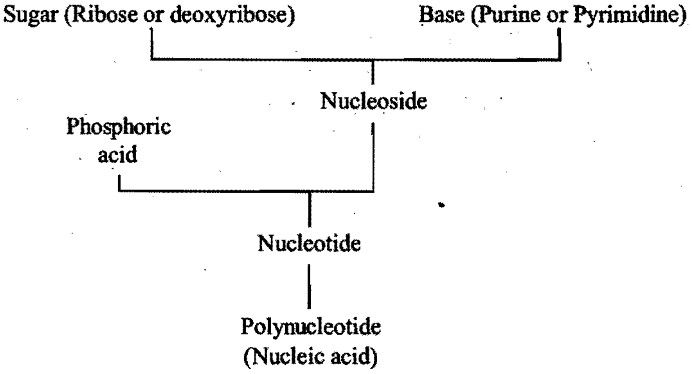


Nucleotide—Adenosine 5′-phosphoric acid

Thus, nucleotide is the building block of both DNA and RNA. The nucleic acids are condensation polymers of the nucleotide monomers and are formed by the creation of an ester linkage from phosphoric residue on one nucleotide to the hydroxy group on carbon 3′ in the pentose of the second nucleotide. The result is a very long chain possessing upto a billion or so nucleotides units in DNA.



Thus, the formation of a nucleic acid can be summarised in the following general way:



Nitrogenous bases, combining with pentose sugars and a phosphate group, form eight types of nucleotide molecules, four for DNA and four for RNA. These are listed as follows:

RNA nucleotides

Base	+ Ribose → (Nucleoside)	+ Phosphoric acid	→ Nucleotide
1. Adenine	+ Ribose → (Adenosine)	+ Phosphoric acid	→ Adenylic acid
2. Guanine	+ Ribose → (Guanosine)	+ Phosphoric acid	→ Guanylic acid
3. Cytosine	+ Ribose → (Cytidine)	+ Phosphoric acid	→ Cytidylic acid
4. Uracil	+ Ribose → (Uridine)	+ Phosphoric acid	→ Uridylic acid

DNA nucleotides

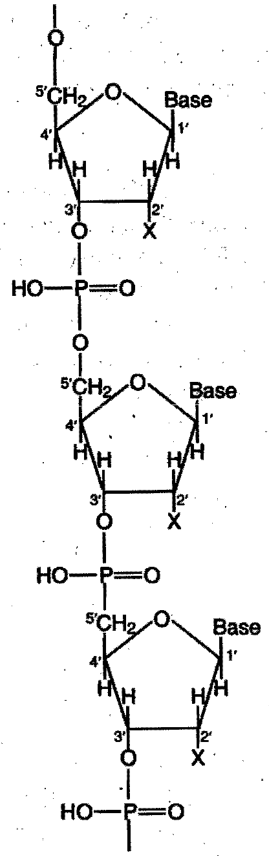
1. Adenine + Deoxyribose sugar + Phosphate → Adenosine phosphate
2. Guanine + Deoxyribose sugar + Phosphate → Guanosine phosphate
3. Cytosine + Deoxyribose sugar + Phosphate → Cytosine phosphate
4. Thymine + Deoxyribose sugar + Phosphate → Thymidine phosphate

Structure of Nucleic Acids

(i) Primary Structure : Nucleic acids are polynucleotides, *i.e.*, they are formed by the combination of thousands of molecules of nucleotides with the elimination of water molecules of RNA (X =OH) and DNA (X =H)

Base (Different purine and pyrimidine bases)

Thus, the backbone of nucleic acid consists of alternating sugar-phosphate residues, each sugar on this backbone is further connected to one of the four nitrogenous bases. Thus, the sequence in which the four nitrogen bases are attached to the sugar-phosphate backbone of a nucleotide chain is called the primary structure of nucleic acids.



Primary structure

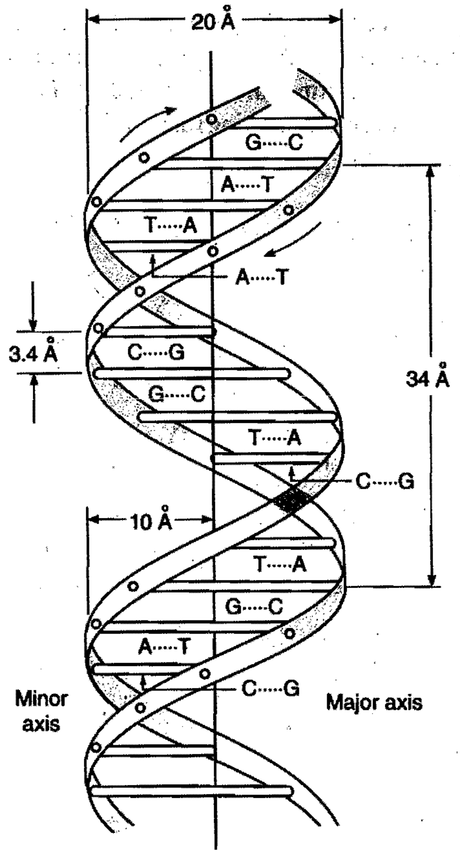
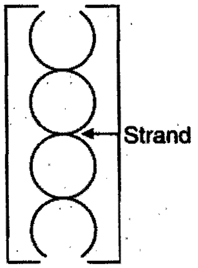
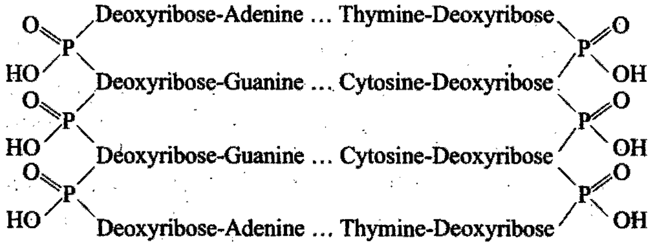


Fig. 15.3 Double helical structure of DNA (Watson and Crick)

(ii) Secondary structure : **Wilkins** (1953) from their X-ray studies showed that the DNA molecule has a helical (spiral) form and the helix contains two intertwined (become twisted) strands (extremes). Furthermore, the two chains are attached in such a manner that pyrimidines and purines bases point towards each other and its H-bonding between pair of bases that holds the helix together.



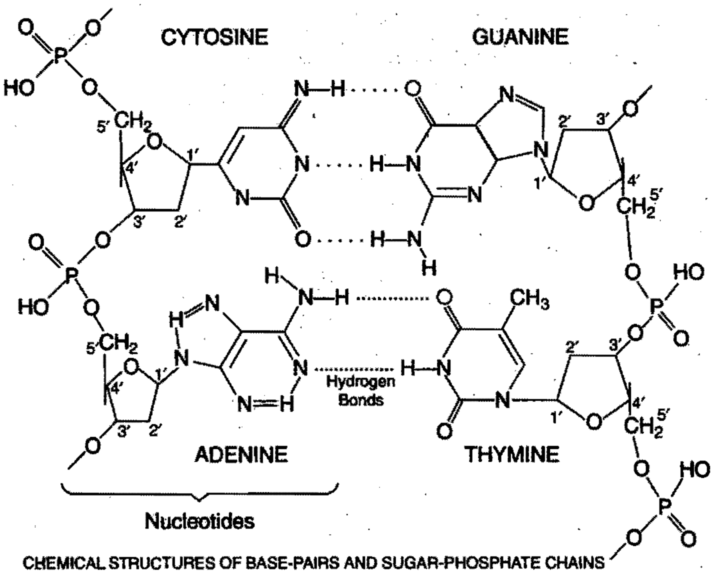
On the above basis and X-ray analysis of DNA, **J.D., Watson** and **F.H.C. Crick** (Shared Nobel Prize in 1962) proposed a three dimensional secondary structure for DNA. They suggested that the DNA molecule consists of two polynucleotide chains, twisted about a common axis, but run in opposite direction to form a right handed helix (Fig. 15.3). The two chains are joined together by specific hydrogen bonds A (Adenine) to T (Thymine) and G (Guanine) to C (Cytosine). The amount (in moles) of adenine was equal to that of thymine (A = T) and that of cytosine was equal to that of guanine (C = G). In other words, the total amount of purines was equal to that of pyrimidines (A + G = C + T). Approximately there are ten nucleotide units in one turn of each strand and the backbone (consisting of 2-deoxyribose and phosphate units) of each nucleotide lies outside the helix of each strand, while the nitrogen bases in each strand lie in the centre of the helix. The diameter of the helix is about 20 Å. The spacing between adjacent pairs is 3.4 Å and the distance between any two turns of the helix is 34 Å.



Double Helix Structure of DNA : The hydrogen bonds are formed between the bases (shown by dotted lines). Because of sizes and geometries of the bases, the only possible pairing in DNA are between G (Guanine) and C (Cytosine) through three H-bonds and between A (Adenosine) and T (Thymine) through two H-bonds (Fig. 15.4). Therefore, GC base pair has more stability as compared to AT base pair. Corresponding to the structure of these bases, the above combination is energetically most favoured.

The other combination of bases are energetically less favoured and hence, do not occur in normal DNA. This means that the two strands of DNA are complimentary to each other. In addition to hydrogen bonds, other forces, *e.g.*, hydrophobic interactions between the bases are also, responsible for stability and maintenance of double helix.

DNA helices can be right handed as well as left handed. The β-conformation of DNA having the right handed helices is the most stable. On heating, the two strands of DNA separate from each other (known as melting) and on cooling these again hybridize (annealing).



CHEMICAL STRUCTURES OF BASE-PAIRS AND SUGAR-PHOSPHATE CHAINS

Fig. 15.4. DNA molecule showing arrangement of base pairs, sugars and phosphoric acid

As regards the secondary structure of RNA, helices are present but only single stranded.

15.9 FUNCTIONS OF NUCLEIC ACIDS

Nucleic acids have two important functions:

1. Replication,
2. Protein synthesis.

1. Replication : The process by which a single DNA molecule produces two identical copies of itself is called replication or cell division. So, DNA has this unique property of duplicating itself. Replication of DNA is an enzyme catalyzed process. The genetic information for the cell is coded in the sequence of bases Adenine (A), Thymine (T), Guanine (G) and Cytosine (C) in the DNA molecule. During division of the cell, DNA molecules replicate and produce exact copies of themselves. Each daughter cell has DNA molecules identical to that of the parent cell. Actually it begins by partial unwinding of the double helix through breaking of the H-bonds between pairs of bases leading to the formation of two isolated strands and each strand serves as a template of pattern for the synthesis of a new strand in the cell environment. Because of the base pairing principle, each new strand in complimentary to its old template strand and DNA replication takes place only in 3′ → 5′ direction. In this way hereditary effects are transmitted from one cell to the other.

2. Protein synthesis : Another important function of DNA is the synthesis of all the proteins present in a cell. The DNA molecules in the cell nucleus hold the code for the protein synthesis. The genetic information is coded in DNA in the form of specific sequence of bases. The DNA directed synthesis of protein occurs in the following two steps:

(i) Transcription,
(ii) Translation.

(i) Transcription : It involves copying of DNA base sequence into a RNA molecule called the messenger RNA (mRNA). The bases of mRNA are complementary to those of the DNA strand. The new chains contain ribose instead of deoxyribose and the base sequence is different which is determined by DNA. Messenger RNA contains only four bases, *i.e.*, Adenine (A), Guanine (G), Cytosine (C) and Uracil (U). DNA molecules contain the four bases, *i.e.*, Adenine (A), Guanine (G), Cytosine (C) and Thymine (T). The complementary base pairs are as follows:

DNA	mRNA
Adenine (A)	Uracil (U)
Guanine (G)	Cytosine (C)
Cytosine (C)	Guanine (G)
Thymine (T)	Adenine (A)

Opposite each Adenine (A) of DNA, there appears on RNA a Uracil (U); opposite Guanine (G) is Cytosine (C); opposite Cytosine (C) is Guanine (G) and opposite Thymine is Adenine. Thus, AATCAGTT on DNA becomes UUAGUCAA on RNA.

After transcription mRNA moves from the nucleus of the cell to a ribosome in the cytoplasm where it serves as template for the protein synthesis.

(ii) Translation : The mRNA directs protein synthesis in the cytoplasm of the cell with the help of ribosome RNA (rRNA) and transfer RNA (tRNA). This process is called translation.

The sequence of bases in mRNA are read in a serial order in groups of three at a time. Each triplet of nucleotides (having a specific sequence of bases) is known as **codon.** Each codon specifies one amino acid. Further since, there are four bases, therefore, $4^3 = 64$ triplets or codons are possible. Out of these 61 triplets code for specific amino acids, while the remaining three (UUA, UGA or UAG) are known to code for chain termination or stop codons. Since, there are only 20-odd amino acids, so that more than one codon can be called the same amino acid. For example, four triplets (*i.e.*, GGU, GGC, GGA, GGG) code for glycine and two triplets (*i.e.*, UUU and UUC) code for phenyl alanine. Similarly, valine has four, leucine has six, lysine has two and tryptophan has only one triplet.

The DNA sequence that codes for a specific protein is called a Gene and thus every protein in a cell has a corresponding gene. The relation between the nucleotide triplets and the amino acids is called the **Genetic Code.** Nirenberg, Hollay and Khorana presented the Genetic Code for which they were awarded Nobel Prize in 1968.

The role of DNA and RNA in the synthesis of protein can be shown by following diagram:

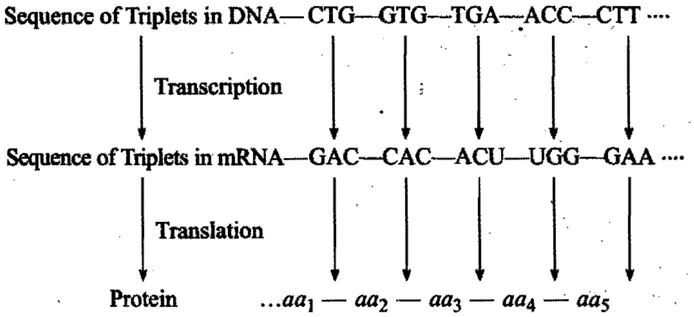


Fig. 15.5 DNA-mediated synthesis of proteins

Mutation : A mutation is a chemical or physical change that alters the sequence of bases in DNA strands that can lead to the synthesis of proteins with altered α-amino acid sequence. Anything that causes mutation is called mutagen. A mutation results from X-ray or ultraviolet light, ionisation radiations, chemicals or viruses. The changes in sequence of bases in DNA are repaired automatically by special enzymes in the cell. If it is not, the protein produced has no biological activity and the cell dies.

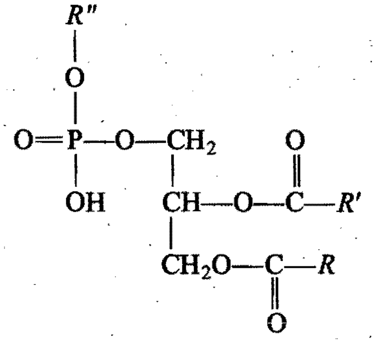
These mutations often prove harmful and give rise to symptoms that cause diseases. Sickle cell anaemia is one such example. Such disease is passed on from one generation to the next generation.

15.10 LIPIDS

Lipids are constituents of plants and tissues which are insoluble in water but soluble in organic solvents such as chloroform, carbon tetrachloride, ether or benzene. They include a large variety of compounds of varying structures such as oils and fats; phospholipids, steroids, etc. Lipids are mainly made of carbon, hydrogen and oxygen. The number of oxygen atoms in a lipid molecule is always small as compared to the number of carbon atoms. Sometimes, small amounts of phosphorus, nitrogen and sulphur are also present. They have a major portion of their structure like a hydrocarbon (aliphatic or fused carbon rings). In the lipids (fats), most of the energy is contained in the long hydrocarbon chains of fatty acids. **Lipids serve as energy reserve** for use in metabolism and as a major structural material in cell membranes for regulating the activities of cell and tissues.

Simple lipids are triesters of glycerol with long chain monocarboxylic acids which can be saturated or unsaturated. These are generally called triglycerides of fats and oils.

Another very important class of lipids is the **phospholipids.** These are **polar lipids** and like the fats, are **esters of glycerol.** In this case, however, only two fatty acid molecules are esterified to glycerol, at the first and second carbon atom. The remaining end position of the glycerol is esterified to a molecule of phosphoric acid, which in turn is also esterified to another alcohol. This gives a general structure.



This structure gives the phospholipids good emulsifying and membrane forming properties and hence they are used as good surfactants.

Cell membranes are composed of phospholipids and proteins in about equal proportion. Phospholipids facilitate the transport of ions and molecules in and out of the cell and regulate the concentration of molecules and ions within the cell. They provide structural support for certain proteins.

The common examples of phospholipids are **lecithins** and **cephalines** which are found in brain, nerve cells and liver of animals. These are also found in egg yolks, yeast, soyabeans and other foods.

Lecithin contains a quaternary nitrogen whereas cephaline contains only primary nitrogen.

The above mentioned lipids are mainly straight chain compounds. There is a third class of lipids which are not straight chain compounds. They are called **Sterols.** The sterols are composed of fused hydrocarbon rings and a long hydrocarbon side chain. **Cholesterol** is most important compound of this class and is found in animals only. It exists either free or as ester with a fatty acid. Cholesterol is also the precursor of hormones. Cholesterol and its esters are insoluble in water. So, they are deposited in the arteries and veins if the blood cholesterol rises. This leads to high blood pressure and heart diseases. Cholesterol is a part of animal cell membrane and is used to synthesise steroid hormones, vitamin-D and bile salts.

Waxes : These are simple lipids and they are esters of long chain fatty acids and monohydric alcohols. General formula of waxes can be given as $RCOOR'$ **(See sec. 13.11).**

Waxes are found as protective layers on fruits, leaves and animals. They are insoluble in water, flexible and non-reactive.

Hormones : These are the chemicals which are secreted by ductless glands and transported to different parts of the body by the blood stream where they control different physiological actions of the body.

The word hormone is derived from Greek language, which means to gear up or to excite. Hormones control cell and tissue growth, heart beat, blood pressure, secretion of digestive enzymes, kidney function, the reproductive system and lactation, etc.

In mammals, the secretion of the hormones is controlled by anterior lobe of the pituitary gland located at the base of brain. These hormones are then carried to other gland such as adrenal, cortex and sex glands to stimulate the production of other hormones.

Classification of hormones : On the basis of structure and composition, hormones are classified into following types:

	Name of Hormones	Source (organ)	Function
	Steroid Hormones		
(a)	**Adrenal cortex hormones**		
	(i) Cortisone or Aldosterone	Adrenal cortex	Controls mineral balance in the body and metabolism of fat, carbohydrates and protein.
(b)	**Sex hormones** **Androgens**		
	(ii) Testosterone	Testes	Regulates and stimulates male sex organs.
	Gestogens		
	(iii) Progesterone	Corpus luteum	It controls the development and maintenance of pregnancy.
	Estrogens		
	(iv) Estrogens, Estrone or Estradiol	Ovary	It maintains the normal function of female sex organs.
(c)	**Amine hormones**		
	(v) Thyroxine	Thyroid gland	It regulates metabolism of lipids, proteins and carbohydrates.
	(vi) Epinephrine or Adrenaline	Adrenal medulla	It controls blood pressure and increases pulse rate. It helps to release fatty acids from fat and glucose from liver glycogen.
(d)	**Peptide hormones**		
	(vii) Insulin	Pancreas	Maintains glucose level in blood and glucose metabolism.
	(viii) Oxytocin	Posterior pituitary gland	It helps to release milk from mammary glands. It also helps to contract uterus after the child birth.
	(ix) Vasopressin	Pituitary glands	It regulates reabsorption of water in the kidney.
	(x) Angiotensin-II	Blood plasma of persons with high blood pressure	Potent vasoconstrictor, *i.e.*, contracts the blood vessels.

15.11 OUR FOOD

The substances which supply the raw materials for various life processes along with energy as to control body functions and maintain its growth are known as food. Food is essential for human beings. Without food life is not possible. Food is required for energy, growth and repair of old parts or tissues.

The food is comprised of the compounds namely : carbohydrates, proteins, lipids, mineral salts, vitamins and water. In addition to these, a proper diet also includes non-digestible roughage. Roughage increases the bulk of the food so that movement of food down the alimentary canal is made easy.

The food, which we take, can broadly be divided into following groups on the basis of their functions:

(i) Energy yielding food — Carbohydrates, fats.
(ii) Body building food — Proteins, minerals.
(iii) Protective food — Vitamins, minerals.

Before discussing the importance of various constituents of food, it is essential to learn about cellular energetics and digestion.

Cellular energetics : Only those chemical reactions occur spontaneously in which the free energy (ΔG) has negative value. The reactions for catabolism are accompanied by negative ΔG, *i.e.*, energy is released. However, a large number of reactions for anabolism are not spontaneous as they require energy, *i.e.*, ΔG is positive.

$$\text{Anabolism; } \Delta G_1 > 0$$

$$\text{Catabolism; } \Delta G_2 < 0$$

In living system, both the reactions occur simultaneously and free energy released during catabolism is used for anabolism. Such reactions are called coupled reactions. For coupled reactions,

$$\Delta G_1 + \Delta G_2 < 0$$

Both catabolic and anabolic reactions proceed through the same intermediate, adenosine triphosphate (ATP), which is referred universal **energy currency of the cell.** The energy produced in catabolic reactions is transferred to ATP and is then carried to various places in the cell where it is released. During anabolic reactions, an ATP molecule releases energy when it is hydrolysed to ADP and AMP.

$$\text{ATP} + H_2O \longrightarrow \underset{\text{(Adenosine diphosphate)}}{\text{ADP}} + PO_4^{3-} + \text{Energy}$$

$$\text{ADP} + H_2O \longrightarrow \underset{\text{(Adenosine monophosphate)}}{\text{AMP}} + PO_4^{3-} + \text{Energy}$$

The energy of ATP is renewed when ADP and AMP are converted into ATP.

$$\text{ADP} + PO_4^{3-} + \text{Energy (provided by food)} \longrightarrow \text{ATP}$$

Digestion : Digestion of food can be summarized in the following form:

1. $$\text{Polysaccharides} \xrightarrow[\left(\begin{array}{c}\text{Saliva (mouth);}\\ \text{Pancreatic juice}\\ \text{(Intestine)}\end{array}\right)]{\text{Amylase}} \underset{\text{(Maltose, etc.)}}{\text{Disaccharides}}$$

$$\xrightarrow[\text{(Intestine)}]{\text{Maltase}} \text{Glucose}$$

2. $$\text{Proteins} \xrightarrow[\text{(Stomach)}]{\text{Pepsin/HCl}} \text{Proteases and Peptones}$$

$$\xrightarrow[\left(\begin{array}{c}\text{Chemotrypsin}\\ \text{Pancreatic juice}\\ \text{(Intestine)}\end{array}\right)]{\text{Trypsin}} \text{Peptides} \xrightarrow[\text{(Intestine)}]{\text{Peptidases}} \text{Amino acids}$$

3. $$\text{Fats} \xrightarrow[\text{(From liver)}]{\text{Bile salts}} \text{Emulsified fats}$$

$$\xrightarrow[\left(\begin{array}{c}\text{Pancreatic and}\\ \text{intestine juice}\end{array}\right)]{\text{Lipases}} \text{Fatty acids} + \text{Glycerol}$$

After digestion, there are present glucose, amino acids, fatty acids along with vitamins and mineral salts. Undigested food and secretions are pushed forward into the reaction from where these are excreted.

COMPONENTS OF FOOD

The various components of our food are as follows:

1. Carbohydrates : These are the compounds of carbon, hydrogen and oxygen. These are energy yielding substances. One gram of carbohydrates yields 4.0 kilocalories. Potatoes, rice, corn and other cereal grains are good sources of carbohydrates. Milk contains lactose, a disaccharide. Sucrose, another disaccharide is obtained from sugarcane and sugar-beet. A number of polysaccharides common in our diet are not nourishing because there are no enzymes to digest them. Cellulose is an example of this type.

Carbohydrate metabolism is a process of converting carbohydrates present in food into monosaccharides by various enzymes during digestion. The glucose is absorbed through the walls of the small intestine into blood stream and then distributed to the other organs. Metabolism of glucose involves two processes:

(i) Glycolysis : The series of reactions that change glucose into pyruvate with the formation of ATP.

(ii) Cellular respiration : Pyruvate can be converted into ethanol, lactate or the acetyl group of the acetyl co-enzyme.

Importance (Functions) of carbohydrates :

(i) Monosaccharides play an important role in all the metabolic reactions of the body.

(ii) Glucose is oxidised in the process of respiration to yield energy.

(iii) Glucose is used in the synthesis of fats and proteins.

(iv) Ribose and deoxyribose sugars form nucleic acid, RNA and DNA.

(v) Excess of monosaccharides in the body are stored as glycogen.

2. Proteins : Proteins are required to repair the old tissues and build new ones. It is said that living beings can live for sufficiently long time without carbohydrates and fats but not without proteins. The name Protein was given by **Mulder** (1838) and was derived from Greek word Protios (meaning to take the first place). Important sources of protein are milk, cheese, eggs, corn, wheat, peas, beans, etc. Protein food also contains essential amino acids. During the process of digestion, the proteins are hydrolysed by enzymes producing amino acids which are absorbed by blood and reach the various tissues.

$$\text{Proteins} \xrightarrow[\text{Proteases}]{\text{Pepsin}} \text{Polypeptides} \xrightarrow[\text{Chemotrypsin}]{\text{Trypsin}} \text{Amino acids}$$

Amino acids have many uses in the body. They are used in the formation of new cells or repair of old cells, synthesis of other amino acids, enzymes, hormones, antibodies, etc. Unlike carbohydrates and lipids which can be stored, there are no storage molecules for amino acids. Some amino acids are metabolised to pyruvate, some to acetyl co-enzyme A and others to various intermediates in glucose metabolism and energy is obtained by their breakdown into CO_2 and H_2O.

3. Fats (Lipids) : Oils and fats are very good fuels for the biological processes in our body. Oils and fats occur widely in animal and plant kingdom. In plants, they are mainly present in seeds. Fats are present in butter, meat, vegetable oils and milk. Fats form part of all membranes and regulate the activities of the cells and tissues. Fats also act as an emulsifying agents, vitamins, hormones and regulators of metabolism. During digestion, fats are hydrolysed to fatty acids and glycerol. The fatty acids are oxidised in mitochondria of liver cells to form acetyl co-enzymes A which enters the citric acid cycle for production of ATP—The universal energy transfer agent. The energy provided by lipids is much more than provided by the metabolism of carbohydrates and proteins.

4. Water : Water is the chief solvent in the body. It is the medium for transportation and it takes part in most of the chemical reactions of the body. Approximately 70% of total body weight is due to water. A normal healthy adult will ingest and excrete about 1.5 to 3.0 litres of water per day. It is essential to maintain water balance in body.

5. Minerals : Minerals of inorganic elements required by man are sodium, potassium, chlorine, sulphur, iodine, magnesium, calcium, phosphorus and iron. Some elements like copper, zinc, cobalt, manganese, molybdenum, fluorine are required in small amounts and are called as trace elements.

Inorganic minerals are involved in various metabolic reactions of the cell and thus help in the growth and development of the cells. Ions play an important role in maintaining osmotic pressure and acid-base balance in the cells.

6. Vitamins : In addition to air, water, carbohydrates, proteins, fats and mineral salts, certain organic substances required for regulating some of the body processes and preventing certain diseases are called **vitamins.** These compounds cannot be synthesised by an organism. These vitamins are required in small amounts and deficiency of any one causes one disease or the other. Thus, vitamins are essential constituents of our diet. Several of these vitamins are known and are designated as A, B, C, D, E and so on. Many of these are now synthesised on commercial scale.

15.12 BALANCED DIET

A balanced diet is a diet which contains all the essential food constituents in proper proportion so that the need for calories, minerals, vitamins and other nutrients is adequately met with. It varies according to age and the amount of work. A balanced diet should have the following three qualities:

(i) It should be rich in various essential constituents.

(ii) It should provide just enough raw materials needed for the growth and development, repair and replacement of cells, tissus and organs of the body.

(iii) It should provide the necessary energy required by the body.

The requirements of various constituents have been determined and these are shown in the table given below:

In metabolism, we generally obtain 4.0 kilo calories of energy from one gram of carbohydrates, 4.0 kilo calories from one gram of protein and about 9.3 kilo calories from one gram of fat. It has been found that we obtain about 50% energy from carbohydrates, 35% from fats and 15% from proteins. The recommended diet for a moderately active adult is given in the following table:

Food	**Recommended amounts (g per day)**	
	Adult man	**Adult woman**
Cereals	520	440
Pulses	50	45
Meat/Fish	30	30
Egg	1	1
Milk	200	150
Fats/Oils	45	25
Sugar	35	20
Roots and tubers	60	50
Green leafy vegetables	40	100
Other vegetables	70	40

TABLE : CONSTITUENTS OF BALANCED DIET

Individual	**Total calories (kcal)**	**Proteins (g)**	**Calcium (g)**	**Iron (mg)**	**Vit. A (ug)**	**Thiamine (mg)**	**Riboflavin (mg)**	**Nicotinamide (mg)**	**Vit. C (mg)**	**Folic acid (ug)**	**Vit. B_{12} (ug)**	**Vit. D (IU)**
Man (Moderately active)	2800	55	0.4–0.5	24	750	1:4	1.7	19	40	100	1	
Woman												
(a) Moderately active	2200	45	0.4–0.5	32	750	1.1	1.3	15	40	100	1	
(b) Pregnant	2700	59	1.0	40	750	1.3	1.5	17	40	300	1.5	
(c) Lactating	2750	70	1.0	32	1150	1.4	1.6	19	80	150	1.5	
Boy (16–18 years)	2820	53	0.5–0.6	25	750	1.4	1.7	19	40	100	1	200
Girl (16–18 years)	2200	44	0.5–0.6	35	750	1.1	1.3	15	40	100	1	200

If a nutrient is not taken in adequate amounts for a long time, symptoms of deficiency of that nutrient appear in the organism. Over nutrition or taking in a large amount of a particular nutrient is also harmful for the body. Thus, proper nutrition, *i.e.*, balanced diet is very essential for good health.

TABLE OF VITAMINS

	Name	Sources	Functions	Effects of deficiency
WATER-SOLUBLE VITAMINS				
1.	**Vitamin B_1** (Thiamine or Aneurin) ($C_{12}H_{18}N_4SOCl_2$)	Rice polishings, wheat flour, pulses meal, eggs, yeast, meat, liver, green vegetables, cereals and fruits, etc.	Major component of co-enzyme co-carboxylase required for carbohydrate and amino acid metabolism.	**Beri-beri,** loss of appetite and vigour, retarded growth, constipation, weak heart beat, muscle atrophy, even paralysis.
2.	**Vitamin B_2 or G** (Riboflavin or Lactoflavin) ($C_{17}H_{20}N_4O_6$)	Cheese, egg white, yeast, tomatoes, green vegetables, liver, kidney, meat, cereals and milk, etc.	Combines with phosphoric acid to form co-enzyme FAD essential for oxidative metabolism.	**Cheilosis** (cracking of lips and corners of the mouth); retarded growth, causes general inflammation of tongue, *i.e.*, dark red tongue (glossitis), scaly dermatitis at angles of nares, corneal opacity, etc.
3.	**Vitamin B_3** (Pantothenic acid) ($C_9H_{17}O_5N$)	All food, more in yeast, liver, kidneys, eggs, meat, milk, sugarcane, groundnut, tomatoes.	Important component of Co-A required for oxidative metabolism.	**Dermatitis,** in cocks; greying of hairs, retarded body and mental growth, reproductive debility.
4.	**Vitamin B_5 or P-P** (Nicotinic acid or Niacin) $C_6H_5NO_2(C_5H_4N—COOH)$	Fresh meat, liver, fish, cereals, milk, pulses, yeast, etc.	Active group in co-enzyme NAD required for oxidative metabolism.	**Pellagra** (Shrivelled skin), dermatitis, diarrhoea, dementia, muscle atrophy, inflammation of mucous membrane of gut.
5.	**Vitamin B_6** (Pyridoxine or Adermin) ($C_8H_{11}O_3N$)	Milk, cereals, fish, meat, egg yolk, liver, yeast synthesised by intestinal bacteria and rice bran, etc.	Important co-enzyme required in protein and amino acid metabolism.	**Dermatitis, anaemia,** pellagra convulsions, nausea, insomnia, vomiting, affects central nervous system, depressed appetite and nervousness.
6.	**Vitamin H** (Biotin) ($C_{10}H_{16}N_2O_3S$)	Yeast, vegetables, fruits, wheat, chocolate, eggs, milk, liver and kidney.	Essential for fat synthesis and energy production.	**Dermatitis** (Skin disease), loss of appetite, weakness, hairfall, paralysis.
7.	**Folic acid group**	Green vegetables, soyabean, yeast, kidneys, liver, synthesised by intestinal bacteria.	Essential for synthesis of DNA and maturation of blood corpuscles.	Retarded growth, **anaemia.**
8.	**Vitamin B_{12}** (Cyanocobalamine) ($C_{63}H_{88}O_{14}N_{14}PCo$)	Meat, fish, liver, eggs, curd, milk, synthesised by intestinal bacteria.	Required for chromosome duplication and formation of blood corpuscles.	**Pernicious anaemia,** RBC deficient in haemoglobin, retarded growth, inflammation of tongue and mouth.
9.	**Vitamin C** (Ascorbic acid) ($C_6H_8O_6$)	Lemon, orange, amla and other citrus fruits, tomatoes, green vegetables, potatoes, carrots, pepper and germinated grains, etc.	Essential for formation of collagen, cartilage, bone, teeth, connective tissue and RBCs and for iron metabolism.	**Scurvy, breakdown of immune defence system,** spongy and **bleeding gums, fragile blood vessels** and **bones,** pyorrhea, exhaustion, nervous breakdown, high fever, wound-healing and growth retarded.
	FAT-SOLUBLE VITAMINS			
10.	**Vitamin A** (Retinol or Axerophthol) ($C_{20}H_{30}O$)	Synthesized in cells of liver and intestinal mucous membrane from carotenoid pigments found in milk, butter, kidneys, egg yolk, liver, fish oil, cod liver, green and yellow vegetables.	Essential for synthesis of visual pigments; growth and division of epithelial cells.	**Xerophthalmia** (hardening of cornea of eye) and soft cornea. Xerosis (dryness of skin, respiratory passages, **night-blindness,** urinary bladder, ureters and intestinal mucosa), **impaired growth, glandular secretion and reproduction.**
11.	**Vitamin D** (Ergocalciferol), (Sun shine vitamin) ($C_{28}H_{44}O$) and Cholecalciferol	Synthesized in skin cells in sunlight from 7-dehydrocholesterol also found in butter, liver, kidneys, egg yolk, fish oil, meat and milk. etc.	Regulates absorption of calcium and phosphorus in intestine, mineral deposition in bones and teeth.	**Rickets** (deformation of bones) in children, osteomalacia (soft bones and joint pain in adults), soft and fragile teeth.
12.	**Vitamin E group** Tocopherols (α, β, γ) ($C_{29}H_{50}O_2$)	Green vegetables, egg yolk, vegetable oils (like wheat germoil, cotton seed oil etc), animal tissues. milk and fish etc.	Essential for proper spermatogenesis, pregnancy, lactation and muscular function.	**Sterility** (impotency), loss of sexual power of reproduction (*i.e.*, increased fragility of RBCs) and muscular atrophy.
13.	**Vitamin K** (Phylloquinone) ($C_{31}H_{46}O_2$) (K_1 and K_2)	Carrots, lettuce, cabbage, tomatoes, liver, egg yolk, fish, meat, cheese; synthesized by colon bacteria.	Essential for synthesis of prothrombin in liver, which is required for blood clotting.	**Haemorrhages,** excessive-bleeding in injury, poor coagulation of blood.

IMPORTANT POINTS TO REMEMBER (SUMMARY)

CARBOHYDRATES

- They occur in all plants, animals and are essential for life. Sugars, starch and cellulose (most abundant in nature) are the best known members of carbohydrate series.
- The general formula for a carbohydrate is $C_x(H_2O)_y$ and appears to be the **hydrates of carbons.** Carbohydrates are often referred to as **Saccharides** because of sweet taste of the simpler members of the class.
- Carbohydrates are **optically active polyhydroxy aldehydes** or **ketones** or substances that give such compounds on acidic or enzymic hydrolysis.
- In carbohydrates, the carbonyl group combines with an alcoholic group of the same molecule to form an **internal hemiacetal.**
- The sweet carbohydrates (monosaccharides and disaccharides) are known as **sugars.** The non-sweet carbohydrates, *e.g.*, starch and cellulose are called **non-sugars.**
- Sugars that reduce Tollens' reagent, Fehling's solution and Benedict's reagent are called as **reducing sugars,** *e.g.*, all monosaccharides and disaccharides like lactose and maltose, etc. Carbohydrates which do not reduce the above reagents are called **non-reducing sugars,** *e.g.*, sucrose (disaccharide) and polysaccharides (starch, cellulose, etc.)

Classification : The carbohydrates are divided into:

(i) Monosaccharides : These are single unit carbohydrates and called simple sugars. They can't be hydrolysed further to simpler sugars.

- Monosaccharides are further classified as **aldoses** (—CHO) and **ketoses** (ketonic group) as well as on the basis of number of carbon atoms present in them (*e.g.*, trioses tetroses, pentoses and hexoses, etc.)

(ii) Oligosaccharides : These are made of 2 to 10 units of monosaccharides.

(a) **Disaccharides ($C_{12}H_{22}O_{11}$) :** These on hydrolysis give two molecules of same or different monosaccharides, *e.g.*,

$$\text{Sucrose} + H_2O \xrightarrow{H^+} \text{Glucose} + \text{Fructose}$$

$$\text{Maltose} + H_2O \xrightarrow{H^+} \text{Glucose (2 molecules)}$$

$$\text{Lactose} + H_2O \xrightarrow{H^+} \text{Glucose} + \text{Galactose}$$

(b) **Trisaccharides ($C_{18}H_{32}O_{16}$) :** These on hydrolysis give three molecules of the same or different monosaccharides, *e.g.*,

$$\text{Raffinose} + 2H_2O \xrightarrow{H^+} \text{Glucose} + \text{Fructose} + \text{Galactose}$$

(c) **Tetrasaccharides ($C_{24}H_{42}O_{21}$) :** These on hydrolysis give four molecules of the same or different monosaccharides, *e.g.*,

$$\text{Stachyose} + 3H_2O \xrightarrow{H^+} \text{Glucose} + \text{Fructose} + \underset{\text{(2 moles)}}{\text{Galactose}}$$

(iii) Polysaccharides ($(C_6H_{10}O_5)_n$) : These carbohydrates are of high molecular weight (polymers) which yield many (> 10) monosaccharides molecules on hydrolysis. *e.g.*,

$$\text{Starch or Cellulose} + nH_2O \xrightarrow{H^+} n\,\text{Glucose}$$

Glucose or Dextrose or Grape-sugar or Blood sugar

- Its important sources are grapes, honey, human blood and urine of diabetic patients.

Preparation

- **From sucrose** (Laboratory method) : By hydrolysis in presence of dilute HCl, sucrose gives a mixture of glucose and fructose. Glucose being insoluble in alcohol (than fructose) crystallizes on cooling leaving behind more soluble fructose in solution and separated by filtration.
- **From starch** (Manufacture method) : Starch on hydrolysis with hot dilute HCl or H_2SO_4 gives glucose.

Fructose or Laevulose or Fruit-sugar

- It is found along with glucose in the juice of ripe fruits and in honey. In combined state it occurs in cane sugar and insulin (a polysaccharide).

Preparation

- **From sucrose** (Cane sugar) : By hydrolysis with dil. HCl or H_2SO_4, cane sugar gives equal molecule of glucose and fructose (called **invert sugar**) and the process is known as **inversion.**
- After neutralisation with $CaCO_3$ and filtration, the filtrate is then concentrated under reduced pressure and crystallized.
- **From insulin :** By hydrolysis with dilute H_2SO_4.

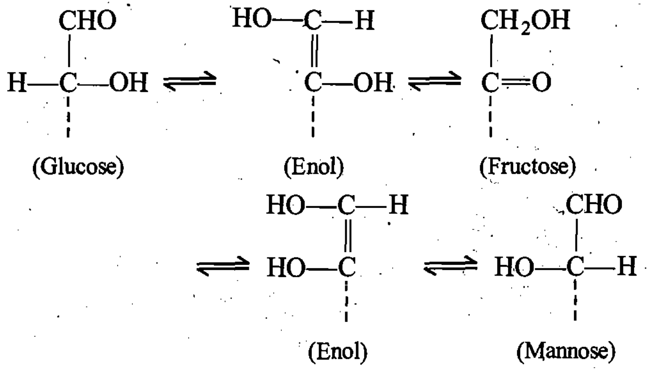
Physical Properties of Glucose and Fructose

- Both glucose and fructose are soluble in water sparingly soluble in alcohol and insoluble in ether. Melting point of glucose is 146°C while fructose is 102°C. Glucose is dextrorotatory while fructose is laevorotatory, but both belong to *D*-family. Both glucose and fructose undergo mutarotation in aqueous solution.

Chemical Properties of Glucose and Fructose

- **Acetylation** (Action of $CH_3COCl/ZnCl_2$ or Ac_2O/CH_3COONa) : Both glucose and fructose forms corresponding penta-acetyl derivatives indicating the presence of 5–OH groups.

- ☐ **Reaction with PCl_5 :** Both forms pentachloride.
- ☐ **Reaction with metallic hydroxide :** With $Ca(OH)_2$, glucose forms calcium glucosate ($C_6H_{12}O_6 \cdot CaO$) which is soluble in water while fructose forms calcium fructosate ($C_6H_{12}O_6 \cdot CaO$) which is insoluble in water.
- ☐ **Reaction with CH_3OH in presence of dry HCl :** Both glucose and fructose on treatment with CH_3OH/dry HCl gas forms α-, and β-methyl glucosides and fructosides respectively indicating that one of the —OH group is different in α- and β- structures (supports the cyclic structure).
- ☐ **Reduction :** P/HI reduces both glucose and fructose into *n*-hexane indicating the presence of a straight chain of six carbon atoms.
- ☐ Reduction with Na-Hg/H_2O or $NaBH_4$, glucose forms *D*-sorbitol while fructose gives a mixture of *D*-sorbitol and *D*-mannitol.
- ☐ **Oxidation :** Depends on the nature of oxidising agent used.
- ☐ **With mild oxidising agents like Br_2 water :** Glucose is oxidised to gluconic acid, $CH_2OH—(CHOH)_4—COOH$ (a monocarboxylic acid), while fructose is not oxidised.
- ☐ **With strong oxidising agents like conc. HNO_3 :** Glucose is oxidised to saccharic acid or glucaric acid, $HOOC—(CHOH)_4—COOH$ (a dicarboxylic acid), while fructose gives a mixture of $HOOC—CH_2OH$ (glycollic acid) and $HOOC—(CHOH)_2—COOH$ (tartaric acid).
- ☐ **Reducing character :** Being easily oxidised, glucose acts as a powerful reducing agent. With **Tollens' reagent** (ammoniacal $AgNO_3$), glucose is oxidised to gluconic acid and reduces Tollens' reagent to **silver mirror.** Similarly, **Fehling's solution** is reduced to give a **red precipitate of cuprous oxide.**
- ☐ Although fructose contains ketonic group, yet it also reduces Tollens' reagent and Fehling's solution. It is due to the fact that dilute solution of alkali present in these reagents convert fructose into an equilibrium mixture of glucose, fructose and mannose (enolisation). So, it has reducing character. For example,



- ☐ **Reaction with HCN :** Both on addition of HCN form cyanohydrin.
- ☐ **Reaction with hydroxylamine (NH_2OH) :** Both form oximes with NH_2OH.
- ☐ **Reaction with phenylhydrazine ($H_2NNHC_6H_5$) :** Both form osazone on treatment with excess of phenylhydrazine.
- ☐ **Fermentation :** Both on fermentation in presence of zymase forms ethyl alcohol and CO_2.
- ☐ **Reaction with alkali :** When heated with concentrated NaOH/KOH, glucose first turns yellow, then brown and finally gives a resinous mass. Fructose is not effected by conc. NaOH.
- ☐ With dilute alkali, both glucose and fructose undergo a rearrangement to give equilibrium mixture of three sugars (glucose, mannose, fructose). This reaction is called **Lobry-de Bruyn Van Ekenstein rearrangement.**
- ☐ *D*-glucose and *D*-mannose are **epimers,** *i.e.*, a pair of diastereomers that differ only in the configuration at C_2 position.
- ☐ **Action of conc. HCl :** Both on heating with conc. HCl give laevulic acid ($CH_3COCH_2CH_2COOH$).

QUESTIONS

❖ Very Short Answer Type

1. Fill in the blanks :
   - (a) A disaccharide consists of two.........joined by......... bonds.
   - (b) A polysaccharide is a polymer of.........
   - (c) A compound that contains both.........and.........is called amino acid.
   - (d) Protein is a polymer of.........
   - (e) Polymer of nucleotides are called.........
   - (f) Loss of biological activity of proteins by physical or chemical changes is termed.........
   - (g) Compounds of living systems that are soluble in organic solvents but insoluble in water, are called ....
   - (h) The formula $C_x(H_2O)_y$ can be assigned to.........
   - (i) The amino acids in polypeptide chain are joined by ....bonds.
   - (j) The glycerides which contain saturated carboxylic acids are called.........
   - (k) Glucose and cane-sugar can be distinguished by......... reagent or.........solution.
   - (l) ATP is.........triphosphate.
   - (m) Pepsin hydrolysis proteins into.........
   - (n) Catabolism and anabolism occur.........in a cell and combination of these is called a.........reaction.
   - (o) An organic substance which is essential in small quantity for maintaining good health is called a.........
   - (p) Lipids $\xrightarrow{\text{Hydrolysis}}$ .... + ...
   - (q) Deficiency of .... causes scurvy.
   - (r) Exposure of body to sunrays produces.........
   - (s) Vitamin C is chemically called.........
   - (t) A normal healthy man requires.........per day.
   - (u) Amino acids are the end products of the digestion of ....
   - (v) Sucrose is non.........sugar.
   - (w) Anaemia is caused by lack of.........and iron.
   - (x) Starch is a polymer of.........while cellulose that of ....
   - (y) Chemical name of vitamin B_{12} is.........
   - (z) In RNA, the sugar is.........whereas in DNA, the sugar is.........

State whether the following statements are **True** or **False :**

- (a) Fructose is an aldose.
- (b) Glycogen is the sugar stored in liver.
- (c) The sugar base present in DNA is ribose.
- (d) Glucose and fructose are both monosaccharides.
- (e) Proteins are the principal source of energy in the body.
- (f) Both animals and plants synthesise carbohydrates.
- (g) Carbohydrate is a polyhydroxy compound that has an aldehydic or a ketonic functional group either free or as hemiacetal or acetal.
- (h) Raffinose is a trisaccharide. On hydrolysis, it gives three molecules of glucose.
- (i) The natural glucose and fructose are *D*-forms.
- (j) Aldohexoses exist in 2^6 optical forms.
- (k) Glucose undergoes oxidation with Fehling's solution or Tollens' reagent.
- (l) Epimers are a pair of diastereomers that differ only in the configuration about a single carbon atom.
- (m) Glucose is more sweeter than fructose.
- (n) Glucose in the form of calcium glucosate is used as medicine in treatment of calcium deficiency.
- (o) Inspite of the fact that glucose possesses an aldehydic group, it does not react with $NaHSO_3$, NH_3 and Schiff's reagent.
- (p) Both α-*D*-glucose and β-*D*-glucose have the same specific rotation.
- (q) The solution having equal molecules of *D*-glucose and *D*-fructose is termed invert sugar.
- (r) Proteins are synthesised by plants only.
- (s) The bond formed between two amino acids by the elimination of a water molecule is called peptide linkage.
- (t) Toxin (snake venom) is also a protein.
- (u) RNA contains the genetic code and directs protein synthesis through DNA.
- (v) A chemical or physical change that alters the sequence of bases in DNA molecule is called mutation.
- (w) Vitamins A, D, E and K are water soluble.
- (x) The energy provided by lipids is much more than provided by the metabolism of carbohydrates and proteins.
- (y) Deficiency of iodine results in a disease, goitre.
- (z) Vitamin C is synthesised in skin cells in sunlight.

3. Match the following :

[A]	1. Glucose	(a) Disaccharide
	2. Hydrolysis of cane sugar	(b) Protein
	3. Zwitter ion	(c) Polysaccharide
	4. Peptide linkage	(d) Insulin
	5. Sucrose	(e) Monosaccharide
	6. Hormone	(f) Biological catalyst
	7. Nucleic acid	(g) Inversion
	8. Starch	(h) Ketose
	9. Fructose	(i) Polymer of nucleotides
	10. Enzyme	(j) α-amino acid
[B]	1. Denaturation	(a) Glucose
	2. Vitamin C	(b) Sucrose
	3. Night-blindness	(c) Photosynthesis
	4. ATP	(d) Pepsin
	5. Reducing sugar	(e) Iodine
	6. Non-reducing sugar	(f) Nucleic acids
	7. Hydrolysis of proteins	(g) Ascorbic acid

8. Synthesis of proteins	(h) Energy transfer reagent
9. Goitre	(i) Loss of biological activity by protein
10. Chlorophyll	(j) Vitamin A

4. Matrix match type questions.
Match the entries of Column I with appropriate entries of Column II. The entries in Column I are labelled A, B, C and D, while the entries in Column II are labelled p, q, r and s. Each entry of Column I can have correct matching with one or more than one options in Column II.

Column I	Column II
(A) Glucose	(p) Osazone
(B) Sucrose	(q) Disaccharide
(C) Lactose	(r) Reducing
(D) Cellulose	(s) Non-reducing

5.

Column I	Column II
(A) Adenine	(p) Purine
(B) Thymine	(q) Pyrimidine
(C) Uracil	(r) RNA
(D) Deoxy ribose	(s) DNA

6. What happens when?
- (i) Glucose is heated with phenyl hydrazine.
- (ii) Glucose is treated with hydroxylamine.
- (iii) Cane-sugar is boiled with dilute sulphuric acid.
- (iv) Cane-sugar is warmed with dilute hydrochloric acid.
- (v) Glucose is made to react with Tollens' reagent.
- (vi) Glucose reacts with bromine water.
- (vii) Glucose solution is heated with Fehling's solution.
- (viii) Glucose is heated with conc. HNO_3.
- (ix) Glucose is treated with HI in the presence of red phosphorus.
- (x) Alanine is treated with nitrous acid.

7. Prove by giving one chemical reaction that:
- (i) glucose has a carbonyl group.
- (ii) glucose has an aldehydic group.
- (iii) glucose has hydroxyl group.
- (iv) glucose is an aldose while fructose is a ketose.
- (v) cane-sugar is a disaccharide.

8. (i) Classify the following into monosaccharides, disaccharides and polysaccharides:
Ribose, glycogen, maltose, deoxyribose, lactose, fructose, glucose, cane-sugar, starch, cellulose.
- (ii) Give one example of each of the following:
  (a) Reducing sugar, (b) Non-reducing sugar.
- (iii) Name the monomers of starch.
- (iv) Name the monomers of cellulose.
- (v) How many naturally occurring amino acids are there?
- (vi) Name the sugars present in nucleic acids.
- (vii) Name the base present in RNA.
- (viii) Name the disease caused due to the deficiency of:
  (a) Vitamin B_{12}, (b) Vitamin C, (c) Vitamin B_1.
- (ix) Name the protein that stores oxygen in the muscle tissue.
- (x) Name the products obtained by hydrolysis of ATP.

❖ Short Answer Type

9. Answer the following:
- (i) What are anomers?
- (ii) What are proteins?
- (iii) What is mutation?
- (iv) What is glucosidic linkage?
- (v) What is mutarotation?
- (vi) What is a peptide bond?
- (vii) What is denaturation of proteins?
- (viii) What is a nucleoside? When does it become nucleotide?
- (ix) What is glycolysis?
- (x) What is digestion?

10. How the following conversions are made?
- (i) Glucose into osazone.
- (ii) Glucose into glucaric acid.
- (iii) Glucose into sorbitol.
- (iv) Glucose into *n*-hexane.
- (v) Glucose into fructose.
- (vi) Fructose into glucose.
- (vii) Glucose into arabinose.
- (viii) Arabinose into glucose.

11. How will you distinguish between?
- (i) Glucose and fructose.
- (ii) Glucose and sucrose (cane-sugar).
- (iii) Glucose and starch.
- (iv) Glucose and glycine.
- (v) Glycine and acetamide.

12. Write short notes on:
- (i) Inversion of cane-sugar.
- (ii) Glycoside linkage.
- (iii) Lipids.
- (iv) Vitamins.
- (v) Zwitter ion.
- (vi) Isoelectric point.
- (vii) Peptide linkage.
- (viii) Coloured tests of proteins.
- (ix) Mutarotation.
- (x) Food digestion.

13. (a) Name the vitamins, deficiency of which cause:
(i) Night-blindness, (ii) Rickets, (iii) Poor coagulation of blood, (iv) Beri-beri and (v) Impotency
(b) Name the sources of following vitamins:
(i) Vitamin A, (ii) Vitamin C, (iii) Vitamin D.

14. (a) How is glucose metabolised in living system?
  (b) How is fat digested in our body?
  (c) Why mineral salts are necessary in food?
  (d) What is the function of water in living system?
  (e) What is glycolysis? Where does it occur? What are the end products of glycolysis?
  (f) What is haemoglobin? What is its function?
  (g) Why does the amylase present in saliva becomes inactive in the stomach?
  (h) How does the acidic medium of stomach helps in the digestion of proteins?

15. Explain the following:
  (i) Why do glucose, mannose and fructose form identical osazone?

[**Ans.** The formation of osazone involves C-1 and C-2. Glucose, mannose and fructose have identical configuration at C-3, C-4 and C-5. Hence, they form same osazone.]

  (ii) Aldoses give positive Tollens', Fehling's and osazone reactions but fail to respond Schiff's and bisulphite tests.

[**Ans.** The open chain form is very very small and Tollens', Fehling's and osazone reactions are irreversible in nature, the equilibrium is thus shifted to restore this small concentration till whole of the aldoses react. Schiff's and bisulphite reactions are reversible, the equilibrium is thus not disturbed and open chain form having —CHO group is not available in good concentrations.]

  (iii) The amino acid in water acts as an ampholyte.

[**Ans.** $H_3\overset{+}{N}CHRCOOH + OH^- \xrightleftharpoons{\text{Acting as an acid}} H_3\overset{+}{N}CHRCOO^- + H_2O$

Cation   Ampholyte

$\xrightleftharpoons{\text{Acting as a base}} H_2NCHRCOO^- + H_3\overset{+}{O}$]

Anion

  (iv) In an electric field, the amino acid migrates towards cathode when pH is below the isoelectric point while it migrates towards anode when pH is higher than isoelectric point.

[**Ans.** Isoelectric point is the pH at which the amino acid has net zero charge and exists as dipolar ion ($H_3\overset{+}{N}CHRCOO^-$). When pH is below the isoelectric point, the cation ($H_3\overset{+}{N}CHRCOOH$) predominates and it migrates to the cathode while at pH higher than isoelectric point the anion ($H_2NCHRCOO^-$) predominates and it migrates to anode.]

  (v) Why is *D*-fructose used for sweetening cold drinks but not hot ones?

[**Ans.** The sweeter form is fructopyranose. The high temperature causes a shift in the pyranose $\rightleftharpoons$ furanose equilibrium towards the less sweet furanose.]

  (vi) The structural feature distinguishes proline from the other α-amino acids.

[**Ans.** Proline is 2° amine and also the amine N is a part of five membered ring.]

  (vii) Despite having an aldehydic group, glucose does not give 2,4-DNP test. What does it indicate?

[**Ans.** Glucose does not have an open chain structure and hence it does not have a free —CHO group. Actually —CHO group combines with C_5—OH to form an hemiacetal ring which is a six membered oxide ring. Thus glucose largely (99%) exist in the cyclic hemiacetal form and so it does not give 2,4-DNP test.]

  (viii) What forces are responsible for the stability of α-helix? Why is it named as 3.6_{13} helix?

[**Ans.** The stability of α-helix structure is due to intramolecular H-bonding between —NH— and —CO groups of the same polypeptide chain. The α-helix is named as 3.6_{13} helix, since each turn of the helix has approximately 3.6 amino acid and a 13-membered ring is formed by H-bonding.]

16. The specific rotation of two glucose anomers are $\alpha = +110°$ and $\beta = +19°$ and for the constant equilibrium mixture is +52.7°. Calculate the per cent composition of the anomers in the equilibrium mixture.

[**Ans.** α-anomer = 36.2% and β-anomer = 63.8%]

[**Hint :** Let *a* and *b* be the mole fractions of α and β-anomers in equilibrium mixture. Thus,

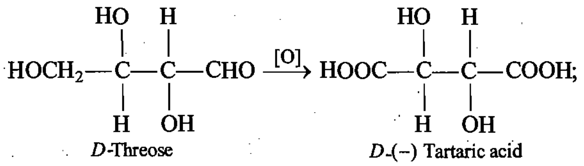
$$a + b = 1$$

$$110° a + 19° b = 52.7°$$

Solving both equations, we get $a = 0.362$ and $b = 0.638$]

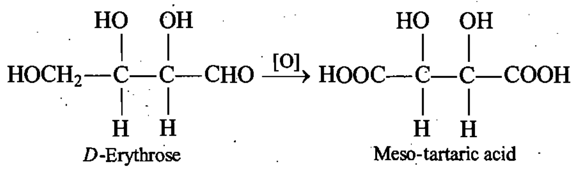
17. Use mild oxidation and reduction separately to differentiate between *D*-erythrose and *D*-threose.

[**Ans.** Threose gives an optically active enantiomer while erythrose gives the optically inactive meso-isomer on mild oxidation.



$HOCH_2—\overset{HO}{\underset{H}{C}}—\overset{H}{\underset{OH}{C}}—CHO \xrightarrow{[O]} HOOC—\overset{HO}{\underset{H}{C}}—\overset{H}{\underset{OH}{C}}—COOH;$

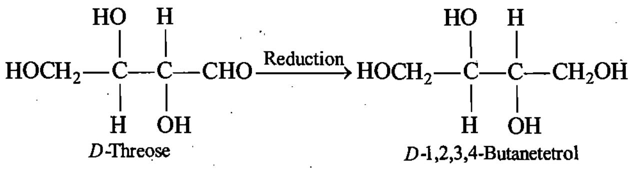
D-Threose   *D*-(−) Tartaric acid



$HOCH_2—\overset{HO}{\underset{H}{C}}—\overset{OH}{\underset{H}{C}}—CHO \xrightarrow{[O]} HOOC—\overset{HO}{\underset{H}{C}}—\overset{OH}{\underset{H}{C}}—COOH$

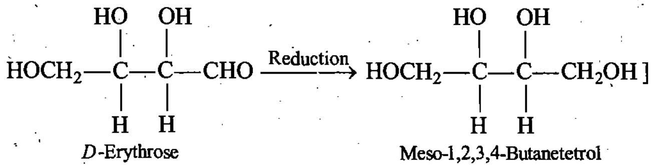
D-Erythrose   Meso-tartaric acid

Threose gives an optically active enantiomer while erythrose gives the optically inactive meso-isomer on mild reduction.



$HOCH_2—\overset{HO}{\underset{H}{C}}—\overset{H}{\underset{OH}{C}}—CHO \xrightarrow{\text{Reduction}} HOCH_2—\overset{HO}{\underset{H}{C}}—\overset{H}{\underset{OH}{C}}—CH_2OH$

D-Threose   *D*-1,2,3,4-Butanetetrol



$HOCH_2—\overset{HO}{\underset{H}{C}}—\overset{OH}{\underset{H}{C}}—CHO \xrightarrow{\text{Reduction}} HOCH_2—\overset{HO}{\underset{H}{C}}—\overset{OH}{\underset{H}{C}}—CH_2OH$]

D-Erythrose   Meso-1,2,3,4-Butanetetrol

18. Define invert sugar. Calculate the specific rotation of invert sugar given that $[\alpha]_D = +52.7^\circ$ for *D*-glucose and $[\alpha]_D = -92.4^\circ$ for *D*-fructose.

[**Ans.** Invert sugar is the equimolar mixture of *D*-glucose and *D*-fructose. It is obtained by hydrolysis of sucrose. The specific rotation is one-half the sum of those of individual monosaccharides : $\frac{1}{2}[+52.7^\circ + (-92.4^\circ)] = -19.9^\circ$]

19. Find the average molecular mass of starch given that an aqueous solution of 10.0 g/L of starch has an osmotic pressure 5.0×10^{-3} atm at 25°C. What is the approximate number of glucose units in this sample of starch?

[**Ans.** Osmotic pressure $= \frac{w}{M \times V} \times R \times T$

or $M = \frac{w}{P \times V} \times R \times T$

$$M = \frac{10}{5 \times 10^{-3} \times 1} \times 0.0821 \times 298 = 48931.6 \text{ g/mol}$$

Each glucose unit in starch has molecular mass $= 180 - 18 = 162$ g/mol

The number of glucose units in the sample of starch $= \frac{48931.6}{162} = 302$]

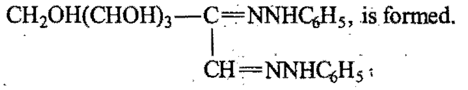
20. Name the monosaccharides which the following give on hydrolysis ?

(a) sucrose, (b) maltose, (c) lactose, (d) starch, (e) insulin.

ANSWERS

1. (a) Monosaccharides, glycoside; (b) monosaccharides; (c) amino and carboxylic groups; (d) α-amino acids; (e) nucleic acids; (f) denaturation; (g) lipids; (h) carbohydrates; (i) peptide; (j) fats; (k) Tollens', Fehling's; (l) adenosine; (m) amino acids; (n) simultaneously, coupled; (o) vitamin; (p) glycerol, monocarboxylic acids; (q) vitamin C; (r) vitamin D; (s) ascorbic acid; (t) 2820 kcal; (u) proteins; (v) reducing; (w) B-complex; (x) α-glucose, β-glucose; (y) cyanocobalamine; (z) ribose, deoxyribose.
2. (a) False—Fructose is a ketose; (b) True; (c) False—The sugar base in DNA is deoxyribose; (d) True; (e) False—Proteins are the building blocks of cells; (f) False—Only plants synthesise carbohydrates; (g) True; (h) False—On hydrolysis, it gives three molecules of monosaccharide units one each of glucose, fructose and galactose; (i) True; (j) False—Aldohexoses exist in $2^4 (= 16)$ optical forms; (k) True; (l) True; (m) False—Fructose is more sweeter than glucose; (n) True; (o) True; (p) False—The specific rotation of α-*D*-glucose is +110° and of β-*D*-glucose is +19°; (q) True; (r) False—Proteins are synthesised by both plants and animals; (s) True; (t) True; (u) False—DNA contains the genetic code and directs protein synthesis through RNA; (v) True; (w) False—Are fat soluble; (x) True; (y) True; (z) False—Vitamin D is synthesised in skin cells in sunlight.
3. [A] (1—e); (2—g); (3—j); (4—b); (5—a); (6—d); (7—i); (8—c); (9—h); (10—f).
   [B] (1—i); (2—g); (3—j); (4—h); (5—a); (6—b); (7—d); (8—f); (9—e); (10—c).
4. (A—p, r); (B—q, s); (C—p, q, r); (D—s).
5. (A—p, r, s); (B—q, s); (C—q, r); (D—s).
6. (i) $CH_2OH(CHOH)_4CHO + H_2N{\cdot}NHC_6H_5 \longrightarrow CH_2OH(CHOH)_4CH{=}NNHC_6H_5$
   Glucose phenylhydrazone

   With excess of phenylhydrazine, glucosazone,

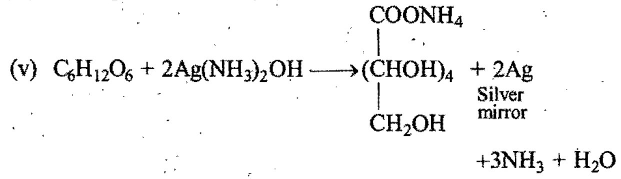


$CH_2OH(CHOH)_3{-}\underset{\displaystyle CH{=}NNHC_6H_5}{\underset{|}{C}}{=}NNHC_6H_5$, is formed.

   (ii) $CH_2OH(CHOH)_4CHO + H_2NOH \longrightarrow CH_2OH{\cdot}(CHOH)_4CH{=}NOH$
   Glucose oxime

   (iii) $\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Dil. } H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

   (iv) Same products as in (iii)



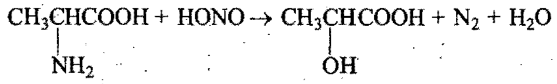
$$\text{(v)}\quad C_6H_{12}O_6 + 2Ag(NH_3)_2OH \longrightarrow \begin{array}{c} COONH_4 \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + \underset{\substack{\text{Silver}\\ \text{mirror}}}{2Ag} + 3NH_3 + H_2O$$

   (vi) $C_6H_{12}O_6 + [O] \xrightarrow{Br_2/H_2O} \underset{\text{Gluconic acid}}{C_6H_{12}O_7}$

   (vii) $C_6H_{12}O_6 + 2Cu(OH)_2 + NaOH \longrightarrow CH_2OH(CHOH)_4COONa + \underset{\text{Red ppt.}}{Cu_2O} + 3H_2O$

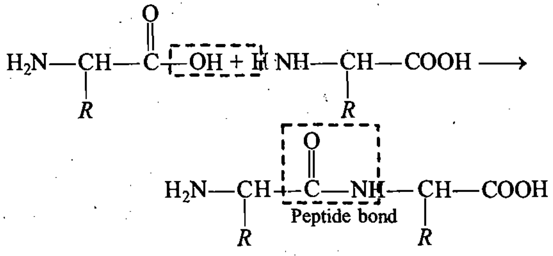
   (viii) $CH_2OH(CHOH)_4CHO + 2[O] \xrightarrow{HNO_3} COOH{\cdot}(CHOH)_4COOH$
   Glucaric acid

   (ix) *n*-Hexane is formed.



   (x) $CH_3\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH + HONO \rightarrow CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCOOH + N_2 + H_2O$
7. (i) Glucose reacts with HCN, NH_2OH and phenylhydrazine respectively.
   (ii) Glucose can be oxidised to gluconic acid by bromine water, Tollens' solution or Fehling's solution.
   (iii) Glucose undergoes acetylation with acetyl chloride.
   (iv) Glucose can be oxidised with bromine water but fructose does not give this reaction.
   (v) Cane-sugar on hydrolysis gives one molecule of glucose and one molecule of fructose, *i.e.*, two monomers.
8. (i) Monosaccharides : Ribose, deoxyribose, glucose, fructose.
   Disaccharides : Maltose, lactose, cane-sugar.
   Polysaccharides : Glycogen, starch, cellulose.
   (ii) Reducing sugar—Glucose; Non-reducing sugar—cane sugar (sucrose).
   (iii) α-Glucose.
   (iv) β-Glucose.
   (v) Twenty.
   (vi) Deoxyribose and ribose.
   (vii) Adenine; cytosine; guanine; uracil.
   (viii) (a) Pernicious anaemia, (b) Breakdown of immune defence system, (c) Beri-beri.
   (ix) Myoglobin.
   (x) ADP and AMP along with phosphate ions and energy.
9. (i) A pair of isomers that differ with respect to orientation of the —OH group at carbon-1.
   (ii) Proteins are polymers of amino acids having peptide linkage.

(iii) Sudden change in the sequence of nitrogenous bases along the DNA strand and can synthesise a new protein with altered amino acid sequence.
(iv) The linkage formed by the combination of hydroxyl group of the hemiacetal carbon of one monosaccharide with the —OH group of the other monosaccharide.
(v) The process that involves the change in the optical rotation of either form of glucose in aqueous solution to that of equilibrium mixture is known as mutarotation.
(vi) The linkage that unites various amino acid units in a peptide molecule is known as peptide bond.



$$\mathrm{H_2N{-}\underset{R}{CH}{-}\overset{O}{\overset{\|}{C}}{-}OH + H{-}NH{-}\underset{R}{CH}{-}COOH \longrightarrow H_2N{-}\underset{R}{CH}{-}\overset{O}{\overset{\|}{C}}{-}NH{-}\underset{R}{CH}{-}COOH}$$

(vii) On heating or on treatment with mineral acids globular proteins undergo coagulation to give fibrous protein. It loses whole or a part of biological activity.
(viii) The molecule in which one of the organic bases is linked with a sugar is called nucleoside. When a phosphate group is also attached to the nucleoside, the compound is known as nucleotide.
(ix) It is the anaerobic conversion of 6-carbon atoms compound, glucose, into two molecules of pyruvic acid.
(x) It is the process of breaking up of a complex food into simple molecules.

10. (i) Treat glucose with excess of phenylhydrazine.
(ii) Treat glucose with nitric acid.
(iii) Treat glucose with $NaBH_4$ or H_2/Pd.
(iv) Treat glucose with phosphorus and hydrogen iodide.
(v) Treat glucose with excess of phenylhydrazine and treat osazone with dil. HCl to form osone. Reduce osone with Zn/CH_3COOH to form fructose.
(vi) Reduce fructose with H_2 in the presence of Ni and treat the alcohol with Fenton's reagent.
(vii) Follow Ruff degradation (or Wohl's method).
(viii) Follow Killiani-Fischer synthesis.

11. (i) Glucose decolourised red colour of bromine water. It is oxidised to gluconic acid. Fructose does not react with bromine water.

Fructose gives a red colour with resorcinol and conc. HCl while glucose does not give any colour.

(ii) Glucose on heating with Tollens' reagent gives silver mirror while sucrose does not. Glucose gives red ppt. with Fehling's solution while sucrose does not.
(iii) Glucose gives positive tests with Tollens' reagent and Fehling's solution while starch does not. Starch gives blue colour with iodine solution while glucose does not.
(iv) Glucose gives positive tests with Tollens' reagent and Fehling's solution while glycine does not.
(v) Acetamide gives an odour of ammonia when heated with NaOH while glycine does not. Glycine gives purple colour with ninhydrin while acetamide does not.

13. (a) (i) Vitamin A, (ii) Vitamin D, (iii) Vitamin K, (iv) Vitamin B_1, (v) Vitamin E.
(b) (i) Synthesised in cells of liver and intestinal mucous membrane from carotenoid pigments found in milk, butter, egg yolk, liver, fish oil, etc.
(ii) Lemon, orange and other citrus fruits, tomatoes, green vegetables, etc.
(iii) Synthesised in skin cells in sunlight, found in butter, liver egg yolk, fish oil, etc.

14. (a) Metabolism of glucose involves two processes :
(i) Glycolysis—The series of reactions that change glucose into pyruvate with the formation of ATP.
(ii) Cellular respiration—Pyruvate can be converted into ethanol, lactate or the acetyl group of the acetyl co-enzyme.

(b) In small intestines, Lipids $\xrightarrow{\text{Bile juice}}$ Emulsified fat

Emulsified fat $\xrightarrow{\text{Lipase}}$ Glycerol + Fatty acids.

(c) Inorganic minerals are involved in various metabolic reactions of the cells. Ions play important role in maintaining osmotic pressure and acid-base balance in the cells.
(d) Water is the medium for transportation in the body. It takes part in most of the chemical reactions of the body.
(e) Conversion of glucose into pyruvic acid. It occurs in cytoplasm of anaerobic cells without oxygen. It is accompanied by release of ATP.
(f) Haemoglobin is a globular protein present in red blood cells. It carries oxygen from one part of the body to the other.
(g) Amylase becomes inactive in stomach due to low pH value.
(h) The acid denatures the proteins and then proteins are hydrolysed.

$$\text{Proteins} \xrightarrow[\text{Proteases}]{\text{Pepsin}} \text{Polypeptides} \xrightarrow[\text{Chemotrypsin}]{\text{Trypsin}} \text{Amino acids}$$

20. (a) Glucose + Fructose, (b) 2 molecules of glucose, (c) Glucose + Galactose, (d) Glucose, (e) Fructose.

OBJECTIVE QUESTIONS

SET I : This set contains the questions with single correct answer.

1. A carbohydrate consists of:
(a) carbon and oxygen ☐
(b) carbon, hydrogen and oxygen ☐
(c) carbon, hydrogen and nitrogen ☐
(d) carbon and hydrogen ☐

2. Which of the following is a monosaccharide?
(a) Sucrose ☐ (b) Galactose ☐
(c) Maltose ☐ (d) Lactose ☐

3. Which of the following carbohydrates is most abundant in nature? **[CPMT 2002]**
(a) Glucose ☐ (b) Fructose ☐
(c) Starch ☐ (d) Cellulose ☐

4. The sweetest of all sugars is: **[PMT (MP) 2007]**
(a) glucose ☐ (b) lactose ☐
(c) sucrose ☐ (d) fructose ☐

5. Sucrose on hydrolysis gives: **[JEE (Orissa) 2006]**
(a) glucose only ☐ (b) glucose and galactose ☐
(c) glucose and fructose ☐ (d) glucose and lactose ☐

6. The commonest disaccharide has the molecular formula:
(a) $C_{10}H_{18}O_9$ ☐ (b) $C_{10}H_{20}O_{10}$ ☐
(c) $C_{11}H_{22}O_{11}$ ☐ (d) $C_{12}O_{22}O_{11}$ ☐

7. The disaccharide present in milk is:
(a) sucrose ☐ (b) lactose ☐
(c) maltose ☐ (d) none of these ☐

8. Which of the following monosaccharides is a pentose?
(a) Glucose ☐ (b) Fructose ☐
(c) Arabinose ☐ (d) Galactose ☐

9. Which gives red colour with Fehling's solution?
(a) Glucose ☐ (b) Cellulose ☐
(c) Benzaldehyde ☐ (d) Cane-sugar ☐

10. Starch is a polymer of:
(a) fructose ☐ (b) glucose ☐
(c) both (a) and (b) ☐ (d) none of these ☐

11. Enzymes are:
(a) carbohydrates ☐ (b) lipids ☐
(c) proteins ☐ (d) none of these ☐

12. On hydrolysis, proteins give:
(a) nucleotides ☐ (b) nucleosides ☐
(c) amides ☐ (d) amino acids ☐

13. Which of the following have coiled helical structure?
(a) Proteins ☐ (b) Lipids ☐
(c) Carbohydrates ☐ (d) Vitamins ☐

14. The change in optical rotation with time of freshly prepared solutions of sugar, is known as:
(a) specific rotation ☐ (b) inversion ☐
(c) rotatory motion ☐ (d) mutarotation ☐

15. Glucose when heated with CH_3OH in presence of dry HCl gas, α- and β-methyl glucosides are formed. This is because it contains:
(a) an aldehydic group ☐ (b) —CH_2OH group ☐
(c) a ring structure ☐ (d) five hydroxyl groups ☐

16. Which of the following carbohydrates is used in silvering of mirrors?
(a) Sucrose ☐ (b) Cellulose ☐
(c) Fructose ☐ (d) Glucose ☐

17. Starch undergoes hydrolysis in presence of mineral acids to:
(a) glucose ☐ (b) fructose ☐
(c) maltose ☐ (d) sucrose ☐

18. Helical structure of proteins is stabilized by:
(a) ionic bond ☐ (b) covalent bond ☐
(c) van der Waals' forces ☐ (d) hydrogen bonds ☐

19. Hydrolysis of sucrose gives:
(a) invert sugar (equal mixture of glucose and fructose) ☐
(b) glucose ☐
(c) fructose ☐
(d) none of the above ☐

20. Digestion is a:
(a) hydrolysis process ☐
(b) catalytic process ☐
(c) both hydrolysis and catalytic process ☐
(d) none of the above ☐

21. Vitamin C is: **[JEE (WB) 2010]**
(a) ascorbic acid ☐ (b) lactic acid ☐
(c) citric acid ☐ (d) paracetamol ☐

22. Iodine deficiency in diet is known to cause:
(a) beri-beri ☐ (b) rickets ☐
(c) night-blindness ☐ (d) goitre ☐

23. When glucose is reacted with bromine water, the major product is:
(a) gluconic acid ☐ (b) saccharic acid ☐
(c) sorbitol ☐ (d) galactose ☐

24. Glucose and fructose are:
(a) optical isomers ☐
(b) functional group isomers ☐
(c) chain isomers ☐
(d) position isomers ☐

25. The number of chiral carbon atoms in β-*D* (+)-glucose molecule is: **[CBSE (Med.) 2004]**
(a) 3 ☐ (b) 5 ☐
(c) 4 ☐ (d) 6 ☐

26. Which of the following is a ketohexose?
(a) Glucose ☐ (b) Fructose ☐
(c) Sucrose ☐ (d) Starch ☐

27. The reagent which may be used to distinguish between cane-sugar and glucose solution is:
(a) Molisch's reagent ☐ (b) Iodine solution ☐
(c) Baeyer's reagent ☐ (d) Fehling's solution ☐

28. The reactions of glucose suggest that it is:
(a) a penta hydroxy aldehyde ☐
(b) hydrate of carbon ☐
(c) a polyhydroxy ketone ☐
(d) an alcohol ☐

29. Glucose is a/an:
(a) oxidising sugar ☐
(b) reducing sugar ☐
(c) reducing and oxidising sugar ☐
(d) none of the above ☐

30. Ascorbic acid is:
(a) a vitamin ☐ (b) an enzyme ☐
(c) a protein ☐ (d) an amino acid ☐

31. Chemical name of vitamin A is:
(a) thiamine ☐ (b) axerophthol (retinol) ☐
(c) ascorbic acid ☐ (d) nicotinamide ☐

32. Glucose reacts with excess of phenylhydrazine and forms: **[CPMT 2006]**
(a) sorbitol ☐
(b) glucose phenylhydrazone ☐
(c) glucosazone ☐
(d) glucose oxime ☐

33. A compound gives both ninhydrin test and Molisch's test. It is:
(a) a carbohydrate ☐ (b) a carboxylic acid ☐
(c) a protein ☐ (d) an amino acid ☐

34. The carbohydrate which serves as a reserve glucose in body is:
(a) sucrose ☐ (b) starch ☐
(c) glycogen ☐ (d) fructose ☐

35. The substances which are even richer sources of energy than carbohydrates are:
(a) fats ☐ (b) proteins ☐
(c) vitamins ☐ (d) hormones ☐

36. Protein is an important constituent of our diet. It functions mainly as:
(a) a source of energy ☐
(b) a construction material ☐
(c) shock absorber ☐
(d) reserve food ☐

37. The coagulation of protein is called:
(a) dehydration ☐ (b) decay ☐
(c) deamination ☐ (d) denaturing ☐

38. Main structural unit of protein is:
(a) ester linkage ☐ (b) ether linkage ☐
(c) peptide linkage ☐ (d) all of these ☐

39. Glucose cannot be classified as:
(a) a hexose ☐ (b) an oligosaccharide ☐
(c) a carbohydrate ☐ (d) an aldose ☐

40. Which one is a disaccharide?
(a) Starch ☐ (b) Lactose ☐
(c) Cellulose ☐ (d) Fructose ☐

41. Point out the wrong statement about proteins:
(a) They are nitrogenous organic compounds of high molecular masses ☐
(b) On hydrolysis by enzymes, they give amino acids ☐
(c) Many of them are enzymes ☐
(d) They do not contain polypeptide linkages ☐

42. The vitamin that is most readily manufactured in our bodies is:
(a) vitamin A ☐ (b) vitamin B ☐
(c) vitamin C ☐ (d) vitamin D ☐

43. Bleeding gums is generally associated with a deficiency of:
(a) thiamine ☐ (b) ascorbic acid ☐
(c) folic acid ☐ (d) vitamin E ☐

44. Vitamin A deficiency leads to a disease known as:
(a) night-blindness ☐ (b) beri-beri ☐
(c) scurvy ☐ (d) TB ☐

45. Which one of the following metal ions is essential inside the cell for the metabolism of glucose/synthesis of proteins ? **[DUMET 2010]**
(a) Na^+ ☐ (b) K^+ ☐
(c) Mg^{2+} ☐ (d) Ca^{2+} ☐

46. The reagent used for the detection of proteins is:
(a) HNO_3 (conc.) ☐ (b) Fehling's solution ☐
(c) Tollens' reagent ☐ (d) Baeyer's reagent ☐

47. Starch is used to test even the small amount of:
(a) urea in blood ☐
(b) iodine in aqueous solution ☐
(c) protein in blood ☐
(d) glucose in aqueous solution ☐

48. Which one of the following contains cobalt?
(a) Chlorophyll ☐ (b) Haemoglobin ☐
(c) Vitamin C ☐ (d) Vitamin B_{12} ☐

49. On heating glucose with Fehling's solution, we get a precipitate whose colour is:
(a) yellow ☐ (b) red ☐
(c) black ☐ (d) white ☐

50. The only amino acid which is non-chiral is: **[DPMT 2007]**
(a) lysine ☐ (b) proline ☐
(c) glycine ☐ (d) histidine ☐

51. The aqueous solution of a carbohydrate gave dark blue colour with iodine solution. The carbohydrate is:
(a) starch ☐ (b) sucrose ☐
(c) fructose ☐ (d) glucose ☐

52. The organic compounds of high physiological importance which are essential in small amounts for the well being of all human beings are:
(a) proteins ☐ (b) vitamins ☐
(c) mineral salts ☐ (d) enzymes ☐

53. Which of the following has magnesium? **[CBSE (Med.) 2000]**
(a) Carbonic anhydrase ☐ (b) Vitamin B_{12} ☐
(c) Chlorophyll ☐ (d) Haemocyanine ☐

54. The hormone which controls the presence of burning of fats, proteins and carbohydrates and liberates energy in the body is: **[CBSE (Med.) 2000]**
(a) thyroxine ☐ (b) adrenaline ☐
(c) insulin ☐ (d) cortisone ☐

55. Which of the following is not a sex hormone? **[DCE 2000]**
(a) Testosterone ☐ (b) Estrone ☐
(c) Estradiol ☐ (d) Cortisone ☐

56. Insulin is secreted from:
(a) thyroid ☐ (b) pancreas ☐
(c) adrenal body ☐ (d) none of these ☐

57. The hormone which transports glucose from blood to tissue is:
(a) glucogen ☐ (b) insulin ☐
(c) thyroxin ☐ (d) heparin ☐

58. A protein is best described as a:
(a) polyamide ☐ (b) polyester ☐
(c) polypeptide ☐ (d) polyurethane ☐

59. A disaccharide, which gives only glucose on hydrolysis, is:
(a) lactose ☐ (b) fructose ☐
(c) sucrose ☐ (d) maltose ☐

60. Methyl-α-*D*(+)-glucoside and methyl-β-*D*(+)-glucoside are called: **[AIIMS 2006; BCECE (Med.) 2007]**
(a) geometrical isomers ☐ (b) anomers ☐
(c) enantiomers ☐ (d) epimers ☐

61. Amino acids are building blocks of:
(a) carbohydrates ☐ (b) fats ☐
(c) proteins ☐ (d) vitamins ☐

62. The reactions with sugars are carried out in neutral or acid medium and not in alkaline medium because in alkaline medium sugars undergo:
(a) decomposition ☐ (b) racemization ☐
(c) inversion ☐ (d) rearrangement ☐

63. Which of the following is found in cod-liver oil?
(a) Vitamin C ☐ (b) Vitamin E ☐
(c) Vitamin A ☐ (d) Vitamin B_1 ☐

64. Proteins can be used:
(a) as food ☐ (b) in textiles ☐
(c) as enzymes ☐ (d) all of these ☐

65. Biuret test is not given by: **[AIEEE 2010]**
(a) proteins ☐ (b) urea ☐
(c) polypeptide ☐ (d) carbohydrates ☐

66. Deficiency of vitamin E causes:
(a) beri-beri ☐ (b) scurvy ☐
(c) antifertility ☐ (d) none of these ☐

67. The enzyme pepsin hydrolyses:
(a) proteins to amino acids ☐
(b) fats to fatty acids ☐
(c) glucose to ethyl alcohol ☐
(d) polysaccharides to monosaccharides ☐

68. Which of the following foodstuffs contain nitrogen?
(a) Carbohydrates ☐ (b) Protein ☐
(c) Fats ☐ (d) None of these ☐

69. Vitamin B_2 is also known as:
(a) riboflavin ☐ (b) pyridoxin ☐
(c) ascorbic acid ☐ (d) none of these ☐

70. The number of amino acids which form proteins in nature is about:
(a) 6 ☐ (b) 10 ☐
(c) 15 ☐ (d) 20 ☐

71. Which one is not the essential constituent of balanced diet?
(a) Hormones ☐ (b) Carbohydrates ☐
(c) Fats ☐ (d) Vitamins ☐

72. The number of tripeptides formed by three different amino acids is: **[DCE 2000]**
(a) five ☐ (b) six ☐
(c) three ☐ (d) four ☐

73. The pH value of a solution in which a polar amino acid does not migrate under the influence of electric field is called:
(a) iso-electric point ☐ (b) iso-electronic point ☐
(c) neutralisation point ☐ (d) none of these ☐

74. The digestion of fat in intestines is aided by:
(a) diffusion ☐ (b) peptization ☐
(c) emulsification ☐ (d) neutralisation ☐

75. The human body does not produce:
(a) vitamins ☐ (b) enzymes ☐
(c) proteins ☐ (d) hormones ☐

76. An enzyme, which helps in the digestion of proteins in living tissues, is:
(a) trypsin ☐ (b) protease ☐
(c) urease ☐ (d) none of these ☐

77. The protein which transports oxygen in the blood stream is:
(a) haemoglobin ☐ (b) insulin ☐
(c) collagen ☐ (d) albumin ☐

78. Which of the following gives maximum energy in metabolic process?
(a) Proteins ☐ (b) Fats ☐
(c) Carbohydrates ☐ (d) Vitamins ☐

79. Hydrolysis of sucrose is called: **[AFMC 2010]**
(a) saponification ☐ (b) hydration ☐
(c) inversion ☐ (d) esterification ☐

80. Enzyme trypsin converts:
(a) amino acids into proteins ☐
(b) glucose into glycogen ☐
(c) starch into sugar ☐
(d) proteins into amino acids ☐

81. Calorific value is in the order of:
(a) fats > carbohydrates > proteins ☐
(b) carbohydrates > fats > proteins ☐
(c) proteins > carbohydrates > fats ☐
(d) fats > proteins > carbohydrates ☐

82. Vitamin B_1 is known as: **[PMT(MP) 2000]**
(a) pyridoxine ☐ (b) thiamine ☐
(c) tocopherol ☐ (d) riboflavin ☐

83. Which of the following base is found only in RNA and not in DNA?
(a) Thymine ☐ (b) Guanine ☐
(c) Uracil ☐ (d) Adenine ☐

84. Which one of the following base found in DNA but not in RNA? **[CET (Gujarat) 2006]**
(a) Cytosine ☐ (b) Guanine ☐
(c) Adenine ☐ (d) Thymine ☐

85. The sequence in which amino acids are arranged in protein is called its:
(a) primary structure ☐ (b) secondary structure ☐
(c) tertiary structure ☐ (d) quaternary structure ☐

86. The relationship between the nucleotide triplets and the amino acid is called:

(a) enzymes ☐ (b) replication ☐
(c) genetic code ☐ (d) mutation ☐

87. Amino acids present in insulin are:
(a) 21 ☐ (b) 51 ☐
(c) 30 ☐ (d) 102 ☐

88. The bond that determines the secondary structure of a protein is:
(a) ionic bond ☐ (b) covalent bond ☐
(c) coordinate bond ☐ (d) hydrogen bond ☐

89. Which has the maximum protein?
(a) Groundnut ☐ (b) Cow-milk ☐
(c) Egg ☐ (d) Wheat ☐

90. At the isoelectric point, amino acids are present as:
(a) $H_2NCHRCOOH$ ☐ (b) $H_3\overset{+}{N}CHRCOO^-$ ☐
(c) $H_3\overset{+}{N}CHRCOOH$ ☐ (d) $H_2NCHRCOO^-$ ☐

91. The most important energy carrier in the living cell is: **[CEE (MP) 2000]**
(a) AMP ☐ (b) ADP ☐
(c) UDP ☐ (d) ATP ☐

92. Emil Fischer was awarded Nobel Prize for his work on:
(a) sugar and protein synthesis ☐
(b) optical activity ☐
(c) ammonia discovery ☐
(d) lipids ☐

93. Glucose and fructose can also be distinguished by:
(a) Molisch's test ☐
(b) acetylation ☐
(c) a concentrated solution of NaOH ☐
(d) phenylhydrazine ☐

94. Which of the following does not show mutarotation? **[CBSE (PMT) Prelims 2010]**
(a) (–) Fructose ☐ (b) (+) Lactose ☐
(c) (+) Maltose ☐ (d) (+) Sucrose ☐

95. Glucose and mannose are: **[AMU (Med.) 2007]**
(a) ketohexoses ☐ (b) anomers ☐
(c) epimers ☐ (d) disaccharides ☐

96. Diabetes is detected by testing urine of the patient with:
(a) Tollens' reagent ☐ (b) Nessler's reagent ☐
(c) Fenton's reagent ☐ (d) Benedict's solution ☐

97. Refrigeration helps in food preservation by:
(a) killing the germs ☐
(b) sealing the food with a layer of ice ☐
(c) greatly reducing the rates of bio-chemical reactions ☐
(d) destroying enzyme action ☐

98. Yeast is:
(a) bacteria ☐ (b) antibiotic ☐
(c) virus ☐ (d) fungi ☐

99. Oxidation of glucose is one of the most important reactions in a living cell. What is the number of ATP molecules generated in cells from one molecule of glucose?
(a) 36 ☐ (b) 12 ☐
(c) 18 ☐ (d) 28 ☐

100. The pH of blood does not appreciably change by a small addition of an acid or a base because blood:
(a) contains serum protein which acts as buffer ☐
(b) contains iron as a part of the molecule ☐
(c) can be easily coagulated ☐
(d) is a body fluid ☐

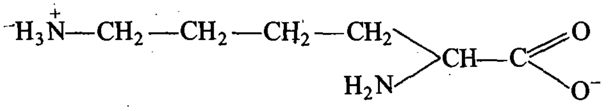
101. Biuret test is used for the detection of:
(a) sugars ☐ (b) fats ☐
(c) proteins ☐ (d) saturated oils ☐

102. The common term used for water soluble proteins is:
(a) glutenin ☐ (b) globulin ☐
(c) albumin ☐ (d) conjugated proteins ☐

103. Which of the following is a protein?
(a) Nylon ☐ (b) Natural silk ☐
(c) Reyon ☐ (d) Terrylene ☐

104. Which protein is main constituent of milk?
(a) Casein ☐ (b) Insulin ☐
(c) Myosine ☐ (d) Keratin ☐

105. The total number of basic groups in the following form of lysine



[IIT 2010]
(a) 0 ☐ (b) 1 ☐
(c) 2 ☐ (d) 3 ☐

106. Which of the following statements is true for proteins?
(a) They act as antibodies ☐
(b) They act as hormones ☐
(c) They catalyse the bio-chemical reactions ☐
(d) They perform all these functions ☐

107. Which of the following gives maximum energy in metabolic process?
(a) Carbohydrates ☐ (b) Fats ☐
(c) Proteins ☐ (d) Vitamins ☐

108. Fibrous proteins are present in:
(a) wool ☐ (b) muscles ☐
(c) silk ☐ (d) all of these ☐

109. Globular proteins are present in:
(a) blood ☐ (b) milk ☐
(c) insulin ☐ (d) all of these ☐

110. Keratin, a fibrous protein is present in:
(a) hair and nails ☐ (b) wool ☐
(c) skin ☐ (d) all of these ☐

111. Which of the following statements about proteins is not true?
(a) Amino acid residues join together to make a protein molecule ☐
(b) Proteins are polymers with formula $(C_6H_{10}O_5)_n$ ☐
(c) Eggs are richer in proteins ☐
(d) Pulses are good source of proteins ☐

112. A metal which can form a complex with insulin is:
(a) copper ☐ (b) iron ☐
(c) zinc ☐ (d) cobalt ☐

113. Secondary structure of protein refers to:
(a) three-dimensional structure, specially the bond between amino acid residues that are distant from each other in the polypeptide chain ☐
(b) regular folding patterns of the polypeptide chain ☐
(c) mainly denatured proteins and structures of prosthetic groups ☐
(d) linear sequence of amino acid residues in the polypeptide chain ☐

114. The enzyme ptylin used for the digestion of food is present in:
(a) blood ☐ (b) intestine ☐
(c) adrenal glands ☐ (d) saliva ☐

115. One of the essential alpha amino acid is:
(a) lysine ☐ (b) glycine ☐
(c) serine ☐ (d) proline ☐

116. Enzymes:
(a) accelerate bio-chemical reactions ☐
(b) consist of amino acids ☐
(c) have optimum activity at body temperature ☐
(d) have all these properties ☐

117. The function of enzymes in the living system is to:
(a) transport oxygen ☐
(b) provide immunity ☐
(c) catalyse bio-chemical reactions ☐
(d) provide energy ☐

118. Which enzyme hydrolysis triglyceride to fatty acids and glycerol?
(a) Lipase ☐ (b) Maltase ☐
(c) Amylase ☐ (d) Pepsin ☐

119. Of the following statements about enzymes, which ones are true?
(i) Enzymes lack in nucleophilic groups
(ii) Enzymes are highly specific both in binding chiral substrates and in catalysing their reactions
(iii) Enzymes catalyse chemical reactions by lowering the activation energy
(iv) Pepsin in proteolytic enzyme
(a) (i) ☐ (b) (i) and (iv) ☐
(c) (i) and (iii) ☐ (d) (ii), (iii) and (iv) ☐

120. Which statement is not correct for enzyme?
(a) It acts as a biocatalyst ☐
(b) It can catalyse any chemical reaction ☐
(c) Its aqueous solution is colloidal ☐
(d) Its catalytic efficiency is temperature dependent ☐

121. The vitamin which is water soluble and antioxidant is:
(a) vitamin C ☐ (b) vitamin B ☐
(c) vitamin E ☐ (d) vitamin D ☐

122. Which of the following vitamins contains nitrogen?
(a) Vitamin A ☐ (b) Vitamin B ☐
(c) Vitamin C ☐ (d) Vitamin D ☐

123. A vitamin that contains both nitrogen and sulphur is:
(a) vitamin A ☐ (b) vitamin B_1 ☐
(c) vitamin B_2 ☐ (d) vitamin B_{12} ☐

124. Which of the following is not a fat soluble vitamin ? **[AMU (Engg.) 2010]**
(a) Vitamin A ☐ (b) Vitamin K ☐
(c) Vitamin E ☐ (d) Folic acid ☐

125. Rickets is caused due to the deficiency of:
(a) vitamin A ☐ (b) vitamin B ☐
(c) vitamin C ☐ (d) vitamin D ☐

126. Which of the following vitamins contains isoprene unit?
(a) Vitamin A ☐ (b) Vitamin B_2 ☐
(c) Vitamin C ☐ (d) Vitamin D ☐

127. Vitamin D is also known as:
(a) ascorbic acid ☐ (b) growth vitamin ☐
(c) reproductive vitamin ☐ (d) sunshine vitamin ☐

128. Identify the vitamin whose deficiency in our food decreases reproductive power:
(a) vitamin A ☐ (b) vitamin C ☐
(c) vitamin D ☐ (d) vitamin E ☐

129. Which of the following is provitamin A?
(a) Ascorbic acid ☐ (b) β-Carotene ☐
(c) Calciferol ☐ (d) Ergosterol ☐

130. Vitamin C is:
(a) alcohol ☐ (b) amide ☐
(c) amine ☐ (d) lactone ☐

131. Vitamin D is:
(a) calciferol ☐ (b) ergosterol ☐
(c) tocoferol ☐ (d) pyridoxin ☐

132. Beri-beri is caused due to:
(a) vitamin A ☐ (b) vitamin B ☐
(c) vitamin C ☐ (d) vitamin D ☐

133. Scurvy is caused due to the deficiency of:
(a) vitamin B_2 ☐ (b) vitamin B_{12} ☐
(c) ascorbic acid ☐ (d) glutamic acid ☐

134. The aldehyde which is formed during photosynthesis of plants is: **[CET (Tamil Nadu) 2001]**
(a) phenyl methanal ☐ (b) propanal ☐
(c) ethanal ☐ (d) methanal ☐

135. A vitamin which plays a vital role in the coagulating property of blood is:
(a) vitamin A ☐ (b) vitamin D ☐
(c) vitamin E ☐ (d) vitamin K ☐

136. Which is not a pyrimidine base?
(a) Uracil ☐ (b) Thymine ☐
(c) Cytosine ☐ (d) Guanine ☐

137. Which statement is incorrect about peptide bond? **[CBSE (Med.) 2001]**
(a) C—N bond length in proteins is smaller than usual bond length of C—N bond ☐
(b) Spectroscopic analysis shows planar structure of —CO—NH group ☐
(c) C—N bond length in proteins is longer than usual bond length of C—N bond ☐
(d) None of the above ☐

138. Bases common to RNA and DNA are:
(a) adenine, guanine, cytosine ☐

(b) adenine, uracil, cytosine ☐
(c) adenine, guanine, thymine ☐
(d) guanine, uracil, thymine ☐

139. The examples of nucleoside are:
(a) adenosine ☐ (b) cytidine ☐
(c) uridine ☐ (d) all of these ☐

140. The examples of nucleotide are:
(a) adenylic acid ☐ (b) guanylic acid ☐
(c) uridylic acid ☐ (d) all of these ☐

141. In nucleic acids, the sequence is:
(a) base-phosphate-sugar ☐
(b) base-sugar-phosphate ☐
(c) sugar-base-phosphate ☐
(d) phosphate-base-sugar ☐

142. A 'base-sugar-phosphate' unit in nucleic acid is called:
(a) base phosphate ☐ (b) phosphotide ☐
(c) nucleotide ☐ (d) nucleoside ☐

143. The function of DNA is:
(a) to synthesis RNA ☐
(b) to synthesis the necessary protein ☐
(c) to carry the heriditary characteristics ☐
(d) all are correct ☐

144. RNA is a:
(a) single helix strand ☐ (b) double helix strand ☐
(c) triple helix strand ☐ (d) none of these ☐

145. Nucleic acids are:
(a) polymers of nucleosides ☐
(b) polymers of nucleotides ☐
(c) polymers of purine bases ☐
(d) polymers of pyrimidine bases ☐

146. Which of the following is responsible for the heridity character of cell?
(a) RNA ☐ (b) DNA ☐
(c) Proteins ☐ (d) Hormones ☐

147. The energy stored in the cells of a living body is in the form of:
(a) fats ☐ (b) glucose ☐
(c) ATP ☐ (d) proteins ☐

148. Which of the following biomolecules contains a non-transition metal ion?
(a) Haemoglobin ☐ (b) Chlorophyll ☐
(c) Insulin ☐ (d) Vitamin B_{12} ☐

149. Lactose is made of: **[PET (Kerala) 2010]**
(a) α-*D*-glucose only ☐
(b) β-*D*-galactose and β-*D*-glucose ☐
(c) α-*D*-glucose and β-*D*-glucose ☐
(d) β-*D*-galactose and α-*D*-glucose ☐
(e) α-*D*-galactose and β-*D*-glucose ☐

150. Which of the following is least related to the other three?
(a) Galactose ☐ (b) Glucose ☐
(c) Mannose ☐ (d) Arabinose ☐

151. The letter '*D*' and '*L*' in carbohydrates represents:
(a) its optical rotation ☐ (b) its mutarotation ☐
(c) its direct synthesis ☐ (d) its configuration ☐

152. Carbohydrates are used by body mainly:
(a) for obtaining vitamins ☐
(b) as a source of energy ☐
(c) for building muscles ☐
(d) for all its development needs ☐

153. Which of the following is a disaccharide?
(a) Glucose ☐ (b) Fructose ☐
(c) Sucrose ☐ (d) Starch ☐

154. Sucrose is made up of:
(a) *D*-glucose + *L*-fructose ☐
(b) *D*-glucose + *D*-fructose ☐
(c) *D*-fructose + *L*-glucose ☐
(d) *L*-fructose + *L*-glucose ☐

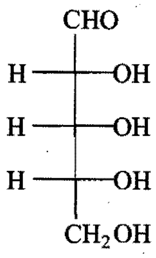
155. α-*D*-glucose and β-*D*-glucose differ from each other due to the difference in one of the carbons with respect to its:
(a) configuration ☐
(b) number of —OH groups ☐
(c) conformation ☐
(d) size of hemiacetal ring ☐

156. When sucrose is heated with conc. HNO_3 in presence of V_2O_5 as catalyst, it gives:
(a) formic acid ☐ (b) oxalic acid ☐
(c) saccharic acid ☐ (d) dinitrosucrose ☐

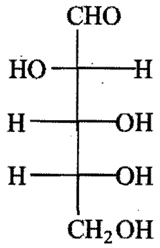
157. The reagent which forms crystalline osazone derivative when reacted with glucose, is:
(a) Fehling's solution ☐ (b) Benedict solution ☐
(c) phenylhydrazine ☐ (d) hydroxylamine ☐

158. The number of asymmetric carbon atoms in fructose is:
(a) 2 ☐ (b) 3 ☐
(c) 4 ☐ (d) 5 ☐

159. Which of the following is the structure of *D*-xylose?

(a)


☐

(b)


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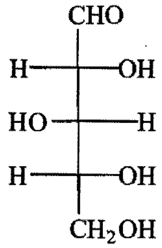
(c)


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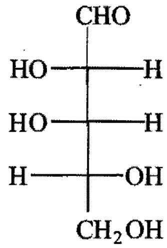
(d)


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160. Sugars are characterised by the preparation of osazone derivatives. Which sugars have identical osazones?
(a) Glucose and fructose ☐ (b) Glucose and arabinose ☐
(c) Glucose and lactose ☐ (d) Glucose and maltose ☐

161. Which one of the following is laevorotatory? **[PMT (MP) 2007]**
(a) Glucose ☐ (b) Fructose ☐
(c) Sucrose ☐ (d) Lactose ☐

162. An example of non-reducing sugar is: **[CET (J&K) 2007]**
(a) sucrose ☐ (b) maltose ☐
(c) lactose ☐ (d) cellobiose ☐

163. Which one of the following is the reagent used to identify glucose?
(a) Neutral $FeCl_3$ ☐ (b) $CHCl_3$ and alc. KOH ☐
(c) Ammoniacal $AgNO_3$ ☐ (d) C_2H_5ONa ☐

164. Starch on hydrolysis by a dilute inorganic mineral acid gives:
(a) glucose ☐ (b) fructose ☐
(c) sucrose ☐ (d) maltose ☐

165. Milk changes after digestion into:
(a) glucose ☐ (b) fructose ☐
(c) lactose ☐ (d) cellulose ☐

166. Raffinose on hydrolysis forms:
(a) glucose ☐ (b) fructose ☐
(c) galactose ☐ (d) all of these ☐

167. Charring of sugar is due to:
(a) oxidation ☐
(b) reduction ☐
(c) dehydration ☐
(d) reduction and hydration ☐

168. Glucose gives silver mirror with ammoniacal silver nitrate because it has: **[MHCET (Med.) 2007]**
(a) ester ☐ (b) aldehyde ☐
(c) ketone ☐ (d) alcoholic $AgNO_3$ ☐

169. Lactose on hydrolysis gives: **[CET (Punjab) 2006]**
(a) glucose ☐ (b) fructose ☐
(c) fructose + glucose ☐ (d) glucose + galactose ☐

170. Cellulose is a linear polymer of:
(a) α-glucose ☐ (b) β-glucose ☐
(c) α-fructose ☐ (d) amylose ☐

171. Fructose reduces Tollen's reagent due to : **[CBSE (PMT) 2010]**
(a) enolisation of fructose followed by conversion to aldehyde by base ☐
(b) primary alcoholic group ☐
(c) secondary alcoholic group ☐
(d) asymmetric carbons ☐

172. Starch is converted into maltose in about half an hour's time by:
(a) zymase ☐ (b) invertase ☐
(c) maltase ☐ (d) diastase ☐

173. On hydrolysis of starch, we finally get:
(a) glucose ☐
(b) fructose ☐
(c) glucose and fructose both ☐
(d) sucrose ☐

174. An aldose is converted into its next higher homologue by:
(a) Wohl's method ☐
(b) Amadori rearrangement ☐
(c) Killiani's reaction ☐
(d) Mutarotation ☐

175. Glucose is stored in our body as:
(a) carbohydrates ☐ (b) fats ☐
(c) glycogen ☐ (d) lipid ☐

176. Molisch test is used for the detection of:
(a) fats ☐ (b) carbohydrates ☐
(c) alkyl halide ☐ (d) alkaloid ☐

177. The aqueous solution of carbohydrate gave a dark blue colour with iodine solution. The carbohydrate is:
(a) glucose ☐ (b) fructose ☐
(c) sucrose ☐ (d) starch ☐

178. Which of the following is used to prepare paper?
(a) Glucose ☐ (b) Sucrose octa acetate ☐
(c) Starch ☐ (d) Cellulose ☐

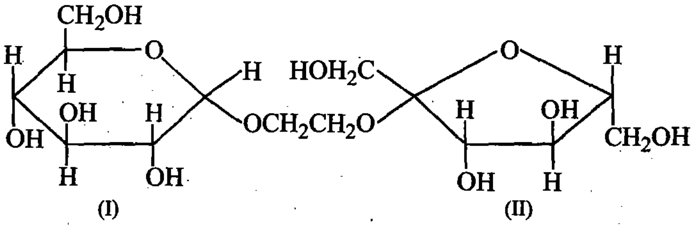
179. Iodine test is shown by: **[BHU 2000; BCECE (Med.) 2007]**
(a) polypeptide ☐ (b) glycogen ☐
(c) starch ☐ (d) glucose ☐

180. Which substance chars when heated with conc. H_2SO_4? **[AIIMS 2001]**
(a) Carbohydrate ☐ (b) Hydrocarbon ☐
(c) Fat ☐ (d) Protein ☐

181. In aqueous solution, an amino acid exists as : **[PMT (Kerala) 2010]**
(a) cation ☐ (b) anion ☐
(c) dianion ☐ (d) zwitter ion ☐
(e) neutral molecule ☐

182. The pK_{a_1} and pK_{a_2} of an amino acid are 2.3 and 9.7 respectively. The isoelectric point of the amino acid is : **[AMU (Med.) 2010]**
(a) 6.0 ☐ (b) 3.7 ☐
(c) 12.0 ☐ (d) 7.4 ☐

183. The correct statement about the following disaccharide is :



[IIT 2010]
(a) ring (I) is pyranose with α-glycosidic link ☐
(b) ring (I) is furanose with α-glycosidic link ☐
(c) ring (II) is furanose with α-glycosidic link ☐
(d) ring (II) is pyranose with β-glycosidic link ☐

184. How many forms are possible for a triglyceride formed from three different acyl groups? **[DPMT 2002]**
(a) Three ☐ (b) Two ☐
(c) More than three ☐ (d) One ☐

185. Secondary structure of protein is mainly governed by : **[PMT (Kerala) 2010]**

(a) hydrogen bonds ☐ (b) covalent bond ☐
(c) ionic bonds ☐ (d) disulphide bonds ☐
(e) dative bonds ☐

186. Which is fight and flight organ? **[UGET (Med.) 2002]**
(a) Adrenal ☐ (b) Thyroid ☐
(c) Pituitary ☐ (d) Kidney ☐

187. In transfer RNA anticodon for the messenger RNA codon G-C-A is: **[DUMET 2010; AMU (Med.) 2010]**
(a) C-G-U ☐ (b) G-C-U ☐
(c) U-G-C ☐ (d) G-U-C ☐

188. Enzymes are made up of: **[CBSE (Med.) 2002; PMT (Pb.) 2007]**
(a) carbohydrates ☐
(b) nitrogen containing carbohydrates ☐
(c) edible proteins ☐
(d) proteins with specific structure ☐

189. Which is not a true statement? **[CBSE (Med.) 2002; PMT (Pb) 2007]**
(a) α-Carbon of α-amino acid is asymmetric ☐
(b) All proteins are found in *L*-form ☐
(c) Human body can synthesize all proteins they need ☐
(d) At pH = 7 both amino acid carboxylic groups exist in ionised form ☐

190. The glucose is an example of: **[CPMT 2002]**
(a) disaccharide ☐ (b) aldohexose ☐
(c) ketohexose ☐ (d) none of these ☐

191. Which of the following is the most abundant carbohydrate found in plants? **[DCE 2006]**
(a) Cellulose ☐ (b) Starch ☐
(c) Lipids ☐ (d) Fructose ☐

192. Which of the following compounds shows aromatic properties? **[CPMT 2003]**
(a) Valine ☐ (b) Leucine ☐
(c) Serine ☐ (d) Tyrosine ☐

193. Which of the following is the sweetest sugar? **[CBSE (Med.) 2003]**
(a) Sucrose ☐ (b) Glucose ☐
(c) Fructose ☐ (d) Maltose ☐

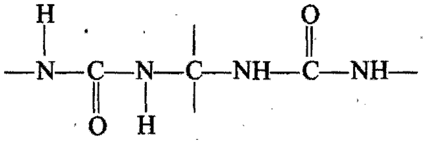
194. Lack of vitamin B_1 causes: **[BHU 2002]**
(a) scurvy ☐ (b) beri-beri ☐
(c) dermatitis ☐ (d) lips inflammation ☐

195. Soaps can be classified as: **[CPMT 2003]**
(a) carbohydrates ☐ (b) ethers ☐
(c) salts of fatty acids ☐ (d) none of these ☐

196. The reason for double helical structure of DNA is operation of: **[AIEEE 2003]**
(a) hydrogen bonding ☐
(b) electrostatic attractions ☐
(c) van der Waals' forces ☐
(d) dipole-dipole interaction ☐

197. Complete hydrolysis of cellulose gives: **[AIEEE 2003]**
(a) *D*-fructose ☐ (b) *D*-ribose ☐
(c) *D*-glucose ☐ (d) *L*-glucose ☐

198. Which of the following structures does represent the peptide chain? **[CBSE (Med.) 2004]**

(a)

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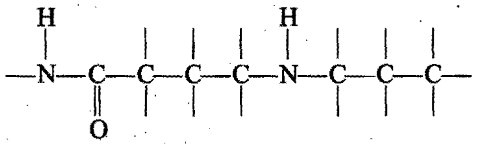
(b)

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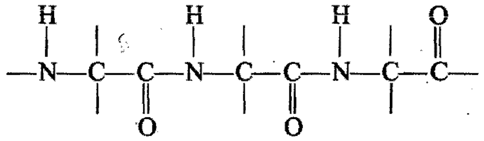
(c)

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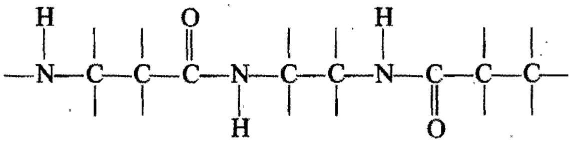
(d)

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199. The enzyme which hydrolysis triglycerides to fatty acids and glycerol is called: **[CBSE (Med.) 2004; UGET (Med.) 2007]**
(a) maltase ☐ (b) lipase ☐
(c) zymase ☐ (d) pepsin ☐

200. The helical structure of protein is stabilized by: **[CBSE (Med.) 2004; UGET (Med.) 2007]**
(a) dipeptide bonds ☐ (b) hydrogen bonds ☐
(c) ether bonds ☐ (d) peptide bonds ☐

201. The purine base present in RNA is: **[AIIMS 2004]**
(a) adenine ☐ (b) cytosine ☐
(c) uracil ☐ (d) thymine ☐

202. A nucleoside on hydrolysis gives: **[CET (Karnataka) 2004]**
(a) an aldopentose and an heterocyclic base ☐
(b) an aldopentose and an orthophosphoric acid ☐
(c) a heterocyclic base and an orthophosphoric acid ☐
(d) an aldopentose, a heterocyclic base and an orthophosphoric acid ☐

203. Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which of the following categories? **[AIEEE 2004; Jamia Millia (Engg.) 2007]**
(a) A co-enzyme ☐ (b) A hormone ☐
(c) An enzyme ☐ (d) An antibiotic ☐

204. The two forms of *D*-glucopyranose obtained from *D*-glucose are known as: **[IIT 2005]**
(a) epimers ☐ (b) anomers ☐
(c) enantiomers ☐ (d) geometrical isomers ☐

205. The group linkage present in fats is: **[AFMC 2005; MGIMS (Med.) 2008]**
(a) ester linkage ☐ (b) peptide linkage ☐
(c) glycosidic linkage ☐ (d) none of these ☐

206. The conversion of maltose to glucose is possible by the enzyme: **[AFMC 2005]**
(a) zymase ☐ (b) lactase ☐
(c) maltase ☐ (d) diastase ☐

207. Which one of the following biomolecules is insoluble in water? **[AIIMS 2005]**
(a) α-Keratin ☐ (b) Haemoglobin ☐
(c) Ribonuclease ☐ (d) Adenine ☐

208. Which one of the following statements is true for protein synthesis (translation)? **[AIIMS 2005]**
(a) Amino acids are directly recognize by *m*-RNA ☐
(b) The third base of the codon is less specific ☐
(c) Only one codon codes for an amino acid ☐
(d) Every *t*-RNA molecule has more than one amino acid attachment ☐

209. Glucose has difference from fructose in that it: **[BHU 2005]**
(a) does not undergo hydrolysis ☐
(b) is a monosaccharide ☐
(c) gives silver mirror with Tollens' reagent ☐
(d) none of the above ☐

210. Which of the following amino acids is optically inactive? **[BHU 2005]**
(a) Phenyl alanine ☐ (b) Glycine ☐
(c) Glutamic acid ☐ (d) Asparagine ☐

211. A certain compound gives negative test with ninhydrin and positive test with Benedict's solution. The compound is: **[DCE 2005]**
(a) a lipid ☐ (b) a protein ☐
(c) an amino acid ☐ (d) a monosaccharide ☐

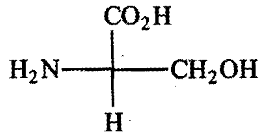
212. Which of the following is not correct? **[EAMCET (Engg.) 2005]**
(a) Chlorophyll is responsible for the synthesis of carbohydrates in plants ☐
(b) The compound formed in the addition of oxygen to haemoglobin is called oxyhaemoglobin ☐
(c) Acetyl salicylic acid is known as aspirin ☐
(d) The metal ion present in vitamin B_{12} is Mg^{2+} ☐

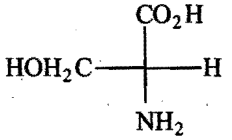
213. DNA multiplication is called: **[AMU (Med.) 2005; PMET (Med.) 2008]**
(a) translation ☐ (b) transduction ☐
(c) transcription ☐ (d) replication ☐

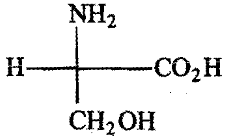
214. The pyrimidine bases present in DNA are: **[AIEEE 2006]**
(a) cytosine and adenine ☐ (b) cytosine and guanine ☐
(c) cytosine and thymine ☐ (d) cytosine and uracil ☐

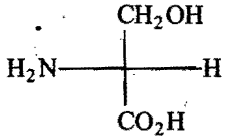
215. The term anomers of glucose refers to: **[AIEEE 2006]**
(a) isomers of glucose that differs in configuration at carbons one and four (C-1 and C-4) ☐
(b) a mixture of (*D*-) glucose and (*L*-) glucose ☐
(c) enantiomers of glucose ☐
(d) isomers of glucose that differ in configuration at carbon one (C-1) ☐

216. Among the following, *L*-serine is: **[AIIMS 2006]**

(a) 
$$\begin{array}{c} CO_2H \\ H_2N-\!\!\!-\!\!+\!\!-\!\!\!-CH_2OH \\ H \end{array}$$
☐

(b) 
$$\begin{array}{c} CO_2H \\ HOH_2C-\!\!\!-\!\!+\!\!-\!\!\!-H \\ NH_2 \end{array}$$
☐

(c) 
$$\begin{array}{c} NH_2 \\ H-\!\!\!-\!\!+\!\!-\!\!\!-CO_2H \\ CH_2OH \end{array}$$
☐

(d) 
$$\begin{array}{c} CH_2OH \\ H_2N-\!\!\!-\!\!+\!\!-\!\!\!-H \\ CO_2H \end{array}$$
☐

217. Thymine is: **[AIIMS 2006]**
(a) 5-methyl uracil ☐ (b) 4-methyl uracil ☐
(c) 3-methyl uracil ☐ (d) 1-methyl uracil ☐

218. Lysine is least soluble in water in the pH range: **[AIIMS 2006]**
(a) 3 to 4 ☐ (b) 5 to 6 ☐
(c) 6 to 7 ☐ (d) 8 to 9 ☐

219. All monosaccharides................Tollens' reagent. **[CET (J&K) 2006]**
(a) oxidise ☐ (b) condense with ☐
(c) reduce ☐ (d) add to ☐

220. RNA differ from DNA in respect of a base: **[AFMC 2006]**
(a) thymine ☐ (b) adenine ☐
(c) cytosine ☐ (d) guanine ☐

221. The best source of vitamin A is: **[AFMC 2006]**
(a) beans ☐ (b) pulses ☐
(c) orange ☐ (d) carrot ☐

222. Which one of the following is a peptide hormone? **[CBSE (Med.) 2006]**
(a) Thyroxin ☐ (b) Adrenaline ☐
(c) Glutathione ☐ (d) Testosterone ☐

223. During the process of digestion, the proteins present in food materials are hydrolysed to amino acids. The two enzymes involved in the process,

$$\text{Proteins} \xrightarrow{\text{Enzyme }(A)} \text{Polypeptides} \xrightarrow{\text{Enzyme }(B)} \text{Amino acids}$$

are respectively: **[CBSE (Med.) 2006]**
(a) pepsin and trypsin ☐ (b) invertase and zymase ☐
(c) amylase and maltase ☐ (d) diastase and lipase ☐

224. Biotin is an organic compound present in yeast. Its deficiency in diet causes dermatitis and paralysis. It is also known as: **[PMT (Kerala) 2006]**
(a) vitamin H ☐ (b) vitamin B_3 ☐
(c) vitamin B_{12} ☐ (d) vitamin D ☐
(e) vitamin E ☐

225. Match **List I** with **List II** and pick the correct matching from the codes given below:

	List I		**List II**
A.	Thymine	1.	Pyrimidine base
B.	Thiamine	2.	Enzyme
C.	Insulin	3.	Cell wall component
D.	Pepsin	4.	Hormone
E.	Phospholipids	5.	Vitamin B_1

Codes: **[PET (Kerala) 2006]**

(a) A—4, B—3, C—1, D—5, E—2 ☐
(b) A—5, B—3, C—4, D—1, E—2 ☐
(c) A—3, B—2, C—1, D—5, E—4 ☐
(d) A—2, B—4, C—1, D—3, E—5 ☐
(e) A—1, B—5, C—4, D—2, E—3 ☐

226. Which of the following exists as Zwitter ion? **[PET (Kerala) 2006; PMT (Kerala) 2008]**

(a) *p*-Amino phenol ☐ (b) Salicylic acid ☐
(c) Sulphanilic acid ☐ (d) Ethanolamine ☐
(e) *p*-Amino acetophenone ☐

227. Insulin regulates the metabolism of: **[CET (Karnataka) 2006]**

(a) minerals ☐ (b) amino acids ☐
(c) glucose ☐ (d) vitamins ☐

228. At pH = 4, glycine exists as: **[CET (Karnataka) 2006]**

(a) $H_3\overset{+}{N}-CH_2-COO^-$ ☐
(b) $H_3\overset{+}{N}-CH_2-COOH$ ☐
(c) H_2N-CH_2-COOH ☐
(d) $H_2N-CH_2-COO^-$ ☐

229. Starch is converted to ethanol by fermentation, the sequence of enzymes used is: **[DPMT 2006]**

(a) amylase, maltase, zymase ☐
(b) diastase, maltase, zymase ☐
(c) amylase, invertase, zymase ☐
(d) amylase, zymase, maltase ☐

230 Configuration of mannose and glucose differ at C-2 position, they are termed as: **[DPMT 2006]**

(a) epimers ☐ (b) anomers ☐
(c) racimers ☐ (d) mesomers ☐

231. Monomer of nucleic acid is: **[DCE 2006; AMU (Engg.) 2007]**

(a) nucleotides ☐ (b) nucleosides ☐
(c) amino acids ☐ (d) carboxylic acid ☐

232. Vitamin B_6 is known as: **[PMT (Haryana) 2006]**

(a) pyridoxine ☐ (b) thiamine ☐
(c) tocopherol ☐ (d) riboflavin ☐

233. A nanopeptide contains..................peptide linkages. **[GGS (Indraprastha Univ.) EE 2006]**

(a) 10 ☐ (b) 8 ☐
(c) 9 ☐ (d) 18 ☐

234. A mixture of amylose and amylopectin is called: **[EAMCET (Med.) 2007; DCE 2008]**

(a) lactose ☐ (b) starch ☐
(c) cellulose ☐ (d) sucrose ☐

235. Which of the following indicates open chain structure of glucose? **[DCE (Engg.) 2007]**

(a) Penta-acetyl derivative of glucose ☐
(b) Cyanohydrin formation with HCN ☐
(c) Reaction with Fehling solution ☐
(d) Reaction with Tollens' reagent ☐

236. Which of the following disaccharide has different type of linkage? **[DPMT 2007]**

(a) Maltose ☐ (b) Galactose ☐
(c) Starch ☐ (d) Sucrose ☐

237. Which of the following hexoses will form the same osazone when treated with excess of phenyl hydrazine? **[PET (Kerala) 2007]**

(a) *D*-glucose, *D*-fructose and *D*-galactose ☐
(b) *D*-glucose, *D*-fructose and *D*-mannose ☐
(c) *D*-glucose, *D*-mannose and *D*-galactose ☐
(d) *D*-fructose, *D*-mannose and *D*-galactose ☐
(e) *D*-glucose, *D*-galactose and *D*-talose ☐

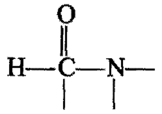
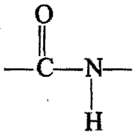
238. The secondary structure of a protein refers to: **[AIEEE 2007]**

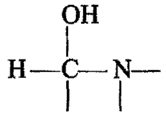
(a) fixed configuration of the polypeptide backbone ☐
(b) α-helical backbone ☐
(c) hydrophobic interactions ☐
(d) sequence of α-amino acids ☐

239. Which one of the following is a conjugated protein? **[BCECE (Med.) 2007]**

(a) Phosphoprotein ☐ (b) Glycoprotein ☐
(c) Chromoprotein ☐ (d) All of these ☐

240. Which one is the correct representation of peptide bond? **[DCE (Engg.) 2007]**

(a) 
$H-\overset{\overset{O}{\|}}{C}-N-$ ☐ (b) 
$-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$ ☐

(c) 
$H-\overset{\overset{OH}{|}}{C}-N-$ ☐ (d) None of these ☐

241. Which functional group participates in disulphide bond formation in proteins? **[JIPMER (Med.) 2007]**

(a) Thioacetone ☐ (b) Thiol ☐
(c) Thioether ☐ (d) Thioester ☐

242. Which one of the following statements about amino acids is not true? **[PMT (Kerala) 2007]**

(a) They are constituents of all proteins ☐
(b) They are all high melting solids ☐
(c) Most naturally occurring amino acids have *D*-configuration ☐
(d) They are characterized by isoelectric point ☐
(e) Glycine is the only naturally occurring amino acid which is optically inactive ☐

243. Polypeptides having, molecular weights above 10,000 are known as: **[CET (J&K) 2007]**

(a) proteins ☐ (b) hormones ☐

(c) amino acids ☐ (d) terminal amino acids ☐

244. Which of the following biomolecules acts as specific catalysts in biological reaction? **[EAMCET (Engg.) 2007]**

(a) Carbohydrates ☐ (b) Lipids ☐

(c) Vitamins ☐ (d) Enzymes ☐

245. RNA and DNA are chiral molecules, their chirality is due to: **[CBSE (Med.) 2007]**

(a) chiral phosphate ester units ☐

(b) *D*-sugar component ☐

(c) *L*-sugar component ☐

(d) chiral bases ☐

246. A sequence of how many nucleotides in messenger RNA makes a codon for an amino acid? **[UGET (Med.) 2007]**

(a) Three ☐ (b) Four ☐

(c) One ☐ (d) Two ☐

247. Which one of the following vitamins is water soluble? **[CBSE (Med.) 2007]**

(a) Vitamin K ☐ (b) Vitamin A ☐

(c) Vitamin B ☐ (d) Vitamin E ☐

248. Vitamin B_{12} contains: **[BCECE (Med.) 2007]**

(a) Co ☐ (b) Mn ☐

(c) Mg ☐ (d) Fe ☐

249. The vitamin which is neither soluble in water nor in fat is: **[PMT (Kerala) 2007]**

(a) biotin ☐ (b) phylloquinone ☐

(c) thiamine ☐ (d) ergocalciferol ☐

(e) pyridoxine ☐

250. The hormone that helps in the conversion of glucose to glycogen is: **[UGET (Med.) 2007]**

(a) cortisone ☐ (b) bile acids ☐

(c) adrenaline ☐ (d) insulin ☐

251. Pickout the statement which is not true? **[PET (Kerala) 2007]**

(a) Tetrazine is harmful edible colour ☐

(b) BHT is an antioxidant ☐

(c) Alitame is an artificial sweetner ☐

(d) Sodium alkyl sulphate is a cationic detergent ☐

(e) The performance of a rocket propellant is measured in terms of specific impulse ☐

252. Insulin is: **[AFMC 2007]**

(a) an amino acid ☐ (b) a protein ☐

(c) a carbohydrate ☐ (d) a lipid ☐

253. Proteins when heated with conc. HNO_3 give a yellow colour. This is: **[AMU (Med.) 2007]**

(a) oxidising test ☐ (b) xanthoprotic test ☐

(c) Hoppe's test ☐ (d) acid-base test ☐

254. The beta and alpha glucose have different specific rotations. When either is dissolved in water, their rotation changes until the some fixed value results. This is called: **[AIIMS 2008]**

(a) epimerisation ☐ (b) racemisation ☐

(c) anomerisation ☐ (d) mutarotation ☐

255. Glucose contains in addition to aldehyde group: **[AFMC 2008; MGIMS (Med.) 2008]**

(a) one secondary —OH and four primary —OH groups ☐

(b) one primary —OH and four secondary —OH groups ☐

(c) two primary —OH and three secondary —OH groups ☐

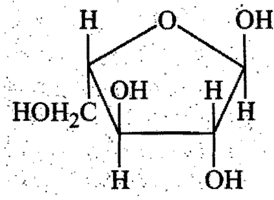
(d) three primary —OH and two secondary —OH groups ☐

256. Which of the following does not form an oxime? **[UGET (Med.) 2008]**

(a) Glucose ☐ (b) Glucose pentaacetate ☐

(c) Arabinose ☐ (d) Galactose ☐

257. Which set of terms correctly identifies the carbohydrate shown? **[PET (Kerala) 2008]**



1. Pentose 2. Hexose 3. Aldose 4. Ketose

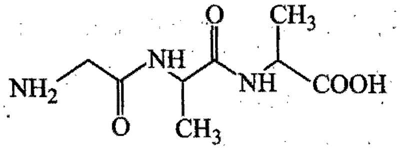
5. Pyranose 6. Furanose

(a) 1, 3 and 6 ☐ (b) 1, 3 and 5 ☐

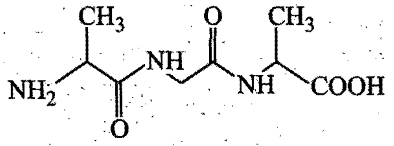
(c) 2, 3 and 5 ☐ (d) 2, 3 and 6 ☐

(e) 1, 4 and 6 ☐

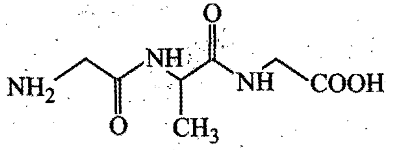
258. A tripeptide is written as Glycine-Alanine-Glycine. The correct structure of the tripeptide is: **[JEE (WB) 2008]**

(a) 

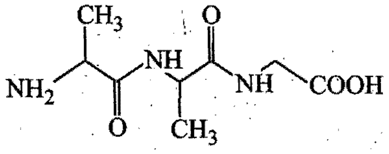
☐

(b) 

☐

(c) 

☐

(d) 

☐

259. Denaturation of protein: **[PMT (Kerala) 2008]**

(a) disrupts the primary or secondary or tertiary structure of protein ☐

(b) disrupts the secondary and tertiary structures only ☐

(c) disrupts all the primary, secondary, tertiary and even the quaternary structures of protein ☐

(d) will not affect the original biological activity ☐
(e) is always irreversible ☐

260. Which of the following sets consists only of essential amino acids? **[VITEEE 2008]**
(a) Alanine, tyrosine, cystine ☐
(b) Leucine, lysine, tryptophan ☐
(c) Alanine, glutamine, lysine ☐
(d) Leucine, proline, glycine ☐

261. In DNA, the complimentary bases are: **[CBSE (Med.) 2008]**
(a) adenine and guanine; thymine and cytosine ☐
(b) uracil and adenine; cytosine and guanine ☐
(c) adenine and thymine; guanine and cytosine ☐
(d) adenine and thymine; guanine and uracil ☐

262. Which of the following is not present in a nucleotide? **[DPMT 2008]**
(a) Cytosine ☐ (b) Guanine ☐
(c) Adenine ☐ (d) Tyrosine ☐

263. Which of the following is an amine hormone? **[CBSE (Med.) 2008]**
(a) Insulin ☐ (b) Progesterone ☐
(c) Thyroxine ☐ (d) Oxypurin ☐

264. A diabetic person carries a packet of glucose with him always, because: **[CET (Karnataka) 2009]**
(a) glucose increases the blood sugar level slowly ☐
(b) glucose reduces the blood sugar level ☐
(c) glucose increases the blood sugar level almost instantaneously ☐
(d) glucose reduces the blood sugar level slowly ☐

265. The two functional groups present in a typical carbohydrate are: **[AIEEE 2009]**
(a) —OH and —COOH ☐
(b) —CHO and —COOH ☐
(c) $>C=O$ and —OH ☐
(d) —OH and —CHO ☐

266. How many tripeptides can be prepared by linking the amino acids glycine, alanine and phenyl alanine? **[EAMCET (Engg.) 2009]**
(a) One ☐ (b) Three ☐
(c) Six ☐ (d) Twelve ☐

267. There are 20 naturally occuring amino acids. The maximum number of tripeptides that can be obtained is: **[CET (Karnataka) 2009]**
(a) 6470 ☐ (b) 7465 ☐
(c) 5360 ☐ (d) 8000 ☐

268. Enzymes actually: **[AFMC 2009]**
(a) are biological catalysts ☐
(b) are biochemical enhancers ☐
(c) decreases rate of reaction ☐
(d) increases activation energy ☐

269. A codon has a sequence of **A**, and specifies a particular **B** that is to be incorporated into a **C**. What are **A**, **B**, **C**? **[EAMCET (Engg.) 2009]**

	A	B	C	
(a)	3 bases	amino acid	carbohydrate	☐
(b)	3 acids	carbohydrate	protein	☐
(c)	3 bases	protein	amino acid	☐
(d)	3 bases	amino acid	protein	☐

270. The segment of DNA which acts as the instrumental manual for the synthesis of the protein is: **[CBSE (Med.) 2009]**
(a) ribose ☐ (b) gene ☐
(c) nucleoside ☐ (d) nucleotide ☐

271. Which of the following hormones contains iodine? **[CBSE (Med.) 2009]**
(a) Testosterone ☐ (b) Adrenaline ☐
(c) Thyroxine ☐ (d) Insulin ☐

272. Which of the following statements is not true? **[DPMT 2009]**
(a) Pheromones are secreted outside the body by the insects ☐
(b) Aspirin is analgesic and antipyretic ☐
(c) Sucrose is a dipeptide commonly known as aspartame ☐
(d) The DNA assists in the synthesis of RNA molecules ☐

SET II : This set contains the questions with two or more correct answers.

273. The essential amino acids are:
(a) glycine ☐ (b) alanine ☐
(c) valine ☐ (d) leucine ☐

274. Carbohydrates have been classified on the basis of:
(a) sugars and non-sugars ☐
(b) reducing character ☐
(c) optical activity ☐
(d) hydrolysis (complexity of structure) ☐

275. Glucose reacts with methanol in presence of dry HCl gas to form:
(a) pentamethyl derivative ☐
(b) tetramethyl derivative ☐
(c) α-methyl glucoside ☐
(d) β-methyl glucoside ☐

276. The disaccharides $(C_{12}H_{22}O_{11})$ are:
(a) cane sugar ☐ (b) raffinose ☐
(c) lactose ☐ (d) maltose ☐

277. Glucose is:
(a) dextrose ☐ (b) grape sugar ☐
(c) aldohexose ☐ (d) ketohexose ☐

278. Fructose is:
(a) grape sugar ☐ (b) fruit sugar ☐
(c) laevulose ☐ (d) ketohexose ☐

279. Fructose may be differentiated from glucose by:
(a) action of lime ☐
(b) the action of concentrated alkali ☐
(c) optical rotation ☐
(d) oxidation with nitric acid ☐

280. Glucose and fructose can be distinguished by:
(a) Fehling's solution test ☐

(b) Furfural test ☐
(c) Selivanoff's test ☐
(d) Molisch test ☐

281. Which one are polysaccharides?
(a) Sucrose ☐ (b) Inulin ☐
(c) Starch ☐ (d) Cellulose ☐

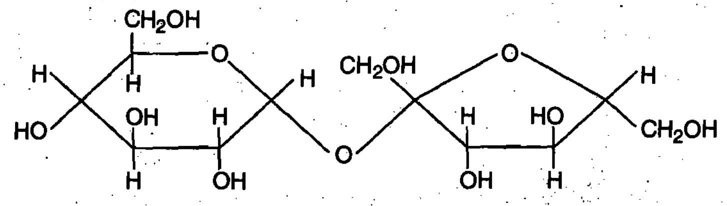
282. Glucose and fructose give same type of reactions:
(a) with phenylhydrazine ☐
(b) on reduction with Na–Hg/H_2O ☐
(c) with Fehling's solution ☐
(d) warming with dilute alkali ☐

283. Glucose does not react with:
(a) NH_2OH ☐ (b) HCN ☐
(c) $NaHSO_3$ ☐ (d) NH_3 ☐

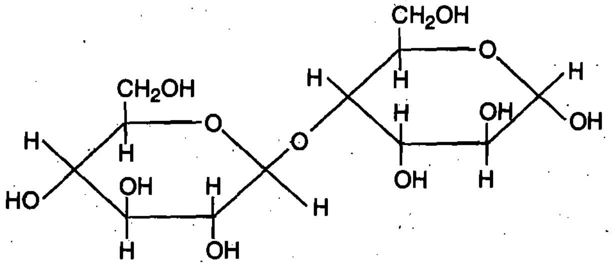
284. Mutarotation is shown by:
(a) glucose ☐ (b) fructose ☐
(c) sucrose ☐ (d) starch ☐

285. Starch is made up of:
(a) α-glucose pyranose ☐ (b) α-glucose furanose ☐
(c) β-fructose pyranose ☐ (d) β-fructose furanose ☐

286. The correct statement (s) about the following sugars *X* and *Y* is (are): **[IIT 2009]**



'X'



'Y'

(a) *X* is a reducing sugar and *Y* is a non-reducing sugar ☐
(b) *X* is a non-reducing sugar and *Y* is a reducing sugar ☐
(c) the glycosidic linkages in *X* and *Y* are α- and β- respectively ☐
(d) the glycosidic linkage in *X* and *Y* are β- and α- respectively ☐

287. Starch and its derivatives are used in:
(a) manufacture of glucose ☐
(b) manufacture of fructose ☐
(c) calicoprinting and textile industry ☐
(d) the manufacture of dextrin and adhesives ☐

288. Raffinose on hydrolysis gives:
(a) mannose ☐ (b) fructose ☐
(c) glucose ☐ (d) galactose ☐

ASSERTION-REASON TYPE QUESTIONS

These questions given below consist of an **Assertion (A)** and the **Reason (R).** Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) All monosaccharides are sweet in taste.
(R) All monosaccharides have the general formula, $C_6H_{12}O_6$.

2. (A) Fructose is the sweetest sugar.
(R) Fructose is a functional isomer of glucose.

3. (A) Fructose does not contain an aldehyde group but still reduces Tollens' reagent.
(R) In presence of dilute solution of alkali, fructose undergoes epimerization to form glucose and mannose.

4. (A) Cellulose is not digested by human beings.
(R) Cellulose is a polymer of β-*D*-glucose.

5. (A) α-amino acids have Zwitter ion structure.
(R) α-amino acids on heating form cyclic amides.

6. (A) Enzymes are proteins but proteins are not enzymes.
(R) Enzymes are biocatalysts and possess a stable configuration having an active site pocket.

7. (A) Uracil occurs in DNA.
(R) RNA undergoes replication.

8. (A) Purine base present in DNA are adenine and guanine.
(R) The base thymine is present in RNA whereas base uracil is present in DNA.

9. (A) Insulin is a globular protein.
(R) Gum is a polymer of more than one type of monosaccharides.

10. (A) A solution of sucrose in water is dextrorotatory but on hydrolysis in presence of little HCl, it becomes laevorotatory.
(R) Sucrose on hydrolysis gives unequal amounts of glucose and fructose as a result of which change in sign of rotation is observed.

11. (A) Glycosides are hydrolysed in acidic conditions.
(R) Glycosides are acetals. **[AIIMS 2003]**

12. (A) Sucrose is a non-reducing sugar.
(R) It has glycosidic linkage. **[AIIMS 2004]**

13. (A) Maltose is a reducing sugar which gives two moles of *D*-glucose on hydrolysis.
(R) Maltose has a 1, 4-β-glycosidic linkage. **[AIIMS 2005]**

14. (A) Alpha (α-) amino acids exist as internal salt in solution as they have amino and carboxylic acid groups in near vicinity.
(R) H^+ ion given by carboxylic (—COOH) group is captured by amino (—NH_2) group having lone pair of electrons. **[AIIMS 2007]**

15. (A) Disruption of the natural structure of a protein is called denaturation.
(R) The change in colour and appearance of egg during cooking is due to denaturation. **[AIIMS 2008]**

ANSWERS

OBJECTIVE QUESTIONS

1. (b)	**2.** (b)	**3.** (d)	**4.** (d)	**5.** (c)	**6.** (d)	**7.** (b)	**8.** (c)	**9.** (a)	**10.** (b)
11. (c)	**12.** (d)	**13.** (a)	**14.** (d)	**15.** (c)	**16.** (d)	**17.** (a)	**18.** (d)	**19.** (a)	**20.** (c)
21. (a)	**22.** (d)	**23.** (a)	**24.** (b)	**25.** (c)	**26.** (b)	**27.** (d)	**28.** (a)	**29.** (b)	**30.** (a)
31. (b)	**32.** (c)	**33.** (c)	**34.** (c)	**35.** (a)	**36.** (b)	**37.** (d)	**38.** (c)	**39.** (b)	**40.** (b)
41. (d)	**42.** (d)	**43.** (b)	**44.** (a)	**45.** (c)	**46.** (a)	**47.** (b)	**48.** (d)	**49.** (b)	**50.** (c)
51. (a)	**52.** (b)	**53.** (c)	**54.** (c)	**55.** (d)	**56.** (b)	**57.** (b)	**58.** (c)	**59.** (d)	**60.** (b)
61. (c)	**62.** (d)	**63.** (c)	**64.** (d)	**65.** (d)	**66.** (c)	**67.** (a)	**68.** (b)	**69.** (a)	**70.** (d)
71. (a)	**72.** (b)	**73.** (a)	**74.** (c)	**75.** (a)	**76.** (a)	**77.** (a)	**78.** (b)	**79.** (c)	**80.** (d)
81. (a)	**82.** (b)	**83.** (c)	**84.** (d)	**85.** (a)	**86.** (c)	**87.** (b)	**88.** (d)	**89.** (a)	**90.** (b)
91. (d)	**92.** (a)	**93.** (c)	**94.** (d)	**95.** (c)	**96.** (d)	**97.** (c)	**98.** (a)	**99.** (c)	**100.** (a)
101. (c)	**102.** (c)	**103.** (b)	**104.** (a)	**105.** (c)	**106.** (d)	**107.** (b)	**108.** (d)	**109.** (d)	**110.** (d)
111. (b)	**112.** (c)	**113.** (b)	**114.** (d)	**115.** (a)	**116.** (d)	**117.** (c)	**118.** (a)	**119.** (d)	**120.** (b)
121. (a)	**122.** (b)	**123.** (c)	**124.** (d)	**125.** (d)	**126.** (a)	**127.** (d)	**128.** (d)	**129.** (b)	**130.** (d)
131. (a)	**132.** (b)	**133.** (c)	**134.** (d)	**135.** (d)	**136.** (d)	**137.** (c)	**138.** (a)	**139.** (d)	**140.** (d)
141. (b)	**142.** (c)	**143.** (d)	**144.** (a)	**145.** (b)	**146.** (b)	**147.** (c)	**148.** (b)	**149.** (b)	**150.** (d)
151. (d)	**152.** (b)	**153.** (c)	**154.** (b)	**155.** (a)	**156.** (b)	**157.** (c)	**158.** (b)	**159.** (c)	**160.** (a)
161. (b)	**162.** (a)	**163.** (c)	**164.** (d)	**165.** (b)	**166.** (d)	**167.** (c)	**168.** (b)	**169.** (d)	**170.** (b)
171. (a)	**172.** (d)	**173.** (a)	**174.** (c)	**175.** (c)	**176.** (b)	**177.** (d)	**178.** (d)	**179.** (c)	**180.** (a)
181. (d)	**182.** (a)	**183.** (a)	**184.** (c)	**185.** (a)	**186.** (a)	**187.** (a)	**188.** (d)	**189.** (b)	**190.** (b)
191. (a)	**192.** (d)	**193.** (c)	**194.** (b)	**195.** (c)	**196.** (a)	**197.** (c)	**198.** (c)	**199.** (b)	**200.** (b)
201. (a)	**202.** (a)	**203.** (b)	**204.** (b)	**205.** (a)	**206.** (c)	**207.** (a)	**208.** (b)	**209.** (c)	**210.** (b)
211. (d)	**212.** (d)	**213.** (d)	**214.** (c)	**215.** (d)	**216.** (c)	**217.** (a)	**218.** (d)	**219.** (c)	**220.** (a)
221. (d)	**222.** (c)	**223.** (a)	**224.** (a)	**225.** (e)	**226.** (c)	**227.** (c)	**228.** (b)	**229.** (b)	**230.** (a)
231. (a)	**232.** (a)	**233.** (b)	**234.** (b)	**235.** (a)	**236.** (d)	**237.** (b)	**238.** (b)	**239.** (d)	**240.** (b)
241. (b)	**242.** (c)	**243.** (a)	**244.** (d)	**245.** (b)	**246.** (a)	**247.** (c)	**248.** (a)	**249.** (a)	**250.** (d)
251. (d)	**252.** (b)	**253.** (b)	**254.** (d)	**255.** (b)	**256.** (b)	**257.** (a)	**258.** (c)	**259.** (b)	**260.** (b)
261. (c)	**262.** (d)	**263.** (c)	**264.** (c)	**265.** (c)	**266.** (c)	**267.** (d)	**268.** (a)	**269.** (d)	**270.** (b)
271. (c)	**272.** (c)	**273.** (c,d)	**274.** (a,b,d)	**275.** (c,d)	**276.** (a,c,d)	**277.** (a,b,c)	**278.** (b,c,d)	**279.** (a,b,c,d)	**280.** (b,c)
281. (b,c,d)	**282.** (a,c,d)	**283.** (c,d)	**284.** (a,b)	**285.** (a,d)	**286.** (b,c)	**287.** (a,c,d)	**288.** (b,c,d)		

ASSERTION-REASON TYPE QUESTIONS

1. (c)	**2.** (b)	**3.** (a)	**4.** (b)	**5.** (a)	**6.** (a)	**7.** (d)	**8.** (c)	**9.** (b)	**10.** (c)
11. (a)	**12.** (b)	**13.** (c)	**14.** (a)	**15.** (b)					

BRAIN STORMING PROBLEMS

1. The function of DNA in biological organism is to :
(a) assist in the synthesis of RNA molecule ☐
(b) store information of heridity characteristics ☐
(c) assist in the synthesis of protein and polypeptide ☐
(d) all of the above ☐

2. A nanopeptide contains how many peptide linkages?
(a) 10 ☐ (b) 8 ☐
(c) 9 ☐ (d) 18 ☐

3. Phospholipids are esters of glycerol with :
(a) three carboxylic acid residues ☐
(b) two carboxylic acid residues and one phosphate group ☐
(c) one carboxylic acid residue and two phosphate groups ☐
(d) three phosphate groups ☐

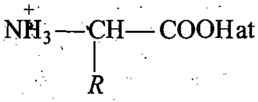
4. Addison's disease is due to the deficiency in the secretions of which harmone?
(a) Adrenals ☐ (b) Testosterone ☐
(c) Progesterone ☐ (d) Diethyl stillbestrol ☐

5. Match **List I** with **List II** and select the correct answer using the codes given below the lists:

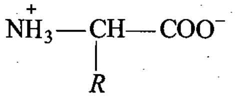
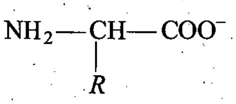
List I (Name of vitamin)	**List II** (Deficiency result)
I. Ascorbic acid	A. Beri-beri
II. Retinol	B. Cracked lips
III. Riboflavin	C. Scurvy
IV. Thiamine	D. Night-blindness

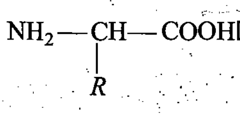
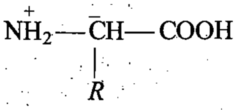
Codes :
(a) I-B, II-A, III-C, IV-D ☐ (b) I-A, II-B, III-C, IV-D ☐
(c) I-D, II-C, III-B, IV-A ☐ (d) I-C, II-D, III-B, IV-A ☐

6. Which of the following exist in Zwitter ionic form?
(a) Alanine ☐ (b) Glucose ☐
(c) Fructose ☐ (d) Ethanamide ☐

7. An α-amino acid exists as,  $\overset{+}{N}H_3—\underset{R}{\underset{|}{CH}}—COOH$ at (pH = 2)

and its isoelectric point is 6. The amino acid at pH 10.97 will exist as :

(a)  $\overset{+}{N}H_3—\underset{R}{\underset{|}{CH}}—COO^-$ ☐ (b)  $NH_2—\underset{R}{\underset{|}{CH}}—COO^-$ ☐

(c)  $NH_2—\underset{R}{\underset{|}{CH}}—COOH$ ☐ (d)  $\overset{+}{N}H_2—\underset{R}{\underset{|}{\bar{C}H}}—COOH$ ☐

8. Semi essential amino acids are :
(a) aspartic acid and histidine ☐
(b) arginine and histidine ☐
(c) lysine and histidine ☐
(d) aspartic acid and arginine ☐

9. Which of the following biomolecules will give blue colouration with Cu^{2+} and purple colour with ninhydrin solution?
(a) Aldehyde ☐ (b) α-Amino acid ☐
(c) Carbohydrate ☐ (d) DNA ☐

10. Match **List I** with **List II** and select the correct answer from the given codes:

List I	**List II**
A. First amino acid synthesised in lab	(i) Glycine
B. Sulphur containing amino acid	(ii) Cystine
C. Amino acid of highest isoelectric point	(iii) Methionine
D. Optically inactive amino acid	(iv) Arginine

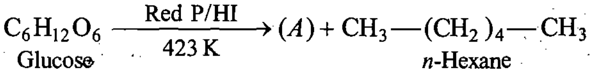
Codes :	**A**	**B**	**C**	**D**	
(a)	(i)	(ii)	(iii)	(iv)	☐
(b)	(iii)	(ii)	(iv)	(i)	☐
(c)	(iii)	(iv)	(ii)	(i)	☐
(d)	(iv)	(iii)	(ii)	(i)	☐

11. Which of the following orders of sweetness is correct?
(a) Sucrose > glucose > fructose > maltose ☐
(b) Fructose > sucrose > glucose > maltose ☐
(c) Fructose > sucrose > maltose > glucose ☐
(d) Glucose > fructose > sucrose > maltose ☐

12. Which among the following is the monomer of starch?
(a) Glucose ☐ (b) Sucrose ☐
(c) Fructose ☐ (d) Lactose ☐

13. Prosthetic group of glycoprotein is:
(a) fat ☐ (b) carbohydrate ☐
(c) protein ☐ (d) nucleic acid ☐

14. In the given reaction,



$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[423\text{ K}]{\text{Red P/HI}} (A) + \underset{n\text{-Hexane}}{CH_3—(CH_2)_4—CH_3}$$

the compound '*A*' is:
(a) 2-iodohexane ☐ (b) 1-iodohexane ☐
(c) 3-iodohexane ☐ (d) 4-iodohexane ☐

15. $A \xrightarrow{HOH/H^+}$ glucose + fructose

$B \xrightarrow{HOH/H^+}$ glucose + glucose

$C \xrightarrow{HOH/H^+}$ glucose + galactose

the disaccharides A, B and C respectively are :
(a) lactose, sucrose, maltose ☐
(b) sucrose, maltose, lactose ☐
(c) sucrose, lactose, maltose ☐
(d) maltose, sucrose, lactose ☐

16. $$\text{Glucose} \xrightarrow[\text{(C}_6\text{H}_5\text{NHNH}_2\text{)}]{\text{Phenylhydrazine}} X$$

$$\text{Fructose} \xrightarrow[\text{(C}_6\text{H}_5\text{NHNH}_2\text{)}]{\text{Phenylhydrazine}} Y$$

X and *Y* are :
(a) different osazones ☐
(b) same osazones ☐
(c) each molecule of glucose reacts with 3 molecules of phenylhydrazine ☐
(d) each molecule of fructose reacts with 2 molecules of phenylhydrazine ☐

17. Amino acid molecules are usually :
(a) laevo ☐ (b) dextro ☐
(c) meso ☐ (d) racemic ☐

18. In a chemical test, a biomolecule gives purple ring on treatment with α-naphthol and conc. H_2SO_4. The chemical test and biomolecule respectively are :
(a) molisch test, protein ☐
(b) molisch test, carbohydrate ☐
(c) ninhydrin test, carbohydrate ☐
(d) ninhydrin test, protein ☐

19. Match **List I** with **List II** and select the correct answer from the codes given below the list:

List I (Name of protein)	**List II** (Type of protein)
A. Haemoglobin	(i) Chromoprotein
B. Mucoproteins	(ii) Phosphoprotein
C. Casein	(iii) Glucoprotein
D. Haemocyanin	(iv) Metalloprotein and chromoprotein

Codes :	A	B	C	D	
(a)	(i)	(ii)	(iii)	(iv)	☐
(b)	(iv)	(i)	(ii)	(iii)	☐
(c)	(iv)	(iii)	(ii)	(i)	☐
(d)	(i)	(iv)	(iii)	(ii)	☐

20. Raffinose is a molecule of carbohydrate. It is a trisaccharide containing:
(a) fructose, glucose, galactose ☐
(b) fructose, glucose, glucose ☐
(c) galactose, galactose, glucose ☐
(d) glucose, fructose, sucrose ☐

21. Which of the following is/are reducing sugar(s)?
(a) Sucrose ☐ (b) Fructose ☐
(c) Maltose ☐ (d) Starch ☐

22. Which of the isoelectric pH can be calculated using following relation?
(a) $\frac{1}{2}[pK_{a_1} + pK_{a_2}]$ ☐ (b) $\frac{1}{2}[pK_{a_1} - pK_{a_2}]$ ☐
(c) $2[pK_{a_1} + pK_{a_2}]$ ☐ (d) $2[pK_{a_1} - pK_{a_2}]$ ☐

23. Match **List I** with **List II** and select the correct answer from the codes given below the list:

List I (Metal)	**List II** (Enzyme)
A. Fe	(i) Ascorbic acid oxidase
B. Cu	(ii) Cytochrome oxidase
C. Ni	(iii) Alcohol dehydrogenase
D. Zn	(iv) Urease

Codes :	A	B	C	D	
(a)	(i)	(ii)	(iii)	(iv)	☐
(b)	(ii)	(i)	(iv)	(iii)	☐
(c)	(iv)	(iii)	(ii)	(i)	☐
(d)	(i)	(iv)	(iii)	(ii)	☐

24. Which one of the following polysaccharides is composed of β- glycosidic link?
(a) Starch ☐ (b) Glycogen ☐
(c) Dextrin ☐ (d) Cellulose ☐

25. Ribose and deoxyribose differ in structure around a single carbon, namely:
(a) C-1 ☐ (b) C-2 ☐
(c) C-3 ☐ (d) C-4 ☐

26. The carbon atoms involved in osazone formation are:
(a) 1 and 2 ☐ (b) 2 and 3 ☐
(c) 3 and 4 ☐ (d) 5 and 6 ☐

27. The bonds in protein structure, that are not broken on denaturation, are:
(a) hydrogen bonds ☐ (b) peptide bonds ☐
(c) ionic bonds ☐ (d) disulphide bonds ☐

28. The number of base pairs present in each turn of DNA helix is:
(a) 9 ☐ (b) 10 ☐
(c) 11 ☐ (d) 12 ☐

29. Functionally active form of vitamin D is:
(a) cholecalciferol ☐ (b) ergocalciferol ☐
(c) dehydro cholesterol ☐ (d) calcitriol ☐

30. Which one of the following is the most important essential fatty acid in the diet?
(a) Linoleic acid ☐ (b) Arachidonic acid ☐
(c) Oleic acid ☐ (d) Palmitic acid ☐

31. The phenomenon of mutarotation is exhibited by :
(a) glucose ☐ (b) fructose ☐
(c) sucrose ☐ (d) maltose ☐

32. Select the carbohydrate which gives only glucose on hydrolysis:
(a) sucrose ☐ (b) lactose ☐
(c) maltose ☐ (d) galactose ☐

33. Match **List I** with **List II** and select the correct answer from the given codes:

List I (Carbohydrate)	**List II** (Source)
A. Glucose	(i) Sugar cane
B. Fructose	(ii) Milk
C. Lactose	(iii) Fruit
D. Sucrose	(iv) Grape

Codes :	**A**	**B**	**C**	**D**	
(a)	(iv)	(iii)	(ii)	(i)	☐
(b)	(i)	(ii)	(iii)	(iv)	☐
(c)	(i)	(iv)	(ii)	(iii)	☐
(d)	(iii)	(i)	(ii)	(iv)	☐

34. Rice does not contain:
(a) alanine ☐ (b) glycine ☐
(c) lysine ☐ (d) leucine ☐

35. Which of the following is not found in nucleotides?
(a) Guanine ☐ (b) Cytosine ☐
(c) Adenine ☐ (d) Tyroxine ☐

36. Which of the following do not undergo hydrolysis?
(a) Glucose ☐ (b) Fructose ☐
(c) Cane sugar ☐ (d) Maltose ☐

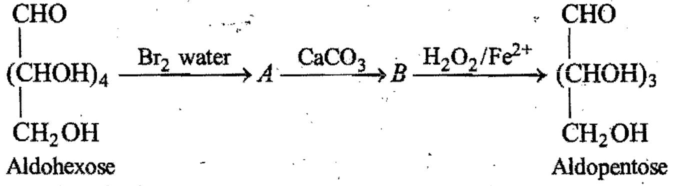
37. The amino acids which has a non-polar side chain is :
(a) lysine ☐ (b) serine ☐
(c) aspartic acid ☐ (d) alanine ☐

38. Insulin has 51 amino acids in two polypeptide chains, these polypeptide chains are cross-linked by :
(a) peroxy link ☐
(b) disulphide bond ☐
(c) diazobond ☐
(d) two carbon-carbon double bonds ☐

39. The pK_{a_1} and pK_{a_2} values of alanine are 2.3 and 9.7 respectively. The isoelectric point of alanine is :
(a) 3 ☐ (b) 7 ☐
(c) 8 ☐ (d) 6 ☐

[**Hint :** Isoelectric point $= \frac{1}{2}[\text{p}K_{a_1} + \text{p}K_{a_2}]$
$= \frac{1}{2}[2.3 + 9.7] = 6$]

40. The reaction,



$$\underset{\text{Aldohexose}}{\begin{array}{c}\text{CHO}\\ |\\ (\text{CHOH})_4\\ |\\ \text{CH}_2\text{OH}\end{array}} \xrightarrow{\text{Br}_2\text{ water}} A \xrightarrow{\text{CaCO}_3} B \xrightarrow{\text{H}_2\text{O}_2/\text{Fe}^{2+}} \underset{\text{Aldopentose}}{\begin{array}{c}\text{CHO}\\ |\\ (\text{CHOH})_3\\ |\\ \text{CH}_2\text{OH}\end{array}}$$

is called :
(a) Ruff degradation ☐
(b) Hofmann's degradation ☐
(c) Killiani-Fischer synthesis ☐
(d) Wacker's synthesis ☐

ANSWERS : BRAIN STORMING PROBLEMS

1. (d)	**2.** (b)	**3.** (b)	**4.** (a)	**5.** (d)	**6.** (a,d)	**7.** (b)	**8.** (b)	**9.** (b)	**10.** (b)
11. (b)	**12.** (a)	**13.** (b)	**14.** (a)	**15.** (b)	**16.** (b,c)	**17.** (a)	**18.** (b)	**19.** (c)	**20.** (a)
21. (b,c)	**22.** (a)	**23.** (b)	**24.** (c)	**25.** (b)	**26.** (a)	**27.** (b)	**28.** (b)	**29.** (d)	**30.** (a)
31. (a,b,d)	**32.** (c)	**33.** (a)	**34.** (c)	**35.** (d)	**36.** (a,b)	**37.** (d)	**38.** (b)	**39.** (d)	**40.** (a)

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Carbohydrates are polyhydroxy aldehydes and ketones and those compounds which on hydrolysis give such compounds are also carbohydrates. The carbohydrates which are not hydrolysed are called monosaccharides. Other carbohydrates are oligosaccharides and polysaccharides. Monosaccharides with aldehydic group are called aldose and those with free ketonic groups are called ketose. Carbohydrates are optically active.

Number of optical isomers = 2^n

Where, n = number of asymmetric carbons. Carbohydrates are mainly synthesised by plants during photosynthesis.

Answer the following questions :

1. Maximum number of monosaccharide units present in oligosaccharides is :
   (a) 8 (b) 10
   (c) 15 (d) 40
2. Aldose sugar present in nucleic acid is :
   (a) arabinose (b) xylose
   (c) deoxyribose (d) all of these
3. First member of ketose sugar is :
   (a) ketotriose (b) ketotetrose
   (c) ketopentose (d) ketohexose
4. First member of aldose sugar is :
   (a) aldotriose (b) aldotetrose
   (c) aldopentose (d) aldohexose
5. In the molecule, $CH_2OHCHOHCHOHCHOHCHOHCHO$, the number of optical isomers will be :
   (a) 16 (b) 8
   (c) 32 (d) 4

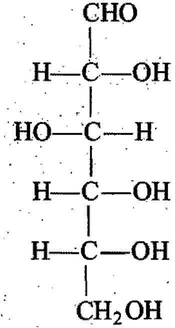
Passage 2

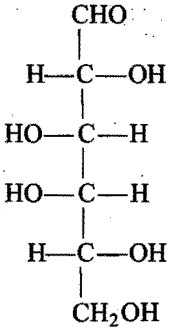
Carbohydrates which differ in configuration at glycosidic carbon (*i.e.*, C-1 in aldoses and C-2 in ketoses) are called anomers. The carbohydrates which differ in configuration at any asymmetric carbon atom other than glycosidic carbon are called epimers. The anomers whose configuration differ at C-1 are diastereomers. The diastereomers are not mirror image of each other and their physical properties are different. Epimers are also configurational diastereomers.

Answer the following questions:

Select whether the following statements are true or false :

1. Glucose and mannose are epimers.
   (a) True (b) False
2. The compounds given below are anomers.


D-Glucose


D-Galactose

   (a) True (b) False
3. α-(D) glucose and β-(D) glucose are anomers.
   (a) True (b) False
4. Glucose $\xrightarrow{\text{Epimerisation}}$ Mannose
   Epimerisation can be achieved by adding aqueous solution of NaOH.
   (a) True (b) False
5. Glucose and fructose are also epimers.
   (a) True (b) False

Passage 3

Three carbohydrate molecules A, B and C were analysed by a scientist for their identification. Their characteristics are tabulated as:

Reagent/Information		*A*	*B*	*C*
1.	Tollens' reagent	Forms silver mirror	Forms silver mirror	No effect
2.	Fehling's solution	Forms red precipitate	Forms red precipitate	No effect
3.	Phenylhydrazine	Osazone (yellow ppt.)	Same osazone (yellow ppt.)	No effect
4.	Resorcinol + HCl (aq.)	No colouration	Red or brown coloured precipitate	Reddish brown precipitate which dissolves in ethanol
5.	Molecular formula	$C_6H_{12}O_6$	$C_6H_{12}O_6$	$C_{12}H_{22}O_{11}$
6.	Hydrolysis in acidic medium	No hydrolysis	No hydrolysis	Gives A and B
7.	Melting point	146°C	102°C	185°C

Answer the following questions :

1. Which of the following is not a reducing sugar ?

(a) *A* (b) *B*
(c) *C* (d) All of these

2. Compound (*C*) has no free carbonyl group. It is a disaccharide named :

(a) sucrose (b) lactose
(c) fructose (d) none of these

3. Match **List I** with **List II** and select the correct answer from the codes given below the list:

List I	**List II**
Compound (*A*)	(i) Sucrose
Compound (*B*)	(ii) Glucose
Compound (*C*)	(iii) Fructose

Codes :	**A**	**B**	**C**	
(a)	Glucose	Fructose	Sucrose	☐
(b)	Fructose	Glucose	Sucrose	☐
(c)	Sucrose	Glucose	Fructose	☐
(d)	Sucrose	Fructose	Glucose	☐

4. Which of the following will not show mutarotation ?

(a) *A* (b) *B*
(c) *C* (d) All of these

5. Compound (*A*) and (*B*) have same configuration at :

(a) C-1 and C-3 (b) C-1 and C-2
(c) C-2 and C-3 (d) C-3 and C-4

ANSWERS :LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	**1.** (b)	**2.** (c)	**3.** (b)	**4.** (a)	**5.** (a)
Passage 2	**1.** (a)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (b)
Passage 3	**1.** (c)	**2.** (a)	**3.** (a)	**4.** (c)	**5.** (d)

16

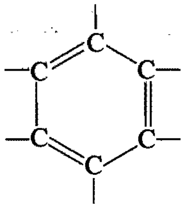
AROMATIC COMPOUNDS

(Benzene and its Derivatives)

16.1 MEANING OF THE TERM AROMATIC

The term **aromatic** has been derived from the Greek word *aroma* meaning pleasant odour. Earlier chemists applied this term to those organic compounds which differed from aliphatic and alicyclic compounds and possessed pleasant odour or derived from odourous compounds. The compounds such as balsams, resins, essential oils, etc., were called aromatic compounds. The term aromatic is, however, a misnomer, as now it is known that all aromatic compounds do not necessarily possess pleasant smell. Not only that, many of the aliphatic compounds also possess fine fragrance.

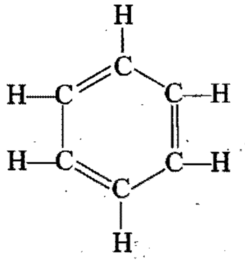
On close examination, it was found that aromatic compounds have a higher percentage of carbon in comparison to aliphatic compounds and were associated with chemical stability. With the development of structural theory, the stable character of aromatic compounds was attributed to the presence of hexagonal ring structure specific of benzene, *i.e.*, they contained at least six carbon atoms connected by a conjugate system of three double bonds, forming a hexagonal ring known as **benzene nucleus.**



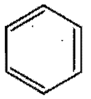
The term aromatic is now reserved for benzene and for all carbocyclic derivatives which resemble with benzene in chemical behaviour. These are also called benzenoid compounds. However, there are some compounds which resemble benzene in their chemical behaviour but do not contain benzene ring. Such compounds are termed as non-benzenoid compounds. Examples are furan, thiophene, pyrrole and pyridine, etc.

All aromatic hydrocarbons (benzene, naphthalene, anthracene, etc.) have been given a new name 'Arenes'. Thus, the term aromatic compounds stands for arenes and their derivatives.

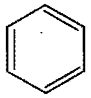
Benzene is the simplest aromatic hydrocarbon. It is represented in one of the following manners:



(i)

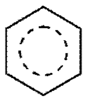


(ii)



(iii)

(iv)

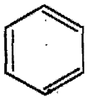
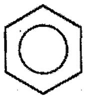
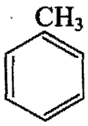
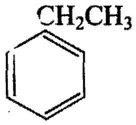
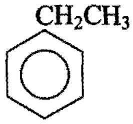
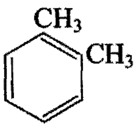
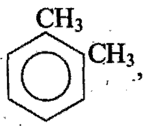
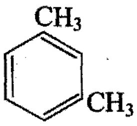
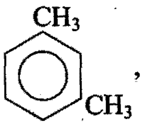
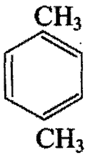
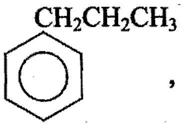
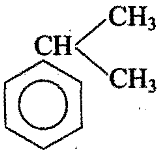
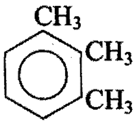
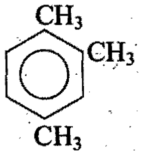
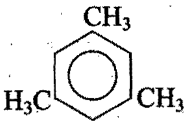


(v)

The common names and structures of some of the aromatic hydrocarbons (arenes) are given below along with classification:

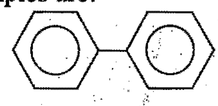
All arenes have general formula, C_nH_{2n-6y} where y is the number of benzene rings and n is not less than six. These are divided into two groups:

(i) Monocyclic aromatic hydrocarbons : These consist of only one benzene ring, *i.e.*, $y = 1$ (General formula: C_nH_{2n-6}) and include benzene and its homologues.

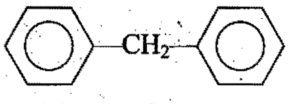
C_6H_6,		or			Benzene
C_7H_8,		or	 ,	$C_6H_5CH_3$	Toluene (Methylbenzene)
C_8H_{10},		or	 ,	$C_6H_5CH_2CH_3$	Ethylbenzene
		or	 ,	$C_6H_4{<}^{CH_3}_{CH_3}$	*Ortho*-xylene (1,2-Dimethylbenzene)
		or	 ,	$C_6H_4{<}^{CH_3}_{CH_3}$	*Meta*-xylene (1,3-Dimethylbenzene)
		or	 ,	$C_6H_4{<}^{CH_3}_{CH_3}$	*Para*-xylene (1,4-Dimethylbenzene)
C_9H_{12},	 ,			$C_6H_5CH_2CH_2CH_3$	*n*-Propylbenzene
	 ,			$C_6H_5CH{<}^{CH_3}_{CH_3}$	Isopropylbenzene (Cumene)
	 ,			$C_6H_3(CH_3)_3$	Adjacent trimethylbenzene (1,2,3)
	 ,			$C_6H_3(CH_3)_3$	Unsymmetrical trimethylbenzene (1,2,4)
	 ,			$C_6H_3(CH_3)_3$	Symmetrical trimethylbenzene (Mesitylene) (1,3,5)

(ii) Polycyclic aromatic hydrocarbons : These contain two or more benzene rings. These are further divided into two classes:

(a) Those which contain **isolated** benzene rings. Examples are:

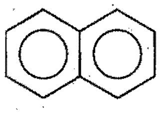


Diphenyl
($C_{12}H_{10}$)

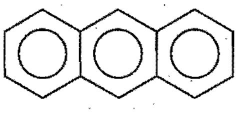


Diphenylmethane
($C_{13}H_{12}$)

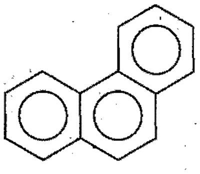
(b) Those in which two or more benzene rings are **fused** or **condensed.** Examples are:



Naphthalene
($C_{10}H_8$)



Anthracene
($C_{14}H_{10}$)

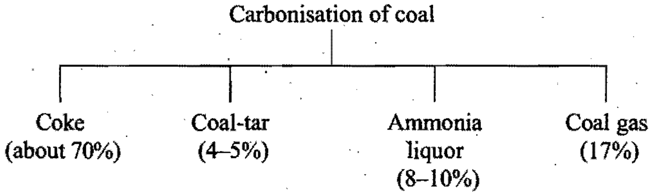


Phenanthrene
($C_{14}H_{10}$)

16.2 SOURCES OF AROMATIC HYDROCARBONS AND AROMATIC COMPOUNDS

Coal and petroleum are the two important sources of aromatic hydrocarbons and other aromatic compounds. Till about 1950, coal was the chief source of these compounds but now petroleum is the main source.

Coal is a complex mixture of aromatic compounds with large quantities of free carbon. When coal is heated in steel retorts at high temperatures in absence of air, it changes into non-volatile material coke. The process is called carbonisation or coking of coal. Carbonisation gives a number of volatile products besides coke.



One of the products of carbonisation is a black viscous oil with unpleasant odour, known as coal-tar which is used as a solvent for dry cleaning and in the manufacture of dyes, drugs, perfumes, explosives and plastics, etc. The actual composition of the coal-tar varies with the nature of the coal and carbonising temperature. Besides suspended carbon particles, the following common substances are present in coal-tar:

(i) Neutral : Benzene, toluene, xylenes, naphthalene, anthracene, etc. Water (about 50%).
(ii) Acidic : Phenol, cresols, etc.
(iii) Basic : Pyridine, quinoline, etc.

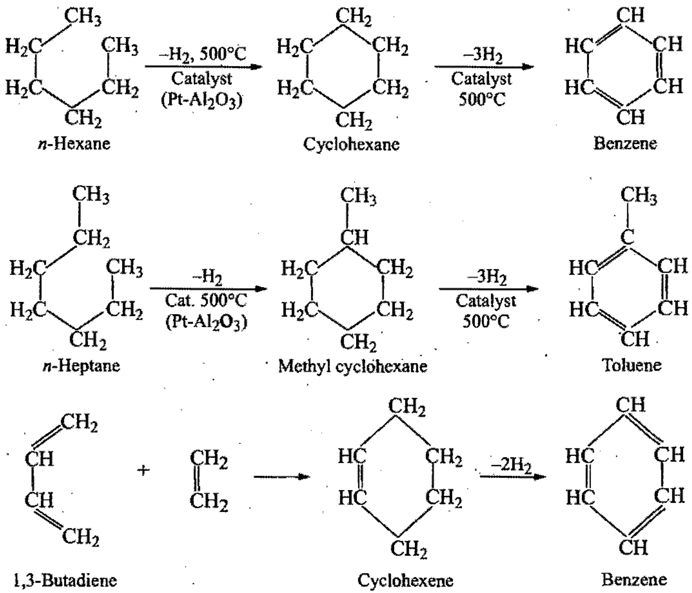
The removal of water is necessary before coal-tar is subjected to fractional distillation.

Coal-tar distillation : Coal-tar still contains about 4% water. It is taken in a preheater where it is heated by a pipe through which the vapours of the still are passing. Here it loses most of the water along with some low boiling hydrocarbons. The following fractions are collected separately at different temperatures:

Main fraction	Temperature range	Chief constituents
1. Light oil or crude naphtha	80–170 °C	Benzene, toluene, xylenes, etc.
2. Middle oil or carbolic acid	170–230 °C	Phenol, naphthalene, pyridine, etc.
3. Heavy oil or creosote oil	230–270 °C	Cresols, naphthalene, quinoline, etc.
4. Green oil or anthracene oil	270–360 °C	Anthracene, phenanthrene, etc.
5. Pitch	Residue	90–94% of carbon

Each fraction is then worked by and its constituents are separated.

Petroleum as a source : Today most of the benzene, toluene and xylenes are obtained from petroleum. These are actually the raw materials for most of the aromatic compounds. C_6 to C_8 fraction of petroleum naphtha is heated over platinum-rhenium-alumina catalyst at 520°C at about 20 atmospheric pressure. This process is termed as **catalyst-reforming.** The process converts alkanes into cyclo alkanes and aromatic hydrocarbons.



16.3 GENERAL CHARACTERISTICS OF AROMATIC COMPOUNDS OR COMPARISON OF AROMATIC AND ALIPHATIC COMPOUNDS

1. Aromatic compounds are ring or closed-chain compounds while aliphatic compounds have open-chain structure.

2. Aromatic compounds are richer in carbon content than the aliphatic ones. The benzene, C_6H_6, contains 92.3% carbon but hexane, C_6H_{14} has 83.7% carbon. On account of being

richer in carbon content, aromatic compounds burn with smoky flame with chloroform and chloral hydrate as an exception.

3. Though aromatic compounds are unsaturated (benzene nucleus consists of three double bonds), yet they are stable. They undergo substitution reactions like halogenation, nitration, sulphonation, etc.

(a) Concentrated nitric acid converts the aromatic hydrocarbons and their derivatives to nitro derivatives (nitration). Direct introduction of —NO_2 group into aliphatic compounds is rather uncommon.

(b) With concentrated sulphuric acid, aromatic compounds form sulphonic acids (sulphonation). Sulphonation is practically unknown in aliphatic compounds.

4. Hydroxy derivatives of aromatic compounds (phenols) are acidic in nature whereas those of corresponding alcohols are neutral.

5. Aromatic amino compounds are less basic than aliphatic amines.

6. Chlorine and bromine form addition as well as substitution products with aromatic hydrocarbons. The substitution is more common. Monohalogen derivatives of benzene are more stable and less reactive than alkyl halides. They are not affected by most of the reagents which react with alkyl halides under normal conditions.

7. Primary amines of aromatic hydrocarbons react with nitrous acid to form diazo compounds (diazotisation). This does not occur in aliphatic amines. Aliphatic primary amines with nitrous acid form alcohols.

8. Homologues of benzene, irrespective of the length of the chain, get oxidised to benzoic acid, *i.e.*, benzene nucleus is stable and side chain gets oxidised. No such relationship is known in the aliphatic series.

9. A number of reactions such as Friedel-Crafts reaction, Perkin reaction, chloromethylation, mercuration, etc., are only shown by aromatic compounds.

10. **Aromaticity :** Aromatic compounds are cyclic and planar. They undergo substitution rather than addition reactions. This property is common to all aromatic compounds and is referred to as **aromaticity** or **aromatic character.** Aromaticity is due to extensive delocalisation of π-electrons in planar ring-system. According to **Hückel rule** all aromatic compounds must have $(4n+2)\pi$ electrons where n is an integer, *i.e.*, $n = 0, 1, 2, 3, \ldots$ and possesses unusual stability due to complete delocalization of π-electrons.

Hückel rule is not applicable to non-aromatic compounds, even if they are cyclic and planar in nature. Taking the following examples, we can prove the validity of Hückel rule:

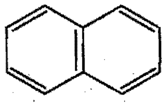
(a) Benzene : In benzene, there are three double bonds (All carbon atoms are sp^2 hybridised), *i.e.*, 6π electrons.

$$4n+2=6$$
$$4n=6-2=4$$
$$n=1$$

Therefore, benzene shows aromatic character.

(b) Naphthalene : There are five double bonds in naphthalene, *i.e.*, 10π electrons.

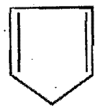
$$4n+2=10$$
$$4n=10-2=8$$
$$n=2$$



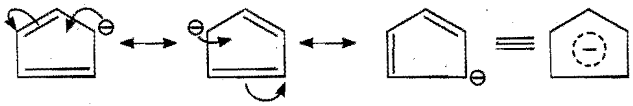
Therefore, naphthalene shows aromatic character.

(c) Cyclopentadiene : The molecule consists of two double bonds (All carbon atoms are not sp^2 hybridised), *i.e.*, 4π electrons.

$$4n+2=4$$
$$4n=4-2=2$$
$$n=0.5 \text{ (not an integer)}$$



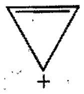
Therefore, cyclopentadiene is non-aromatic.
Cyclopentadienide ion is aromatic.



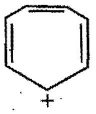
It has 6π electrons used in delocalisation (including one lone pair)

∴ $(4n+2)\,\pi$ Hückel rule is verified for $n=1$. Hence, it is aromatic.

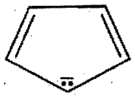
In addition to these compounds, there are a number of monocyclic ions which are aromatic in character according to Hückel's rule. Examples are:



Cyclopropenyl
cation (2π '*e*')
(Cyclopropenium salt)



Cycloheptatrienyl
cation
(6π '*e*')



Cyclopentadienide
anion
(6π '*e*')

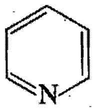
Therefore, **aromaticity** may be defined as **"An aromatic compound having a reasonably planar cyclic structure with $(4n+2)\pi$ electron clouds and possessing unusual stability due to delocalization of π-electrons".**

SOME SOLVED EXAMPLES

Problem 1. *Show whether the following compounds exhibit aromaticity.*

(a) Pyridine, (b) Cyclo-octatetraene, (c) Pyrrole,
(d) Cyclobutadiene, (e) Furan, (f) Thiophene.

Solution : (a) Pyridine has the following structure:

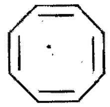


It has three double bonds, *i.e.*, 6π electrons.

$$4n+2=6$$
$$4n=6-2=4$$
$$n=1$$

Therefore, pyridine shows aromaticity.

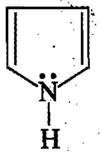
(b) Cyclo-octatetraene has the following structure:

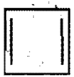


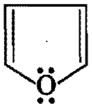
It has four double bonds, *i.e.*, 8π electrons.

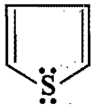
$$4n+2=8$$
$$4n=8-2=6$$
$$n=1.5 \text{ (not an integer)}$$

Therefore, cyclo-octatetraene does not show aromaticity.

(c) Pyrrole,  shows aromaticity.

(d) Cyclobutadiene,  is non-aromatic.

(e) Furan,  shows aromaticity.

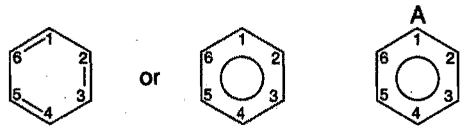
(f) Thiophene,  shows aromaticity.

16.4 ISOMERISM AND NOMENCLATURE OF BENZENE DERIVATIVES

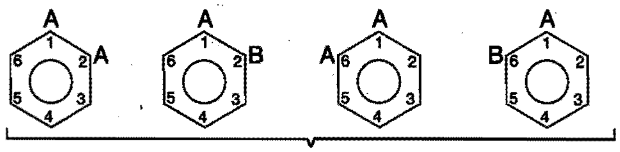
Benzene derivatives are obtained by the replacement of one, two, three, four, five or six hydrogen atoms from the benzene molecule with equal number of univalent groups.

$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow[+X]{-H} \underset{\text{Monosubstituted}}{C_6H_5X} \xrightarrow[+X]{-H} \underset{\text{Disubstituted}}{C_6H_4X_2} \xrightarrow[+X]{-H} \underset{\text{Trisubstituted}}{C_6H_3X_3} \;\ldots\ldots\; \underset{\text{Polysubstituted}}{C_6X_6}$$

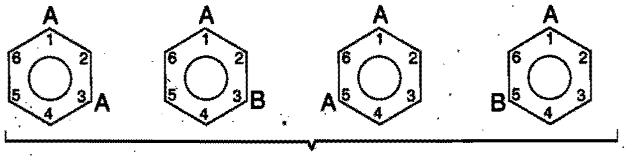
Since, all the six hydrogen atoms in benzene are equivalent, **only one monosubstituted derivative is possible.** Thus, any one carbon atom in the benzene ring can be numbered as 1 but for uniformity the top carbon atom of the nucleus is numbered as 1, while the rest are numbered in clockwise direction, as shown below:



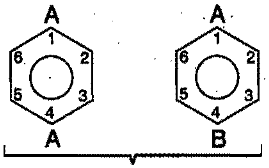
When two hydrogen atoms in benzene are replaced by two univalent groups (which may be same or different), three position isomers are possible. Since, the six hydrogen atoms in benzene are equivalent, the position 1,2 and 1,6 are equivalent. The 1,2 (or 1,6) disubstituted benzene derivative is known as the ***ortho* (*o*-)** compound. The 1,3 and 1,5 positions are equivalent and a 1,3 (or 1,5) disubstituted derivative is known as the ***meta* (*m*-)** compound. The 1,4 disubstituted derivative is known as the ***para* (*p*-)** compound.



Ortho (*o*-) isomer



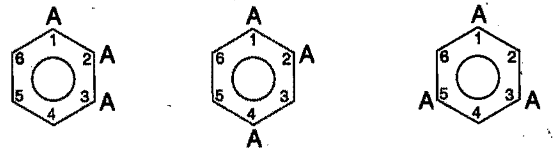
Meta (*m*-) isomer



Para (*p*-) isomer

In the case of trisubstituted derivatives of benzene, the number of isomers depends on the nature of substituents.

(a) If the three substituent groups are same, then three isomers are possible. They are termed adjacent (1,2,3), unsymmetrical (1,2,4) and symmetrical (1,3,5) isomers.



Adjacent isomer Unsymmetrical isomer Symmetrical isomer

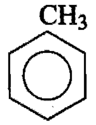
(b) If two substituent groups are identical and third different, then six isomers are possible.

(c) If all the three substituent groups are different, then ten isomers are possible.

The following guidelines are followed in naming benzene derivatives. Many of the benzene derivatives have been given special names which are generally more common in use.

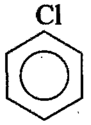
1. A six membered closed-chain structure with alternate single and double bond or with delocalization of π-electrons is known as benzene nucleus or ring. The root word for benzene derivatives is benzene.

2. The names of the mono substituted benzene compounds are usually derived by prefixing the name of the substituent before the word benzene. The special names are given in brackets in the following examples:

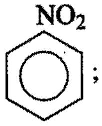


Methylbenzene (Toluene);

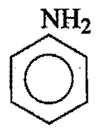
Ethylbenzene;



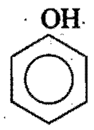
Chlorobenzene;



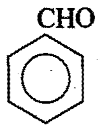
Nitrobenzene;



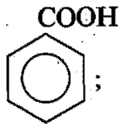
Aminobenzene (Aniline) or Benzenamine;



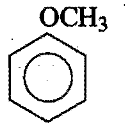
Hydroxybenzene (Phenol);



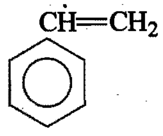
Formylbenzene (Benzaldehyde);



Carboxybenzene (Benzoic acid)

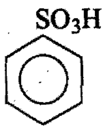


Methoxybenzene (Anisole);



Vinylbenzene (Styrene)

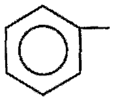
In certain cases, there is apparent departure from the said point. For example :



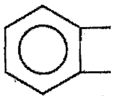
Benzene sulphonic acid

Benzene diazonium chloride

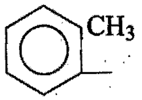
3. A carbon chain connected to one of the carbon atoms of the benzene ring through a carbon atom, other than those of simple functional groups like —CHO, —COOH, >CO, —COX, etc., is called a side-chain. Thus, $—CH_3$, $—CH_2CH_3$, $—CH{=}CH_2$, $—CH_2Cl$, $—CH_2NH_2$, etc., when linked to benzene nucleus constitute a side-chain. The side-chain substituted compounds are generally named as aliphatic compounds in which the aromatic portion is shown as a substituent. The following names are given to residues formed by the loss of one or more hydrogen atoms from the benzene and toluene:



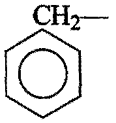
$[C_6H_5—]$
Phenyl



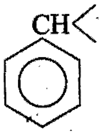
$[C_6H_4<]$
o-Phenylene



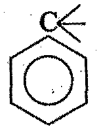
$[C_6H_4(CH_3)—]$
o-Tolyl



$[C_6H_5CH_2—]$
Benzyl
(Phenylmethyl)

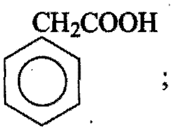


$[C_6H_5CH<]$
Benzal
(Benzylidene)

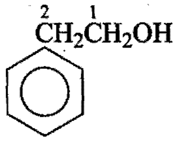


$[C_6H_5C\lessdot]$
Benzo
(Benzylidyne)

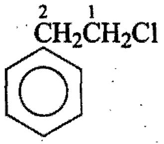
Examples :



2-Phenyl ethanoic acid

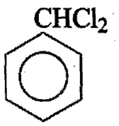


2-Phenylethanol

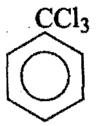


1-Chloro-2-phenyl ethane

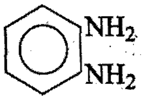
1-Chloro-1-phenyl methane
(Benzyl chloride)



1,1-Dichloro-1-phenyl-methane
(Benzal chloride)



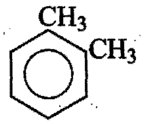
1,1,1-Trichloro-1-phenylmethane
(Benzo chloride)



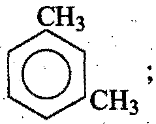
1,2-Diaminobenzene
(*o*-Phenylene diamine)

2-Chlorotoluene
(*o*-Tolyl chloride)

4. (a) When two similar substituents are attached to the benzene ring, the relative position of the substituents must be indicated by adding the symbols *o*-(1,2), *m*-(1,3) or *p*-(1,4) before the prefix.

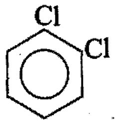


1,2-Dimethyl-benzene
(*o*-Xylene)

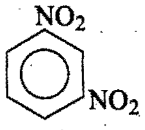


1,3-Dimethyl-benzene
(*m*-Xylene)

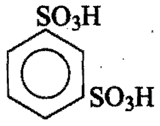
1,4-Dimethyl-benzene
(*p*-Xylene)



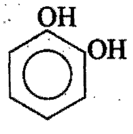
1,2-Dichlorobenzene
(*o*-Dichlorobenzene)



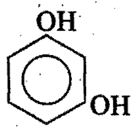
1,3-Dinitrobenzene
(*m*-Dinitrobenzene)



1,3-Benzene disulphonic acid (*m*-Benzene disulphonic acid)



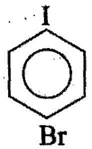
o-Dihydroxy benzene
(Catechol)



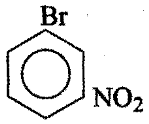
m-Dihydroxy benzene
(Resorcinol)

p-Dihydroxy benzene
(Hydroquinone)

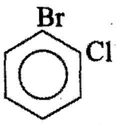
(b) If two substituents are different and the compound has no special name on account of any of the substituents, the two substituents are named successively in alphabetical order and the name ends with suffix benzene. Examples are :



1-Bromo-4-iodobenzene
(*p*-Bromoiodobenzene)

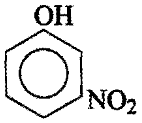


1-Bromo-3-nitrobenzene
(*m*-Bromonitrobenzene)

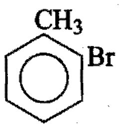


1-Bromo-2-chlorobenzene
(*o*-Bromochlorobenzene)

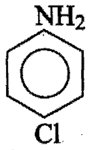
(c) If one of the two groups is such that it gives a special name to the molecule, then the compound is named as the derivative of that special compound and the special (principal) functional group is numbered as 1.



3-Nitrophenol
(*m*-Nitrophenol)

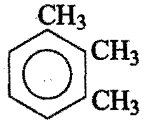


2-Bromotoluene
(*o*-Bromotoluene)

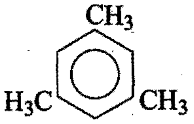


4-Chloroaniline
(*p*-Chloroaniline)

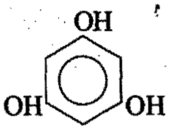
5. The positions of substituents in tri or polysubstituted benzene derivatives are generally shown by suitable numerical prefixes.



1,2,3-Trimethyl-benzene



1,3,5-Trimethyl-benzene (Mesitylene)

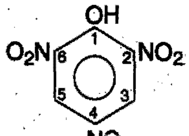


1,3,5-Trihydroxy-benzene (Phloroglucinol)

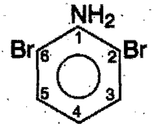
If one of the groups is such that it gives a special name to the compound, the compound is named as its derivative and special group is assigned the position 1. The order of decreasing properties of common substituents is:

$$-SO_3H, -COOH, -CN, -CHO, >C=O, -OH, -NH_2, -R, -NO_2, -X.$$

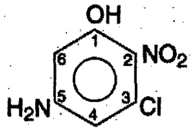
The positions of groups are always designated by the lowest combination of numbers.



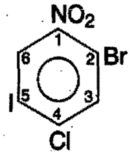
2,4,6-Trinitrophenol (Picric acid)



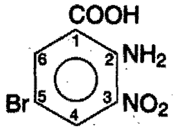
2,4,6-Tribromoaniline



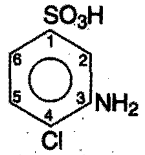
5-Amino-3-chloro-2-nitrophenol



2-Bromo-4-chloro-5-iodonitrobenzene

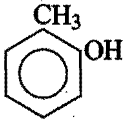


2-Amino-5-bromo-3-nitro benzoic acid

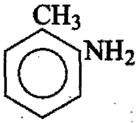


3-Amino-4-chloro-benzene sulphonic acid

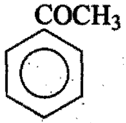
The following list includes the aromatic compounds which are generally named by special names:



o-Cresol



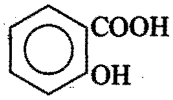
o-Toluidine



Acetophenone

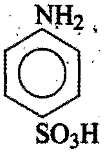
Salicylaldehyde

Phthalic acid

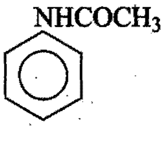


Salicylic acid

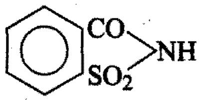
Anthranilic acid



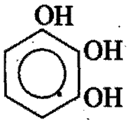
Sulphanilic acid



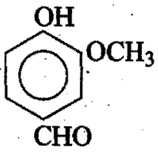
Acetanilide



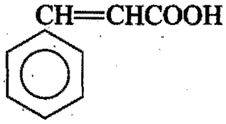
Saccharin



Pyrogallol



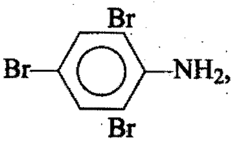
Vanillin

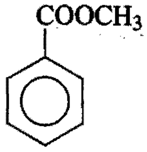


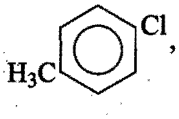
Cinnamic acid

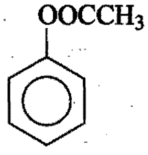
Problem 2. *Write the IUPAC names of the following:*

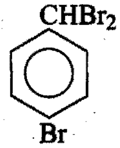
(*i*) *Orthobromotoluene* ; (*ii*) $C_6H_5CH_2COOH$,

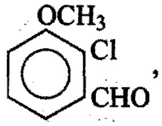
(*iii*)


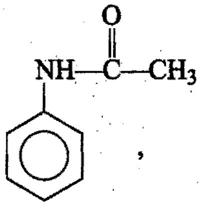
(*iv*)


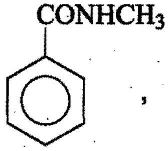
(*v*)


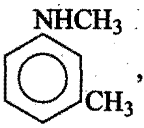
(*vi*)


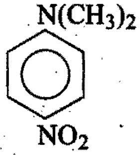
(*vii*)


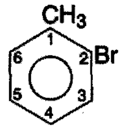
(*viii*)


(*ix*)


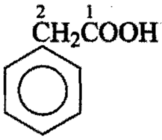
(*x*)


(*xi*)


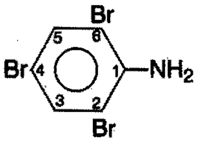
(*xii*)


Solution : (i)


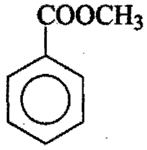
2-Bromotoluene or 2-Bromo-1-methylbenzene

(ii)


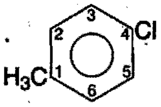
2-Phenyl ethanoic acid

(iii)


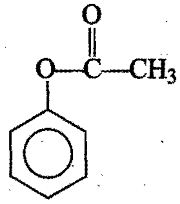
2,4,6-Tribromoaniline

(iv)


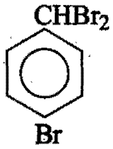
Methyl benzoate

(v)


4-Chlorotoluene

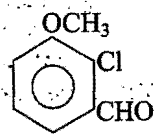
(vi)


Phenyl ethanoate

(vii)


4-Bromo-1,1-dibromo-1-phenylmethane (4-Bromobenzal bromide)

(viii)



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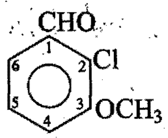
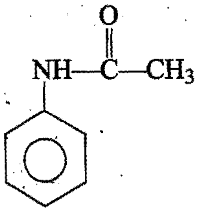


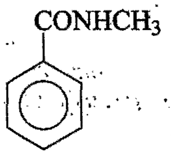
2-Chloro-3-methoxy benzaldehyde

(ix)



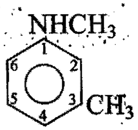
N-Phenyl ethanamide

(x)



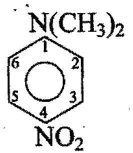
N-Methyl benzamide

(xi)



3-Methyl-*N*-methyl aniline
(3-Methyl-*N*-methylbenzenamine)

(xii)



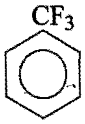
4-Nitro-*N*,*N*-dimethyl aniline
(4-Nitro-*N*,*N*-dimethylbenzenamine)

Problem 3. *Write the structural formulae for :*

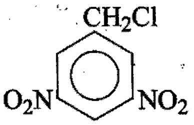
(*a*) *Benzotrifluoride,*
(*b*) *3,5-Dinitrobenzyl chloride,*
(*c*) *Trityl bromide (Triphenylmethyl bromide),*
(*d*) *Biphenyl,*
(*e*) *2,4′-Dimethyl diphenylmethane,*
(*f*) *1,3-Diphenylbutane,*
(*g*) *Tosyl chloride (p-toluene sulphonyl chloride),*
(*h*) *Phenylnitromethane.*

Solution :

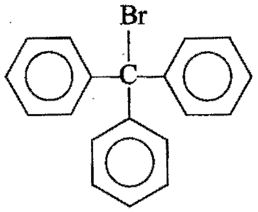
(a)



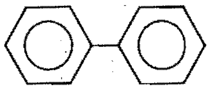
(b)



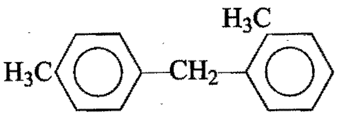
(c)



(d)

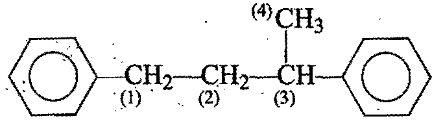


(e)

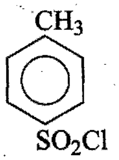


Note :(′) on second number indicates that one of substituents is present in the second ring.

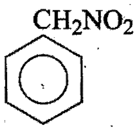
(f)



(g)



(h)

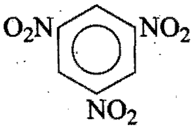


Problem 4 *Correct each of the following and write its corresponding structure.*

(*a*) 2,4,6-*Trinitrobenzene,* (*b*) 4-*Chloro-meta-xylene,*
(*c*) 2-*Aminonitrobenzene,* (*d*) 1-*Ethyl*-4-*butylbenzene,*
(*e*) 1-*Chloro-2-chloropropylbenzene.*

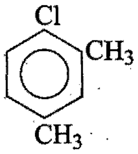
Solution :

(a) Numbering should be 1,3,5.

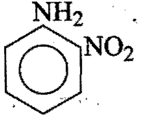


1,3,5-Trinitrobenzene

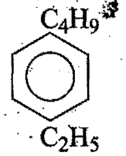
(b) '*meta*' is used only for disubstituted derivatives. The correct name is 1-chloro-2,4-dimethylbenzene.



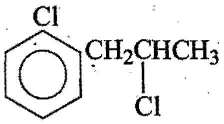
(c) Amino group has priority over nitro group. The correct name is 2-nitroaniline.



(d) Substituents have not been listed in alphabetical order. The correct name is 1-butyl-4-ethylbenzene.

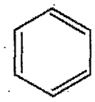


(e) The position of the 2-Chloropropyl group is uncertain. The correct name should be 1-chloro-2-(2′-chloropropyl) benzene.

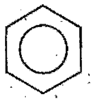


16.5 BENZENE

C_6H_6,



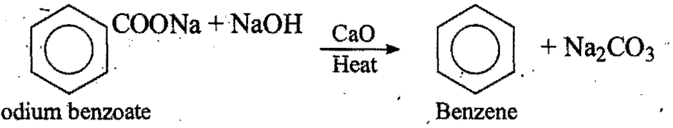
or



Benzene is the first member of aromatic hydrocarbon series. It was first discovered by Faraday in 1825 in oil gas obtained by the destructive distillation of whale oil. In 1833, Mitscherlich obtained it by distilling benzoic acid with lime. In 1845, Hofmann obtained it from coal-tar, which is still a commercial source of benzene. Large quantities of benzene are obtained now-a-days from petroleum.

Methods of Preparation

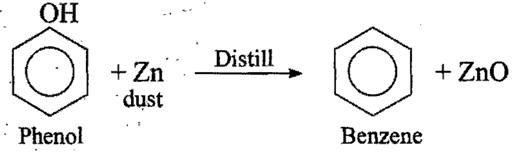
1. Decarboxylation of aromatic acids (Laboratory preparation): Benzene is conveniently prepared in the laboratory by heating the mixture of sodium benzoate and soda lime. This reaction is called decarboxylation.



Benzoic acid and phthalic acid (*o*- benzene dicarboxylic acid) also gives benzene on distillation with lime.

2. From benzene derivatives :

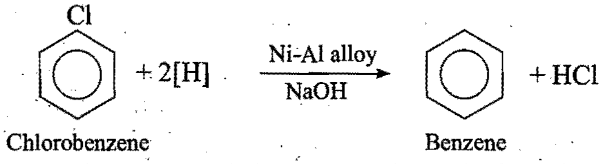
(i) From phenol : Benzene is obtained by reduction of phenol with red hot zinc powder.



[—OH group of the benzene nucleus is replaced by —H in this reaction.]

(ii) From chlorobenzene : Chlorine of the benzene nucleus can be substituted by hydrogen in two ways:

By doing reduction with Ni–Al alloy and NaOH.

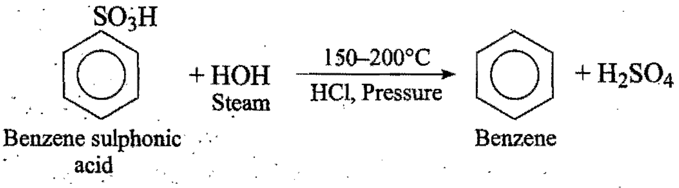


or by preparing its Grignard reagent and then hydrolysing it.

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} \xrightarrow[\text{Dry ether}]{Mg} \underset{\text{Phenyl magnesium chloride}}{C_6H_5MgCl} \xrightarrow{H_2O} \underset{\text{Benzene}}{C_6H_6} + Mg\left\langle\begin{matrix}OH\\Cl\end{matrix}\right.$$

(iii) From benzene sulphonic acid : (Replacement of sulphonic acid group —SO_3H).

Benzene is obtained by boiling benzene sulphonic acid with dilute hydrochloric acid under pressure at 150–200°C or hydrolysing it with superheated steam.

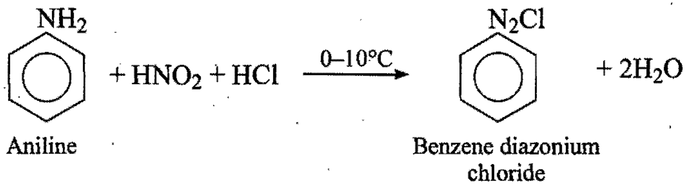


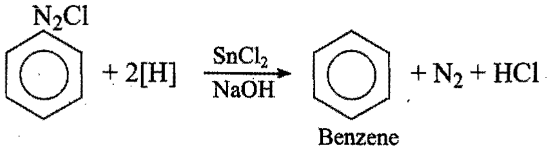
It is known as **desulphonation.**

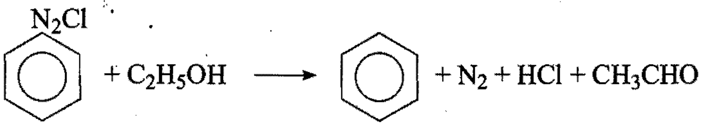
(iv) From aniline : (Replacement of —NH_2 group)

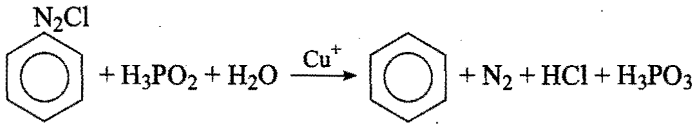
Aniline is first diazotised with sodium nitrite and hydrochloric acid at 0–10°C when benzene diazonium chloride is formed which is then reduced to benzene by $SnCl_2$ and NaOH or absolute ethyl alcohol or hypophosphorous acid (H_3PO_2).

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

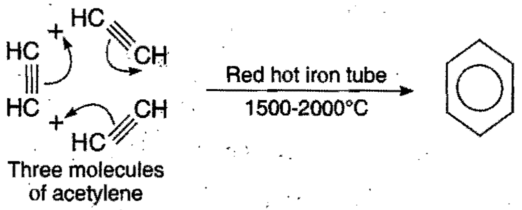


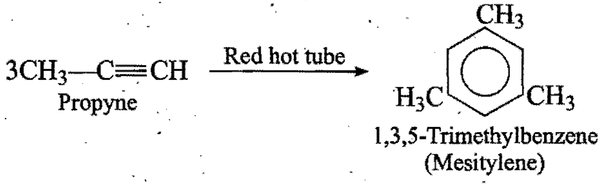


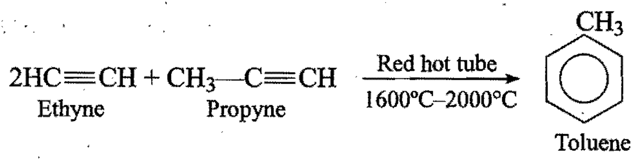


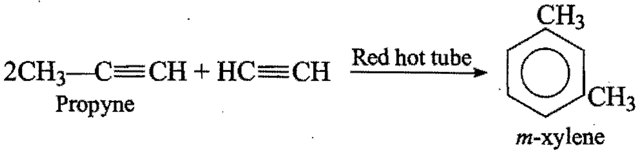


3. Synthesis from ethyne : When acetylene is passed through a red hot metallic tube, cyclic polymerisation takes place and benzene is formed.









+ *o*- and *p*-isomers

4. Manufacture : Benzene is obtained on a large scale from the following sources :

(i) From coal-tar : See **section 16.2.**

(ii) From petroleum : See **section 16.2.**

5. Aromatisation : By cyclization of long chain alkanes on heating at 500 – 550°C under high pressure in presence of oxides of Cr, V or Mo (catalyst) supported over alumina or Pt-Al_2O_3, (*i.e.*, catalytic reforming).

$$\underset{n\text{-Hexane}}{C_6H_{14}} \xrightarrow[\text{at high pressure}]{Cr_2O_3/V_2O_5/Mo_2O_3,\ 500°C} \underset{\text{Benzene}}{C_6H_6} + 4H_2$$

Properties of Benzene

Physical : (i) Benzene is a colourless, mobile and volatile liquid. Its boiling point is 80°C and freezing point is 5.5°C. It has characteristic odour.

(ii) It is highly inflammable and burns with sooty flame.

(iii) It is lighter than water. Its specific gravity at 20°C is 0.8788.

(iv) It is immiscible with water but miscible with organic solvents such as alcohol and ether.

(v) Benzene itself is a good solvent. Fats, resins, rubber, etc., dissolve in it.

(vi) It is a non-polar compound and its dipole moment is zero.

(vii) It is an extremely poisonous substance. Inhalation of vapours or absorption through skin has a toxic effect.

Chemical : Benzene is a stable compound. Even though its molecular formula, C_6H_6, indicates a high degree of unsaturation, it is not so reactive as alkenes or alkynes. It does not show the usual reactions of unsaturated hydrocarbons. Benzene does not form any addition product with halogen acids and hypochlorous acid. It resists oxidation by alkaline $KMnO_4$, (*i.e.*, no decolourisation) and does not decolourise bromine solution. However, under special conditions, it shows some addition reactions.

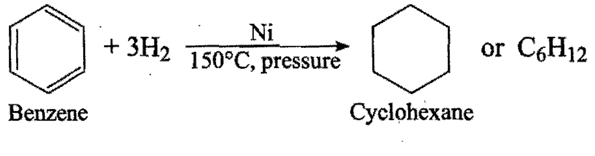
In many respects benzene behaves like a saturated hydrocarbon as it gives substitution reactions, *i.e.*, hydrogen atoms are replaced by other atoms or groups (benzene is more reactive than alkanes). Benzene is not affected by alkalies.

The principal reactions of benzene can be studied under three heads:

(i) Addition reactions,
(ii) Electrophilic substitution reactions,
(iii) Oxidation reactions.

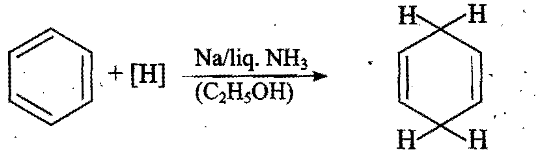
(i) Addition reactions (Reactions in which benzene behaves like unsaturated hydrocarbons) :

(a) Addition of hydrogen (Hydrogenation) : Benzene reacts with hydrogen in the presence of nickel (or platinum) catalyst at 150°C under pressure to form cyclohexane.



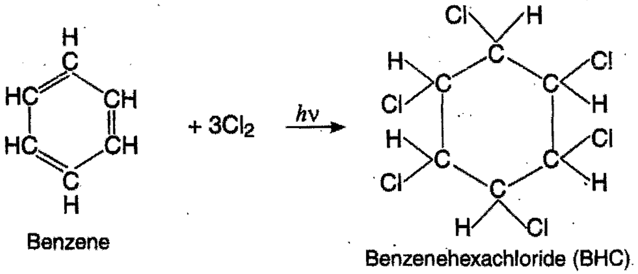
$$\left(\underset{\text{Benzene}}{C_6H_6} + 3H_2 \longrightarrow \underset{\text{Cyclohexane}}{C_6H_{12}}\right)$$

Birch reduction takes place in presence of lithium or Na metal and liquid NH_3.



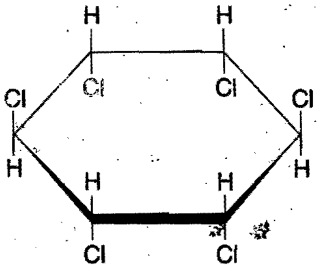
1,4-Cyclohexadiene

(b) Addition of halogen : Benzene reacts with chlorine or bromine but not with iodine in presence of sunlight or ultraviolet light to produce crystalline hexachlorides and hexabromides, respectively.



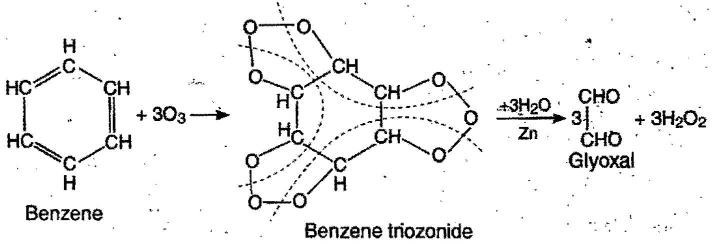
$$C_6H_6 + 3Cl_2 \xrightarrow[\text{Light}]{\text{UV}} \underset{\text{(BHC)}}{C_6H_6Cl_6}$$

Out of nine theoretically possible isomers of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane), the γ-isomer is the most important one and is used as a powerful insecticide under the name of **'gammexane'** or '666' or **'lindane'**. It is also used extensively as a pesticide in agriculture for killing termite (white ants) from soil. This addition reaction involves a free-radical mechanism. The γ-isomer can be represented as:



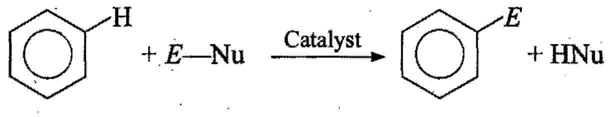
Gammexane

(c) Addition of ozone : When treated with ozone in presence of an inert solvent such as CCl_4, $CHCl_3$ or CH_2Cl_2 at low temperature (196-200K), benzene triozonide is produced which on decomposition with zinc dust and water yields glyoxal.



(ii) Electrophilic substitution reactions : The reactions in which hydrogen atom of the benzene ring is replaced by an electrophile are called electrophilic aromatic substitution **(EAS)** reactions. **Benzene undergoes electrophilic**

substitution reactions because it is an electron rich system due to delocalized π-electrons. The reactions can be represented as:



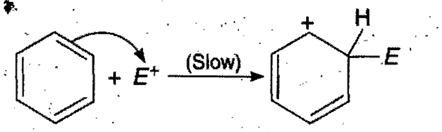
$$E—Nu \longrightarrow E^+ + \bar{N}u\!:$$

Mechanism

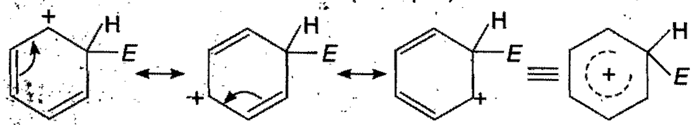
In all electrophilic aromatic substitution reactions, the first step is the formation of an electrophile, E^+. The important electrophiles **used in the aromatic substitution are the following:**

Electrophile (E^+)	Name	Source	Name of substitution reaction
Cl^+	Chloronium	$Cl_2 + AlCl_3$ or $FeCl_3$	Chlorination
Br^+	Bromonium	$Br_2 + AlBr_3$ or $FeBr_3$	Bromination
$\overset{+}{N}O_2$	Nitronium	$HNO_3 + H_2SO_4$	Nitration
SO_3 or $\overset{+}{S}O_3H$	Sulphur trioxide	Conc. H_2SO_4, Fuming sulphuric acid	Sulphonation
R^+	Alkyl carbocation	$RX + AlX_3$ ($X = Cl$ or Br), $ROH + H^+$	Friedel-Crafts (Alkylation)
$R—\overset{+}{C}—O$	Acyl carbocation	$RCOCl + AlCl_3$	Friedel-Crafts (Acylation)

In the **second step,** the electrophile (E^+) attacks the aromatic ring to form intermediate carbocation called **σ-complex** (or arenium ion) which is stabilized by resonance.



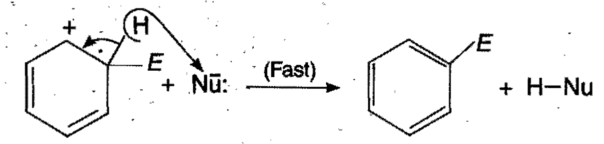
Carbocation (σ-complex)



Resonance forms of carbocation (arenium ion)

Resonance hybrid

In the **third step,** the carbocation loses the proton to form the substitution product.



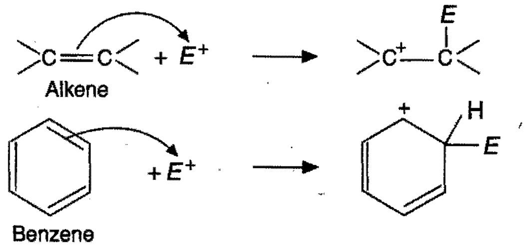
Carbocation

Substitution product

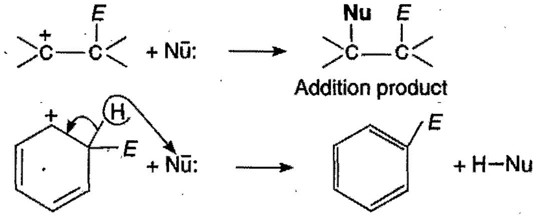
The second step is slow one while the third step is fast. Thus, electrophilic substitution in benzene ring is believed to be a bimolecular [S_{E^2}] reaction.

Note Benzene undergoes electrophilic substitution while alkenes undergo electrophilic addition.

Both react with electrophiles to form carbocations (point of similarity).



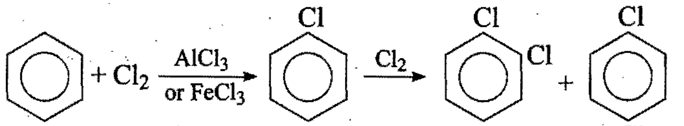
The carbocation formed by alkene usually combines with the nucleophile to form the addition product while nucleophile removes a proton from benzene carbocation to form substitution product as to maintain the aromatic character (point of dissimilarity).



Addition product

Substitution product

(a) Halogenation : Benzene undergoes chlorination when it is treated with chlorine in presence of Lewis catalyst such as $AlCl_3$ or $FeCl_3$ and in absence of light.



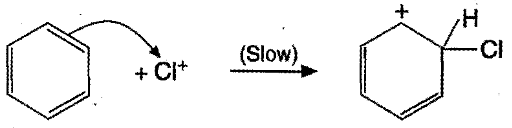
Benzene Chlorobenzene o-Dichlorobenzene p-Dichlorobenzene

Mechanism

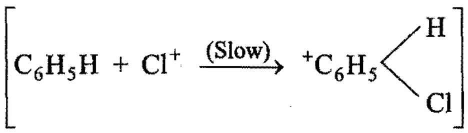
Step 1. Formation of the electrophile (Cl^+).

$$Cl—Cl + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$$

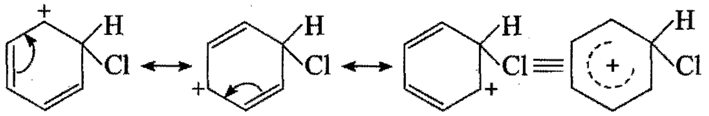
Step 2. The electrophile attacks the benzene ring to give an intermediate carbocation which is stabilized by resonance.



Benzene Carbocation



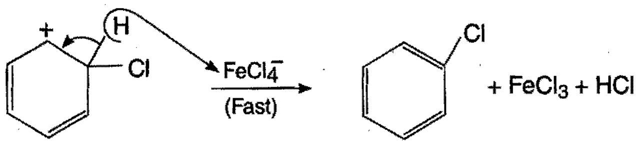
$$\left[C_6H_5H + Cl^+ \xrightarrow{(Slow)} {}^+C_6H_5\!\begin{matrix}H\\Cl\end{matrix}\right]$$



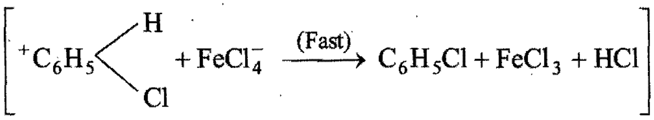
Resonance stabilized carbocation

Resonance hybrid

Step 3. Removal of proton gives chlorobenzene.

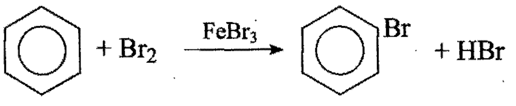


Chlorobenzene



$$\left[{}^{+}C_6H_5\langle^{H}_{Cl} + FeCl_4^- \xrightarrow{(Fast)} C_6H_5Cl + FeCl_3 + HCl\right]$$

Similarly, benzene undergoes bromination when it is treated with bromine in presence of $FeBr_3$ or $AlBr_3$, but not so fast as chlorination.



Bromobenzene

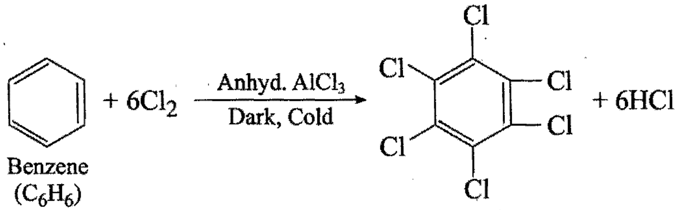
But iodination of benzene is reversible and slow ($Cl_2 > Br_2 > I_2$). Therefore, iodination takes place in presence of an oxidising agent, *i.e.*, HIO_3 or HgO to remove HI formation, (which is a strong reducing agent).

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Direct fluorination is impossible due to explosion.

$$C_6H_6 + 3F_2 \longrightarrow 6HF + 6C$$

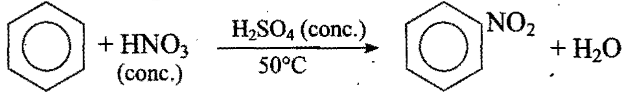
With excess of halogens in presence of anhydrous $AlCl_3$ (catalyst) and dark, all the hydrogen atoms of benzene ring may be successively replaced. For example,



Benzene (C_6H_6)

Hexa chlorobenzene (C_6Cl_6)

(b) Nitration : Benzene undergoes nitration when treated with concentrated nitric acid in presence of concentrated sulphuric acid (nitrating mixture), *i.e.*, nitrobenzene is formed. The reaction is carried at 40–50°C, when one of the H atom from the benzene ring is replaced by nitro group (NO_2^+, *i.e.*, nitronium ion is attacking species).



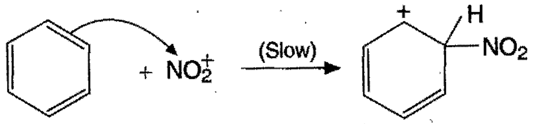
Nitrobenzene

Mechanism

First step : Formation of the electrophile (NO_2^+).

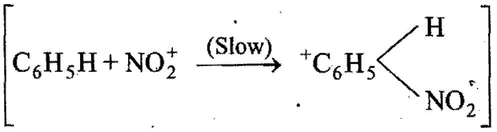
$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

Second step : The electrophile attacks the benzene ring to give an intermediate carbocation which is stabilized by resonance.

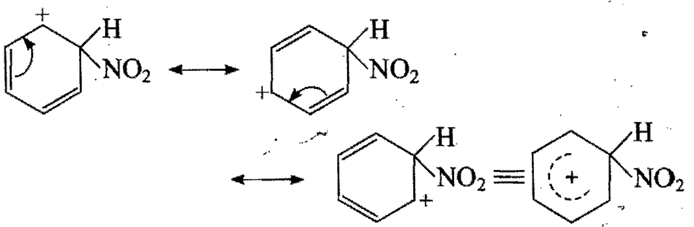


Benzene

Carbocation



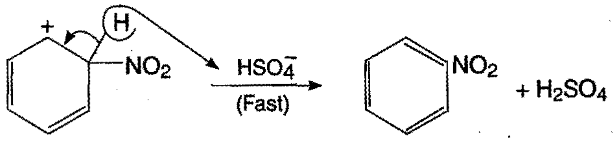
$$\left[C_6H_5H + NO_2^+ \xrightarrow{(Slow)} {}^{+}C_6H_5\langle^{H}_{NO_2}\right]$$



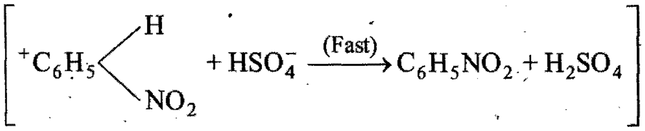
Resonance forms of carbocation

Resonance hybrid

Third step : Removal of proton from carbocation gives nitrobenzene.

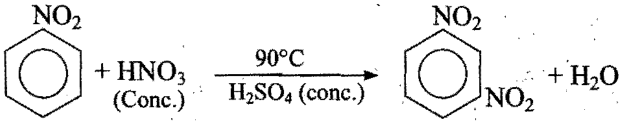


Nitrobenzene



$$\left[{}^{+}C_6H_5\langle^{H}_{NO_2} + HSO_4^- \xrightarrow{(Fast)} C_6H_5NO_2 + H_2SO_4\right]$$

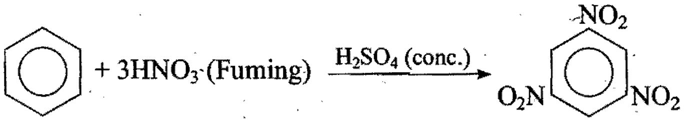
If nitrobenzene is further nitrated or benzene is heated with nitrating mixture (conc. HNO_3 + conc. H_2SO_4) at about 90°C, *m*-dinitrobenzene is obtained.



Nitrobenzene

m-Dinitrobenzene

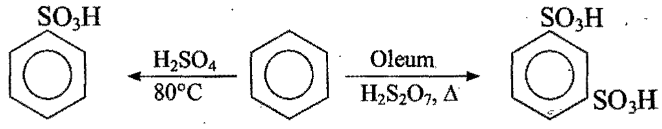
On heating benzene with fuming nitric acid and conc. H_2SO_4, 1,3,5-(sym-) trinitrobenzene is formed which is used as a powerful explosive.



s-Trinitrobenzene

+ $3H_2O$

(c) Sulphonation : Benzene forms benzene sulphonic acid with hot concentrated sulphuric acid while with fuming sulphuric acid or oleum (conc. $H_2SO_4 + SO_3$) at high temperature, *m*-benzene disulphonic acid is formed.

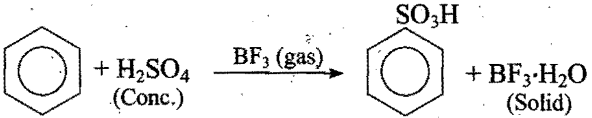


Benzene sulphonic acid

Benzene

m-Benzene disulphonic acid

Sulphonation can also be carried out at room temperature in presence of BF_3 catalyst.



Benzene

So for sulphonation, it must be **hot and conc. H_2SO_4** and the attacking species is SO_3 (neutral) or $\overset{+}{S}O_3H$.

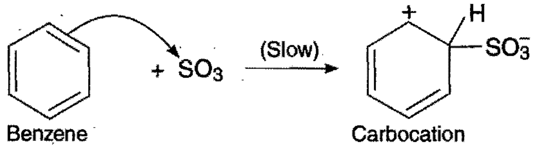
Mechanism

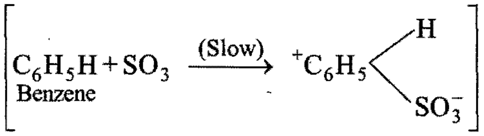
First step : Formation of the electrophile SO_3 or $\overset{+}{S}O_3H$.

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + SO_3$$

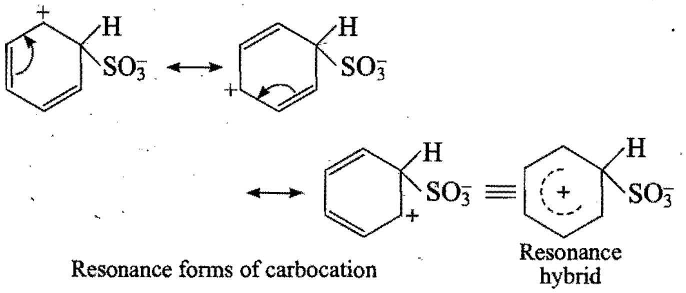
$$[SO_3 + H_3O^+ \longrightarrow \overset{+}{S}O_3H + H_2O]$$

Second step : The electrophile attacks the benzene nucleus to form carbocation which is stabilized by resonance.



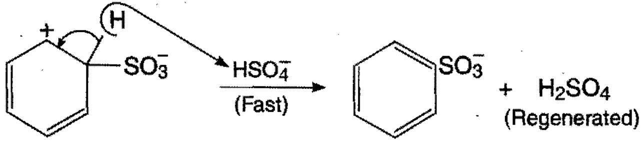


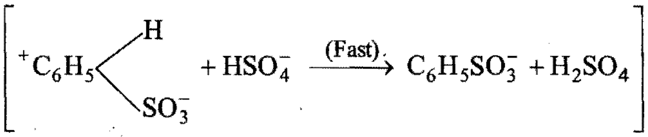
$$\left[\underset{\text{Benzene}}{C_6H_5H} + SO_3 \xrightarrow{\text{(Slow)}} {}^+C_6H_5\!\begin{array}{l}\diagup H\\ \diagdown SO_3^-\end{array}\right]$$



Resonance forms of carbocation

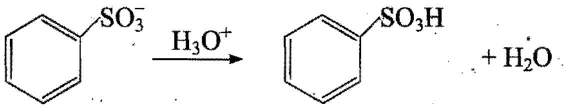
Third step : Carbocation loses the proton.





$$\left[{}^+C_6H_5\!\begin{array}{l}\diagup H\\ \diagdown SO_3^-\end{array} + HSO_4^- \xrightarrow{\text{(Fast)}} C_6H_5SO_3^- + H_2SO_4\right]$$

Fourth step :



Benzene sulphonic acid

$$[C_6H_5SO_3^- + H_3O^+ \longrightarrow C_6H_5SO_3H + H_2O]$$

(d) Friedel-Crafts reaction : This reaction was discovered by Friedel and Craft in 1877 and used for introducing an alkyl or acyl group in benzene nucleus by an alkylating or acylating agent in presence of a suitable catalyst.

The alkylating agent is usually an alkyl halide, an alcohol or an alkene, while the acylating agent may be an acid chloride or acid anhydride. The catalyst may be $AlCl_3$, $FeCl_3$, $SnCl_4$, BF_3, BCl_3 or $ZnCl_2$. Out of these, anhydrous aluminium chloride ($AlCl_3$) is the best and gives satisfactory results. A few examples are given below :

1. Alkylation (Formation of Benzene Homologues)

(i) $\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$

(ii) $C_6H_6 + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Ethylbenzene}}{C_6H_5C_2H_5} + H_2O$

(iii) $C_6H_5H + \underset{\text{Ethylene}}{C_2H_4} \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Ethylbenzene}}{C_6H_5C_2H_5}$

(iv) $2C_6H_5H + CH_2Cl_2 \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Diphenylmethane}}{(C_6H_5)_2CH_2} + 2HCl$

(v) $3C_6H_5H + CHCl_3 \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Triphenylmethane}}{(C_6H_5)_3CH} + 3HCl$

(vi) $\underset{\text{Benzene}}{C_6H_5H} + \underset{n\text{-Propyl chloride}}{CH_3CH_2CH_2Cl} \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Isopropylbenzene}}{C_6H_5CH(CH_3)_2} + HCl$

In this reaction, the primary carbocation $(CH_3CH_2\overset{+}{C}H_2)$ rearranges to a more stable secondary carbocation $(CH_3—\overset{+}{C}HCH_3)$ to form isopropyl benzene.

(vii) $C_6H_6 + \underset{\text{Propene}}{CH_3CH{=}CH_2} \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Isopropylbenzene}}{C_6H_5CH(CH_3)_2}$

(viii) $C_6H_6 + \underset{\text{Ethene}}{H_2C{=}CH_2} \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3}$

(ix) $C_6H_6 + CH_3OH \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Methyl benzene}}{C_6H_5CH_3} + H_2O$

(x) $C_6H_6 + \underset{\text{Dimethyl sulphate}}{(CH_3)_2SO_4} \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Toluene}}{C_6H_5CH_3} + CH_3HSO_4$

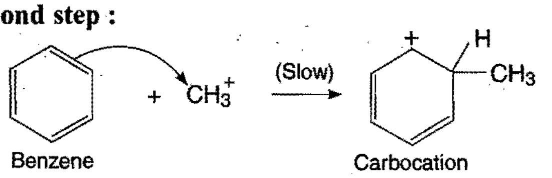
(xi) $C_6H_6 + \underset{\text{Diethyl sulphate}}{(C_2H_5)_2SO_4} \xrightarrow[\Delta]{\text{Anhyd. }AlCl_3} \underset{\text{Ethylbenzene}}{C_6H_5C_2H_5} + C_2H_5HSO_4$

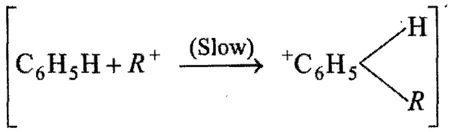
Mechanism

First step : $CH_3Cl + AlCl_3 \longrightarrow \underset{\text{Electrophile}}{CH_3^+} + AlCl_4^-$

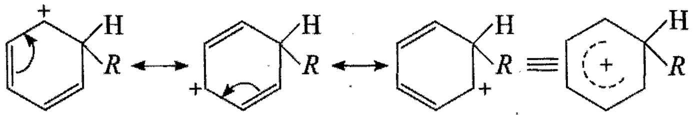
$$[RCl + AlCl_3 \longrightarrow R^+ + AlCl_4^-]$$

Second step :





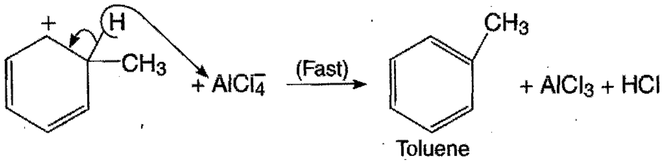
$$\left[C_6H_5H + R^+ \xrightarrow{\text{(Slow)}} {}^+C_6H_5\!\!<^{H}_{R}\right]$$

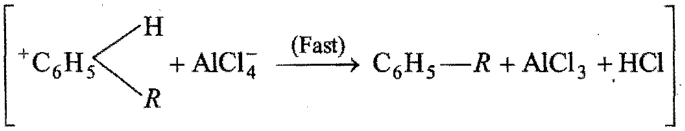


Resonance forms

Resonance hybrid

Third step :



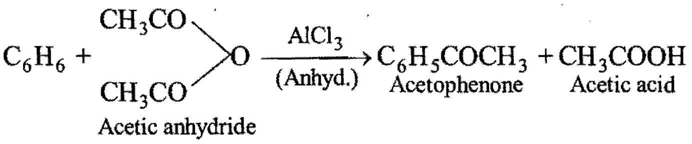


$$\left[{}^+C_6H_5\!\!<^{H}_{R} + AlCl_4^- \xrightarrow{\text{(Fast)}} C_6H_5—R + AlCl_3 + HCl\right]$$

Toluene readily undergoes Friedel-Crafts reaction.

2. Acylation (Formation of Ketones)

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Acetyl chloride}}{ClCOCH_3} \xrightarrow[\text{(Anhyd.)}]{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$



$$C_6H_6 + \underset{\text{Acetic anhydride}}{\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>O} \xrightarrow[\text{(Anhyd.)}]{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + \underset{\text{Acetic acid}}{CH_3COOH}$$

This also follows electrophilic substitution. The electrophile RCO^+ is first formed (same mechanism).

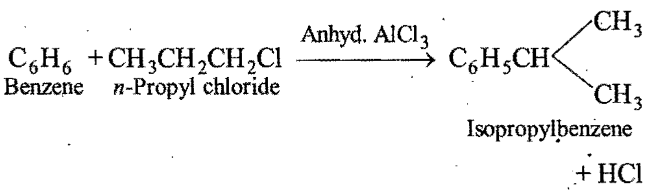
$$RCOCl + AlCl_3 \longrightarrow \underset{\text{Acyl carbocation}}{RCO^+} + AlCl_4^-$$

Therefore, Friedel-Crafts reaction proceeds through the intermediate formation of R^+ or RCO^+.

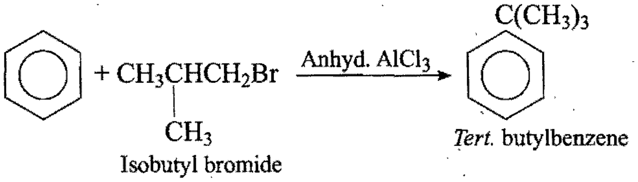
Friedel-Crafts reaction has the following drawbacks :

(i) Mono alkyl derivative readily undergoes further alkylation to produce poly-substituted derivatives.

(ii) It is easy to introduce methyl, ethyl or isopropyl group but usually difficult to introduce *n*-propyl or *n*-butyl group as isomeric change may occur.

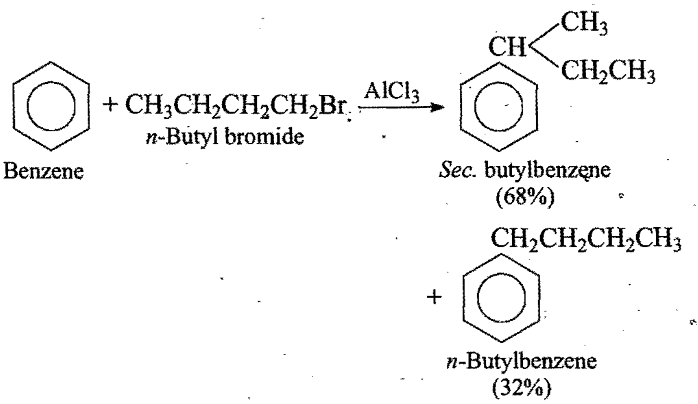


$$\underset{\text{Benzene}}{C_6H_6} + \underset{n\text{-Propyl chloride}}{CH_3CH_2CH_2Cl} \xrightarrow{\text{Anhyd. }AlCl_3} \underset{\text{Isopropylbenzene}}{C_6H_5CH\!\!<^{CH_3}_{CH_3}} + HCl$$



Isobutyl bromide

Tert. butylbenzene



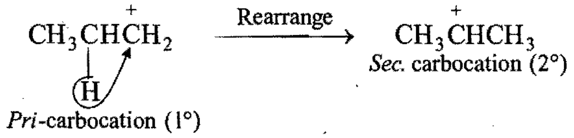
Benzene

n-Butyl bromide

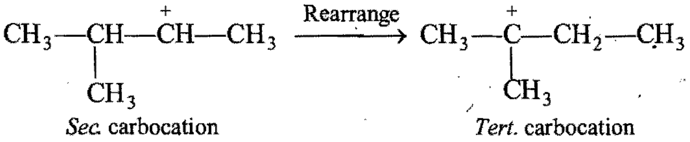
Sec. butylbenzene (68%)

n-Butylbenzene (32%)

In the mechanism of alkylation, the carbocation (R^+) formed from an alkyl halide (or alkene or alcohol) can rearrange (1,2-hydride shift) to a more stable carbocation ($T > S > P$) and so the major product obtained from the reaction is usually the one from the more stable carbocation, *i.e.*,



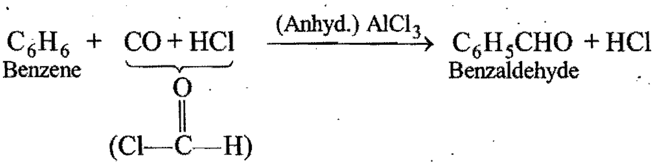
$$\underset{Pri\text{-carbocation (1°)}}{CH_3CH\overset{+}{C}H_2} \xrightarrow{\text{Rearrange}} \underset{Sec.\text{ carbocation (2°)}}{CH_3\overset{+}{C}HCH_3}$$



$$\underset{Sec.\text{ carbocation}}{CH_3—\underset{\begin{matrix}|\\CH_3\end{matrix}}{CH}—\overset{+}{C}H—CH_3} \xrightarrow{\text{Rearrange}} \underset{Tert.\text{ carbocation}}{CH_3—\underset{\begin{matrix}|\\CH_3\end{matrix}}{\overset{+}{C}}—CH_2—CH_3}$$

(iii) The presence of *m*-directing group in the benzene ring hinders the reaction, because they deactivate the ring for further substitution. For example, nitrobenzene, benzoic acid and benzene sulphonic acid, etc., do not undergo Friedel-Crafts reaction.

Besides alkylation and acylation, this reaction has recently been applied in number of other cases. For example,



$$\underset{\text{Benzene}}{C_6H_6} + \underbrace{CO + HCl}_{(Cl—\overset{\overset{\displaystyle O}{\|}}{C}—H)} \xrightarrow{\text{(Anhyd.) }AlCl_3} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Chloroformamide}}{ClCONH_2} \xrightarrow{\text{(Anhyd.) }AlCl_3} \underset{\text{Benzamide}}{C_6H_5CONH_2} + HCl$$

$$C_6H_6 + \underset{\text{Carbonyl chloride}}{ClCOCl} \xrightarrow{\text{(Anhyd.) }AlCl_3} \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + HCl$$

The electrophile, $\overset{+}{C}OCl$ is first formed.

$$(COCl_2 + AlCl_3 \longrightarrow \overset{+}{C}OCl + AlCl_4^-)$$

(e) Mercuration : Benzene when heated with alcoholic solution of mercuric acetate at (100–150°C), a hydrogen atom is replaced by acetoxy mercuric acid group and forms acetoxy mercury benzene.

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Mercuric acetate}}{(CH_3COO)_2Hg} \xrightarrow{\Delta} \underset{\text{Phenyl mercuric acetate}}{C_6H_5HgOOCCH_3} + CH_3COOH$$

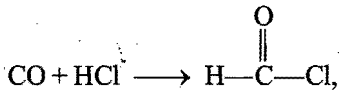
This reaction is called mercuration and is employed in the preparation of certain medicines and other organic compounds.

$$\underset{\text{Acetoxy mercury benzene}}{C_6H_5HgOOCCH_3} + Br_2 \longrightarrow \underset{\text{Bromobenzene}}{C_6H_5Br} + BrHgOOCCH_3$$

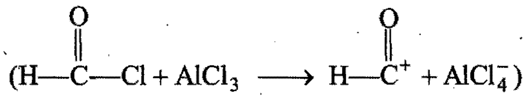
(f) Formylation : It is a direct method for introducing an aldehydic group ($-\overset{O}{\overset{\|}{C}}-H$) in benzene. It is called **Gattermann-Koch** synthesis when a mixture of dry HCl gas and carbon monoxide is used in presence of anhydrous aluminium chloride.

$$\underset{\text{Benzene}}{C_6H_6} + CO + HCl \xrightarrow[\Delta]{\text{Anhyd. AlCl}_3} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

The electrophile, $H-\overset{O}{\overset{\|}{C^+}}$ is first formed.



$$CO + HCl \longrightarrow H-\overset{O}{\overset{\|}{C}}-Cl,$$



$$(H-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow H-\overset{O}{\overset{\|}{C^+}} + AlCl_4^-)$$

(g) Gattermann-aldehyde reaction : The synthesis of aldehyde with HCN is virtually the same reaction and is called Gattermann synthesis.

$$\underset{\text{Benzene}}{C_6H_5H} + HC{\equiv}N + HCl \xrightarrow[\Delta]{\text{Anhyd. AlCl}_3} C_6H_5CH{=}NH{\cdot}HCl \xrightarrow{\text{HOH}} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + NH_3{\cdot}HCl$$

The electrophile, $H\overset{+}{C}{=}NH$ is first formed.

$$H-C{\equiv}N + HCl \longrightarrow ClHC{=}NH$$

$$(ClHC{=}NH + AlCl_3 \longrightarrow H\overset{+}{C}{=}NH + AlCl_4^-)$$

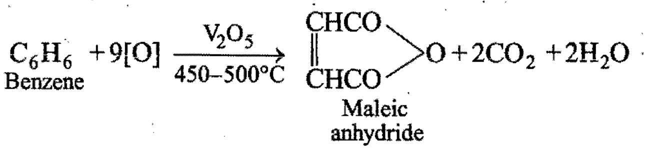
(h) Chloromethylation (Blance reaction) : A chloromethyl group, $-CH_2Cl$, is introduced in benzene nucleus by heating it with formaldehyde and HCl in presence of either anhydrous $ZnCl_2$ or $AlCl_3$ as catalyst to form benzyl chloride. The process is known as chloromethylation.

$$\underset{\text{Benzene}}{C_6H_6} + HCHO + HCl \xrightarrow[\Delta]{\text{Anhyd. AlCl}_3} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + H_2O$$

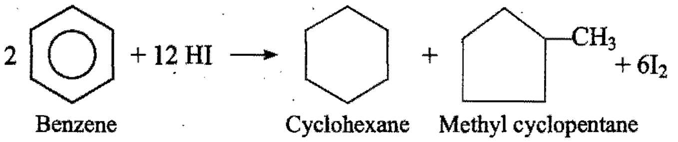
(iii) Oxidation reactions : Benzene is a stable compound. It is not attacked by ordinary oxidising agents. Acidified potassium permanganate, chromic acid, *i.e.*, strong oxidising agents convert benzene slowly into carbon dioxide and water on heating. Being inflammable liquid it burns in air with smoky flame **(combustion).**

$$2C_6H_6 + 15O_2 \xrightarrow{\text{Burn}} 12CO_2 + 6H_2O$$

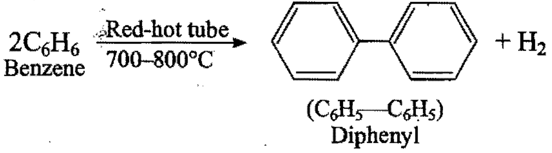
When vapours of benzene and air are passed over vanadium pentoxide at 450–500°C, maleic anhydride is obtained **(catalytic oxidation).**



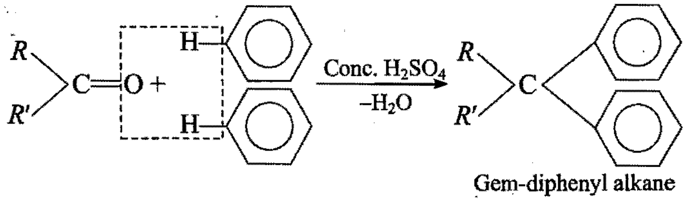
(iv) Reduction : On reduction with hydroiodic acid (HI) at 250°C, benzene forms cyclohexane and methyl cyclopentane.



(v) Action of heat : Benzene vapours on passing through red-hot tube of iron or molten lead at 700–800°C gives biphenyl (diphenyl).



(vi) Condensation with carbonyl compounds : Aldehydes and ketones react with benzene in the presence of conc. H_2SO_4 to give gem-diphenyl alkane.



Uses : Benzene is used,

(a) in dry-cleaning, (b) as a motor fuel when mixed with petrol, (c) as a solvent, (d) in the manufacture of gammexane (as insecticide), (e) in the preparation of nitrobenzene, chlorobenzene, benzene sulphonic acid, aniline, styrene, etc. Many of these are employed for making dyes, drugs, plastics, insecticides, etc.

16.6 STRUCTURE OF BENZENE

1. Molecular formula : On the basis of analysis and molecular mass determination, the molecular formula of benzene comes to be C_6H_6.

2. Unsaturation : The molecular formula, C_6H_6, indicates that it has high degree of unsaturation as it has eight hydrogen atoms less than the corresponding paraffin, C_6H_{14}. Thus, benzene is an unsaturated compound containing double and triple bonds.

3. Open-chain structure : Assuming carbon atom to be tetravalent and hydrogen monovalent, the following open-chain structures can be proposed for benzene molecule:

(i) $CH_3—C{\equiv}C—C{\equiv}C—CH_3$
(ii) $H_2C{=}C{=}CH—CH{=}C{=}CH_2$
(iii) $HC{\equiv}C—CH_2—CH_2—C{\equiv}CH$
(iv) $H_2C{=}CH—C{\equiv}C—CH{=}CH_2$

All the above open-chain structures were rejected because these were having different properties than the properties of benzene.

(a) Benzene adds six hydrogen atoms or six chlorine atoms.

$$\underset{\text{Benzene}}{C_6H_6} + 3H_2 \xrightarrow[200\text{–}250°C]{\text{Raney Ni}} \underset{\text{Cyclohexane}}{C_6H_{12}}$$

$$\underset{\text{Benzene}}{C_6H_6} + 3Cl_2 \xrightarrow{\text{Sunlight}} \underset{\substack{\text{Benzenehexachloride}\\ \text{(BHC)}}}{C_6H_6Cl_6}$$

(b) Benzene forms a triozonide.

$$\underset{\text{Benzene}}{C_6H_6} + 3O_3 \xrightarrow{CH_2Cl_2} \underset{\text{Benzene triozonide}}{C_6H_6(O_3)_3}$$

(c) Halogen acids and hypochlorous acid do not add on to benzene while in the above structures addition should take place readily.

(d) Benzene is resistant to oxidation (like saturated compounds) even with strong oxidising agents like $K_2Cr_2O_7/H_2SO_4$ or acidic $KMnO_4$ etc. Further alkaline $KMnO_4$ also does not react with benzene in cold. Similarly, benzene does not decolourise bromine solution. These are typical tests of all unsaturated alkenes and alkynes.

The above points thus confirm that benzene is a unsaturated compound but different than aliphatic unsaturated hydrocarbons. Hence, it cannot be represented by an open-chain structure similar to alkenes or alkynes. The properties (a) and (b) suggest that the molecule of benzene possesses three double bonds.

4. Ring structure : The following are some more points which are in favour of different structure of benzene (which behaves like a saturated compound) and probably the ring structure.

(a) Benzene gives substitution reactions like halogenation, nitration, sulphonation, etc.

$$\text{(i) } \underset{\text{Benzene}}{C_6H_6} + Cl_2 \xrightarrow{FeCl_3} \underset{\text{Chlorobenzene}}{C_6H_5Cl}, \text{ (Halogenation)}$$

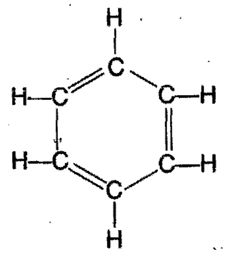
$$\text{(ii) } C_6H_6 + \underset{\text{(Conc.)}}{HNO_3} \xrightarrow{H_2SO_4\text{ (conc.)}} \underset{\text{Nitrobenzene}}{C_6H_5NO_2}, \text{ (Nitration)}$$

$$\text{(iii) } C_6H_6 + \underset{\text{(Conc.)}}{H_2SO_4} \xrightarrow{\text{Heat}} \underset{\substack{\text{Benzene}\\ \text{sulphonic acid}}}{C_6H_5SO_3H}, \text{ (Sulphonation)}$$

Benzene gives only one mono-substituted product. It shows that all the hydrogen atoms are equally and symmetrically distributed among the six carbon atoms.

(b) Benzene forms three isomeric disubstituted products (*ortho, meta, para*).

5. Kekule's formula : In view of the above facts, Kekule in 1865 suggested a ring structure of benzene in which the ring was composed of six carbon atoms, each of which carries one atom of hydrogen. To satisfy the fourth valency of the carbon atom, he suggested three alternate double bonds.

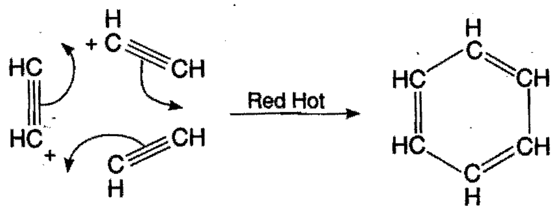


Evidences in favour of Kekule's Structure

(i) X-ray crystallographic studies of benzene show the presence of hexagonal structure with carbon centres at a distance of 1.4 Å and carbon-hydrogen distances are 1.09 Å. Electron diffraction and Raman spectra also confirm this view.

(ii) Studies on magnetic rotation and molecular refraction show the presence of three double bonds and a close conjugated system.

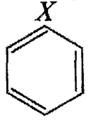
(iii) Benzene combines with three molecules of hydrogen or three molecules of chlorine. It also combines with three molecules of ozone to form triozonide. These reactions confirm the presence of three double bonds.



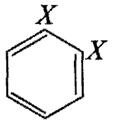
Acetylene (3 moles) Benzene

(iv) The synthesis of benzene from three molecules of acetylene also favours Kekule's structure.

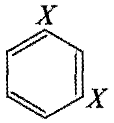
(v) The formation of only one monosubstituted product confirms that all the six hydrogen atoms are equivalent.



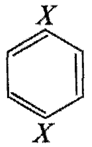
(vi) The formation of three isomers of disubstituted products confirms this structure.



ortho (i)
(1,2)

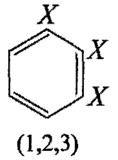


meta (ii)
(1,3)

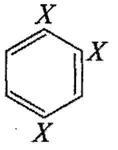


para (iii)
(1,4)

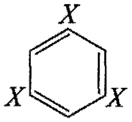
(vii) The formation of three isomers of trisubstituted products also confirms Kekule's structure.



(1,2,3)



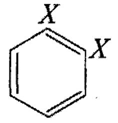
(1,2,4)



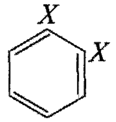
(1,3,5)

Objections against Kekule's Formula

First objection : Ladenberg pointed out that on the basis of Kekule's formula, the *ortho* disubstituted derivative of benzene should exist in two forms and not one form.

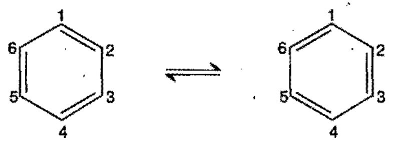


Double bond between two adjacent carbon atoms



Single bond between two adjacent carbon atoms

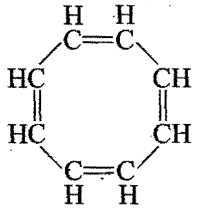
Kekule explained this objection by proposing that double bonds in benzene ring were continuously oscillating between two adjacent positions.



Thus, the positions 2,6 are really symmetrical with respect to position 1 and the *ortho* isomers 1,2 or 1,6 represent the same compound.

Second objection : Inspite of the fact that benzene molecule consists of three double bonds, it is stable towards oxidising agents. Actually benzene behaves as a saturated and extra stable molecule as it does not decolourise bromine water and Baeyer's reagent. It shows substitution reactions. It was shown by **Willstatter** that a similar closed-chain compound cyclo-octatetraene, though contains alternate single and double bonds similar to benzene, is not so stable as benzene.

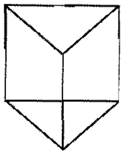
To explain the second objection, many modifications were suggested by proposing other formulae but none of them was found to be entirely satisfactory.



Cyclo-octatetraene

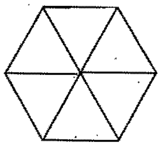
6. Some other formulae of benzene :

(i) Ladenberg's prism formula : Each carbon atom is linked with three other carbon atoms and fourth valency is satisfied by hydrogen. This is a stable structure as there is no unsaturation. Further, this formula demands two *ortho* derivatives.

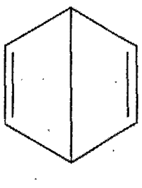


Ladenberg's formula is a three dimensional structure whereas X-ray studies of benzene molecule indicate a planar structure. The formula fails to account for reduction and addition reactions.

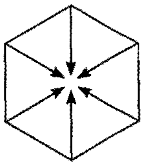
(ii) Claus-diagonal formula : Each carbon is linked to three other carbon atoms, *i.e.*, two neighbours and one diagonally opposite. The formula fails to account the reduction and addition products. However, the formula explains the simultaneous formation of *ortho* and *para* isomers. Lengthening of bonds brings instability, thus the formula is against the stability of benzene molecule.

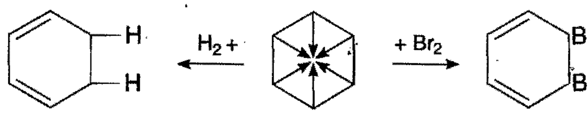


(iii) Dewar's parallel formula : The formation of benzoquinone by electrolytic oxidation of quinol supports this formula but it was rejected on the ground that it was not symmetrical. X-ray determination shows that length of all C—C linkages should be 1.40 Å but the length of *para* bond in this formula is 2.80 Å which is very high.



(iv) Armstrong and Baeyer's centric formula : In this formula, fourth valency of each carbon atom is directed towards the centre. By the mutual action of these valencies, a state of equilibrium is reached in the ring which accounts for the aromatic properties. These valencies become very active during the course of reaction. When one molecule of hydrogen or bromine is added, the state of equilibrium is disturbed and two double bonds appear in the compound. This compound behaves as a typical diolefin.

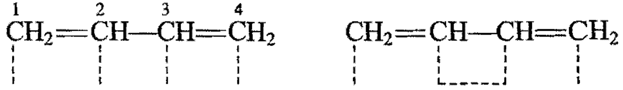




(C_6H_8) (C_6H_6) ($C_6H_6Br_2$)

However, this formula had no satisfactory explanation for the behaviour of polynuclear hydrocarbons and therefore was rejected.

(v) Thiele's formula : Thiele (in 1899) introduced a useful concept of partial valencies. He considered each carbon atom of a double bond to possess a certain partial valency, represented by a dotted line.

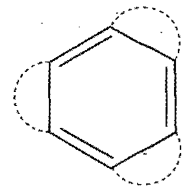


$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2$ $\quad CH_2{=}CH{-}CH{=}CH_2$

(1,3-Butadiene) or Conjugated system

In butadiene molecule, the valencies at carbon 2 and 3 mutually satisfy each other leaving valencies at 1 and 4 free for addition. [Butadiene shows 1,4-addition]

Thiele noted that Kekule's formula is a closed conjugated system without terminal carbon atoms as in butadiene. Hence, all the partial valencies neutralise and more stability comes to benzene molecule.



This formula was rejected because the same concept could not explain the stability of cyclo-octatetraene possessing four conjugated system.

7. Present day position regarding the structure of benzene : The **stability** and the **structure of benzene** has been explained on the basis of two **modern theories.** These theories are:

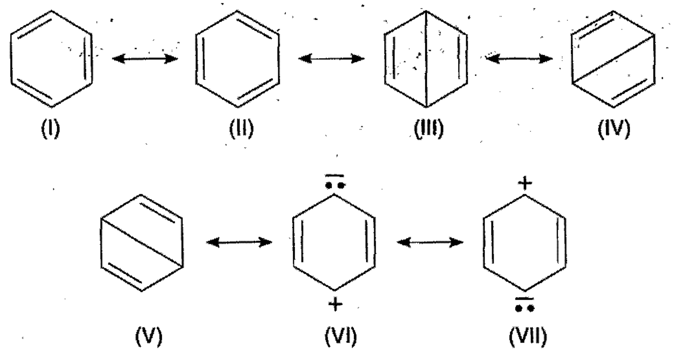
(i) Resonance or valence-bond theory.

(ii) Molecular orbital theory.

(i) Resonance theory or valence-bond theory : If a compound can be represented by more than one structural formula from the point of view of electronic configuration, then none of them represents the compound. These different structures must be such that the position of the nucleus remains the same in each of the structure but the position of electrons can change. The structural formula of such a compound is somewhat intermediate (hybrid) between the various proposed formulae. This state is known as **'Resonance'.** It is also observed that the compound which is in state of resonance is much more stable than the expectation from the known structure.

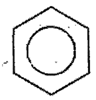
On the basis of resonance theory, benzene is believed to be a resonance hybrid of the following canonical structures:

(I) and (II) structures (Kekule) are far more stable than the rest of the structures. Thus, these two Kekule structures contribute far more to resonance (80%) than the rest of the structures.



Since, the two Kekule's structures are equivalent, the stability of the resulting resonance hybrid is very high. Resonance gives each C—C bond in benzene some double bond character and this has been confirmed by measuring bond length between two adjacent carbon atoms in various compounds of benzene. The bond length C—C (single bond as in ethane) is 1.54 Å and C=C (double bond as in ethene) is 1.33 Å. The carbon to carbon bond length in benzene has been found to be 1.39 Å which lies between single and double bond length values.

Resonance can occur in a molecule if it is planar. Thus, all the C and H are expected to be planar. Instead of using two Kekule's structures, the hybrid is represented for the sake of convenience only, by one structure as shown below : (Actually hybrid form cannot be represented on paper).

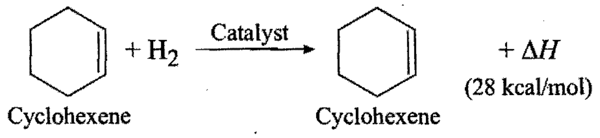


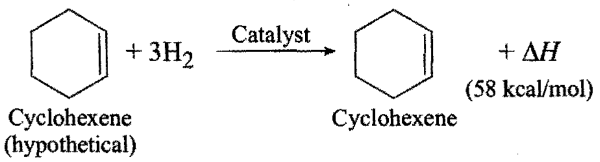
Hybrid formula of benzene

Resonance Energy

The **resonance energy** which is responsible for stability can be calculated from the heat of hydrogenation and heat of combustion datas.

Heat of hydrogenation is the amount of heat evolved when one mole of an unsaturated compound is hydrogenated in presence of a catalyst.





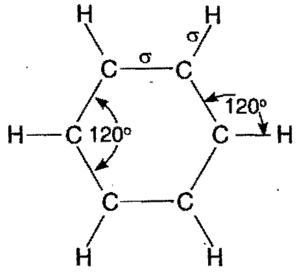
Actually when benzene is fully hydrogenated, it gives cyclohexane and 49 kcal/mol of heat is evolved. **So benzene is said to be stabilized by a resonance energy of 36 (85–49) kcal/mol.** Therefore, resonance energy (R.E.) is the difference in the energy contents of contributing (hypothetical) structures and the most stable (actual) of the resonance hybrid structure. Thus, the actual molecule of benzene is 36 kcal (150 kJ) more stable than the hypothetical molecule. In other words, 36 kcal/mol is the **resonance energy of benzene.**

Hence, benzene (and other members of the arene family) behave like a stable compound and give mainly substitution reactions rather than addition reactions.

Note: (i) According to Kekule, each structure was real, but changed rapidly from one form to another.

(ii) According to resonance theory, both Kekule's structure are imaginary. The real structure of benzene is hybrid, not a mixture of the two Kekule's forms.

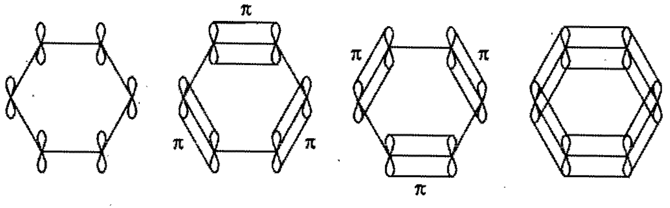
(ii) Molecular orbital theory applied to benzene structure : All six carbon atoms in benzene are sp^2-hybridized. The sp^2-hybrid orbitals overlap with each other and with *s*-orbitals of the six hydrogen atoms forming C—C and C—H σ-bonds. Since, **the bonds result from the overlap of planar sp^2-orbitals, all carbon and hydrogen atoms in benzene lie in the same plane and all the bond angles are 120° as shown below:**



(C—H) bond length = 1.09 Å

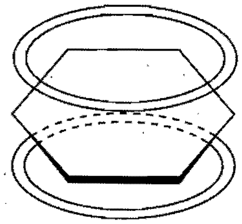
(C—C) bond length = 1.40 Å

After the formation of six C—C and six C—H σ-bonds, one $2p$-unhybridized orbital is left unused on each carbon atom. They are parallel to each other and perpendicular to the plane of sp^2-orbitals. The lateral overlap of these p-orbitals produces 3π-molecular orbitals containing six electrons as shown in (b) and (c). As the overlapping on both sides is equal, all the six p-orbitals unite to form a continuous π-molecular orbital containing six electrons as shown in (d) given below.



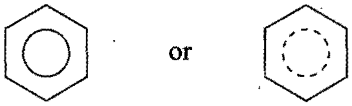
(a) (b) (c) (d)

The formation of continuous molecular orbital suggests that there is delocalization of π-electrons and all the six π-electrons are free to move over the six carbon atoms. Since the delocalised electrons have lower energy than localised electrons, the **benzene molecule becomes more stable.**



The energy of delocalization (energy of localized electrons minus the energy of delocalized electrons) is equivalent to resonance energy. Due to delocalization the π-molecular orbital acquires the shape of an electron cloud composed of two dough nut shapes of full hexagonal symmetry. One lobe lies above and other lies below the plane of σ-bonds.

The molecular orbitals picture of benzene explains all the known facts about the benzene, *i.e.*, planarity of the molecule, bond angles, equal C—C bond lengths and stabilization of molecule. Due to delocalization of π-electrons, benzene molecule acts as a source of electrons and is easily attacked by electrophiles. However, to preserve the delocalization and the corresponding stability, the molecule of benzene tends to undergo substitution rather than addition with electrophilic reagents. To show the delocalization of 6π-electrons benzene is represented by a continuous circle or a dotted line circle as shown below:



Summary

1. Benzene has a cyclic, planar hexagonal structure.
2. All the six carbon atoms in benzene are equally reactive and so, all the hydrogen atoms in benzene are equivalent. Only one monosubstituted product is formed.
3. All carbon atoms in benzene are sp^2-hybridized. All carbon-carbon bond lengths are identical (1.39 or 1.40 Å). The bond angles are 120°.

16.7 DIRECTIVE INFLUENCE OF FUNCTIONAL GROUPS IN MONOSUBSTITUTED BENZENE

A substituent already present on the benzene ring exercises two types of influence on further substitution.

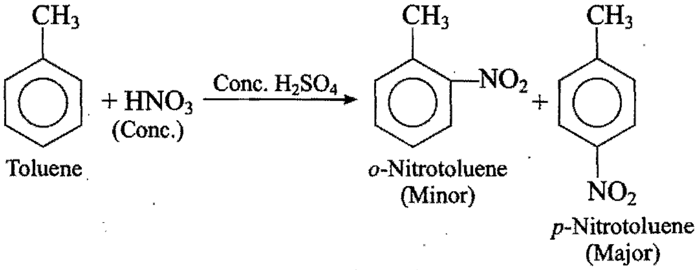
(i) Directive or Orientation effect : The substituent already present on the benzene ring directs the incoming substituent to occupy *ortho* (2 or 6), *meta* (3 or 5) or *para* (4) position. This direction depends on the nature of the first substituent and is called **directive** or **the orientation effect.**

(ii) Activity effects : The substituent already present can increase or decrease the rate of further substitution, *i.e.*, it either activates or deactivates the benzene ring towards further substitution. These effects are called **activity effects.**

1. Directive influence of substituents : On the basis of extensive experiments it has been shown that when the second substituent, *i.e.*, incoming group (guest) enters the benzene nucleus, the main product is either a mixture of *ortho-* and *para*-isomers or the *meta*-isomer, depending on the nature of the first substituent, *i.e.*, the group already present to the benzene nucleus (host). Thus, there are two types of substituents—(i) Those which direct the incoming group to *ortho-* and *para*-positions simultaneously (neglecting *meta* altogether). (ii) Those which direct the incoming group to *meta*-position only (neglecting *ortho* and *para*-positions altogether).

Class-I (*o*-, *p*-directing groups) :

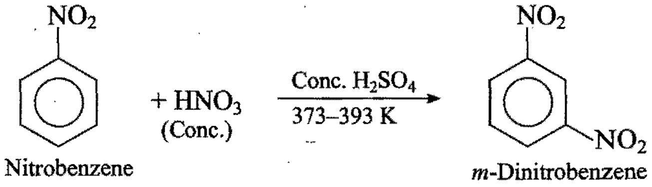
$-R$ (alkyl), —OH, —SH, —NH_2, —O^-, —OR, —NHR, —NR_2, —NHCOR, —Cl, —Br, —I, —CH_2Cl, —CH_2OH, —CH_2NH_2, —CH_2CN, —CH_2COOH, —CH=CH_2, —CH=CHCOOH, —C_6H_5, —N=N, —NC, etc.



(—CH_3 group is *o*-, *p*-directing)

Class-II (*m*-directing groups) :

—SO_3H, —NO_2, —CHO, —COOH, —CN, —NH_3Cl, —SO_2Cl, —COCl, —COOR, —COR, —$CONH_2$, —CCl_3, —CF_3, —$\overset{+}{N}H_3$, —$\overset{+}{N}H_2R$, —$\overset{+}{N}HR_2$, —$\overset{+}{N}R_3$, etc.



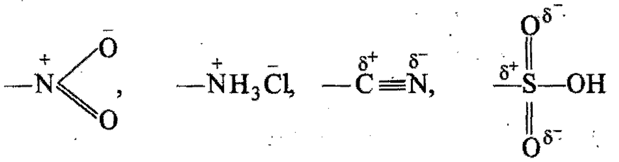
(—NO_2 group is *m*-directing)

It is further noted that all *ortho-para* directing substituents possess a non-bonding electron pair on the 'key atom'.

$$-\ddot{\underset{\bullet\bullet}{\text{Cl}}}:,\ -\ddot{\underset{\bullet\bullet}{\text{Br}}}:,\ -\underset{\bullet\bullet}{\ddot{\text{O}}}\text{H},\ -\ddot{\text{O}}\text{CH}_3,\ -\ddot{\text{N}}\text{H}_2$$

The only exception to the said rule is the methyl or alkyl group.

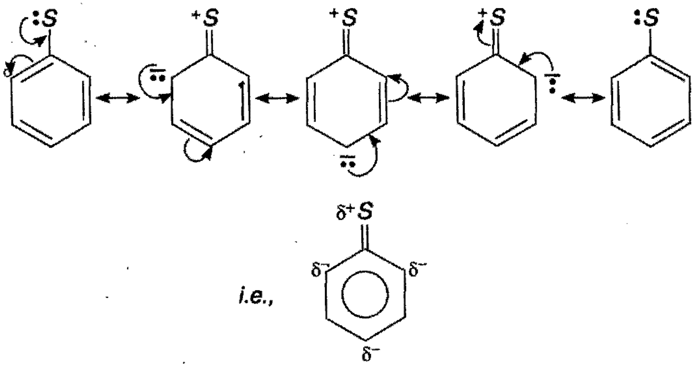
Substituents which have a positive (or partial positive) charge on the key atom (atom adjacent to the ring) are *meta* directors.



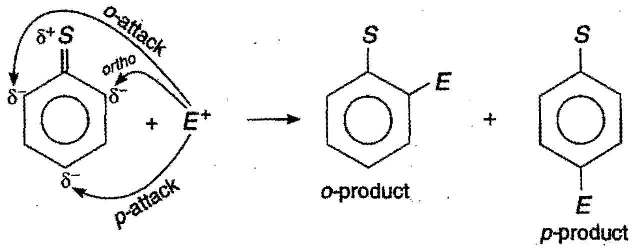
$-\overset{+}{N}O_2$, $-\overset{+}{N}H_3\overset{-}{Cl}$, $-\overset{\delta+}{C}\equiv\overset{\delta-}{N}$, $-\overset{\delta+}{S}O_2-OH$

Theory of directive effects :The resonance theory clearly explains why certain substituents are *ortho-para*-directing, while others are *meta*-directing.

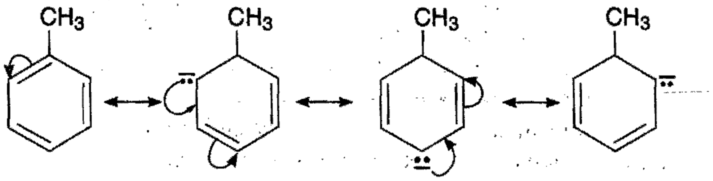
***Ortho-para*-directing**:All of these *ortho* and *para* -directors have atleast one pair of non-bonding electrons on the atom adjacent to the benzene ring. This non-bonding electron pair present on the key atom of the substituent is distributed into the ring by interaction with the π-system (electron donating) with a result that *ortho* and *para*-positions attain greater electron density and the electrophile (E^+) would naturally attack at these electron-rich centres forming *ortho* and *para* isomers.



Resonance hybrid



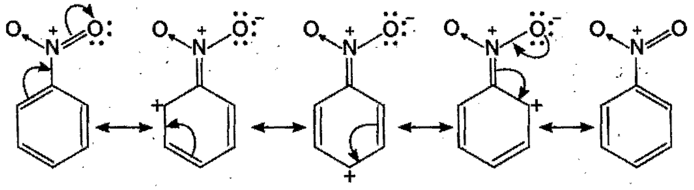
The above mechanism is followed when *S* is —OH, —NH$_2$, —Cl, —Br, —I, —O*R*, —N*R*$_2$, —NHCO*R*, etc.



In methyl or alkyl group, the +*I* effect of the methyl group or alkyl group initiates the resonance effect. Thus, methyl or alkyl group directs all electrophiles to *ortho* and *para* -positions.

In general, all electron donating groups (**EDG**) *are o-, p-directing.*

***Meta*-directing** :The substituent, *S* withdraws electrons from *ortho* and *para*-positions. Thus, *m*-position becomes a point of relatively high electron density and further substitution by electrophile occurs at *meta*-position. For example, —NO$_2$ group is a *meta*-directing (electron withdrawing). Its mechanism can be explained as:



In these structures, there is a positive charge at the *ortho* and *para* positions. Therefore, they are unreactive to the attacking electrophile which is also positively charged. Hence, electrophilic substitution becomes difficult.

In general, all electron withdrawing groups (**EWG**) *are m-directing.*

2. Effect of substituents on reactivity :Toluene is more reactive than benzene while chlorobenzene is less reactive than benzene. Thus, substituent already present on a benzene ring not only directs the position of an incoming group but also influences the rate of reaction.

A substituent which activates the benzene ring to further substitution is called an activating substituent while substituent which deactivates the benzene ring is called a deactivating substituent.

In general, it has been observed that :

***Ortho-para*-directing groups activate the benzene ring towards electrophilic substitution while *meta*-directing groups deactivate the benzene nucleus towards electrophilic substitution.**

—F, —Cl, —Br and —I (halogens) are exceptions to the above rule. These groups are *o*-, *p*-directing but deactivate the benzene ring.

Any substituent or group which repels or releases (donates) electrons into the ring, (*i.e., o-, p*-directing) activates the benzene ring for further substitution. The substituent which attracts or withdraws electrons (*m*-directing) from the ring deactivates the benzene ring for further substitution.

The abnormal behaviour of halogens is attributed to the fact that two opposing effects operate simultaneously. A halogen substituent releases electrons due to resonance but withdraws electrons also due to its high electronegativity [—*I* (inductive) effect]. The inductive effect is more pronounced than the resonance effect and the net result is that the benzene ring is rendered electron deficient and less liable to electrophilic substitution.

Effect of substituents on electrophilic aromatic substitution:

***Ortho-para* Directors**	***Meta*-Directors**
Strongly activating	Moderately deactivating
$-\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{H}R, -\ddot{\text{N}}R_2, -\underset{\bullet\bullet}{\overset{\bullet\bullet}{\text{O}}}\text{H}, -\underset{\bullet\bullet}{\overset{\bullet\bullet}{\text{O}}}\text{:}^-$	$-\text{C}\equiv\text{N}, -\text{SO}_3\text{H}, -\text{COOH}, -\text{COO}R, -\text{CHO}, -\text{CO}R$
Moderately activating	Strongly deactivating
$-\ddot{\text{N}}\text{HCOCH}_3, -\ddot{\text{N}}\text{HCO}R, -\underset{\bullet\bullet}{\overset{\bullet\bullet}{\text{O}}}\text{CH}_3, -\underset{\bullet\bullet}{\overset{\bullet\bullet}{\text{O}}}R$	$-\text{NO}_2, -\overset{+}{\text{N}}R_3, -\text{CF}_3$
Weakly activating $-\text{CH}_3, -\text{C}_2\text{H}_5, -R, -\text{C}_6\text{H}_5, -\text{CH}=\text{CH}_2$	$-\overset{+}{\text{N}}\text{H}_3, -\overset{+}{\text{N}}\text{H}_2R$
Weakly deactivating	Weakly deactivating
$-\underset{\bullet\bullet}{\overset{\bullet\bullet}{\text{F}}}\text{:}, -\underset{\bullet\bullet}{\overset{\bullet\bullet}{\text{Cl}}}\text{:}, -\underset{\bullet\bullet}{\overset{\bullet\bullet}{\text{Br}}}\text{:}, -\underset{\bullet\bullet}{\overset{\bullet\bullet}{\text{I}}}\text{:}$	$-\text{CCl}_3-$

Introduction of a Third Substituent into Benzene Ring

The position occupied by a third substituent group entering the benzene ring is mainly decided by the nature of the two groups already present on the benzene ring.

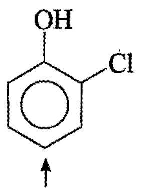
(i) When both the groups belong to class I (***o*-, *p*-directing**), the directive influence of each group is in the following order :

$$O^- > NR_2 > NH_2 > OH > OMe, NHCOCH_3 > CH_3 > X$$

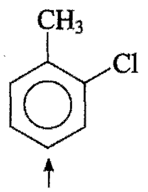
$$(X = -F > -Cl > -Br > -I)$$

Out of the *ortho-* and *para*-positions, the new group enters *p*-position preferably with respect to more powerful group.

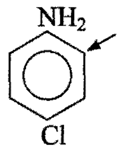
For example, in *o*-chlorophenol, since —OH group is more powerful than —Cl, the third group enters the position *para* to —OH as indicated by arrow.



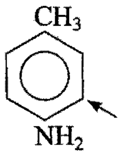
, other example is :



In case, the *p*-position is blocked, the third group enters the position *ortho* to more powerful group. For example, in *p*-chloroaniline, —NH_2 is more powerful than —Cl, the new entrant is directed to *ortho*-position as indicated by arrow because the *p*-position being blocked.



, other example is :

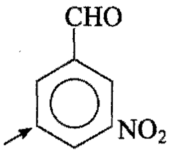


(ii) When both the groups belong to class II (***meta*-directing**) the third group is accommodated on benzene ring with difficulty. The directive influence of each group is in the following order :

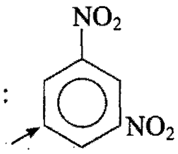
$$Me_3\overset{+}{N} > NO_2 > CN > SO_3H > CHO > COMe > COOH$$

The new entrant occupies *meta*-position with respect to more powerful group.

For example, in *m*-nitrobenzaldehyde, the new group is directed to position shown by arrow.

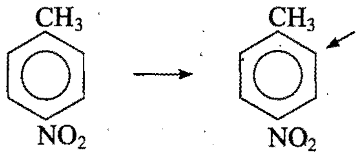


, other example is :



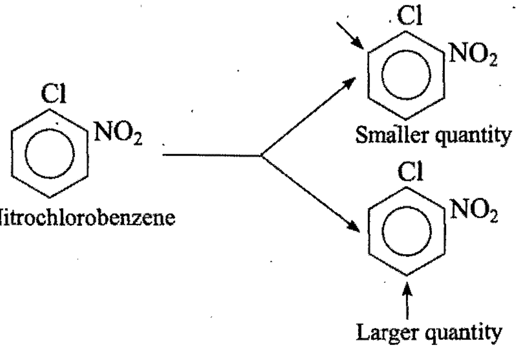
(iii) When the two groups exert different directive influences the group belonging to class I takes precedence. In case, the influences of two groups reinforce each other, the third group enters almost entirely in one position.

Examples are given below to explain the above point.

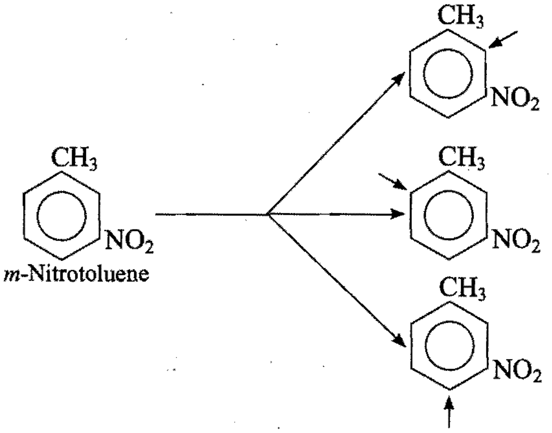


p-Nitrotoluene

(Position *ortho* to —CH_3 and *meta* to —NO_2)



o-Nitrochlorobenzene



m-Nitrotoluene

16.8 MECHANISM OF AROMATIC SUBSTITUTION

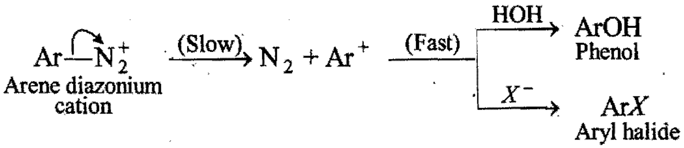
There are three possible mechanisms for aromatic substitution:

(1) Electrophilic, (2) Nucleophilic and (3) Free radical mechanism.

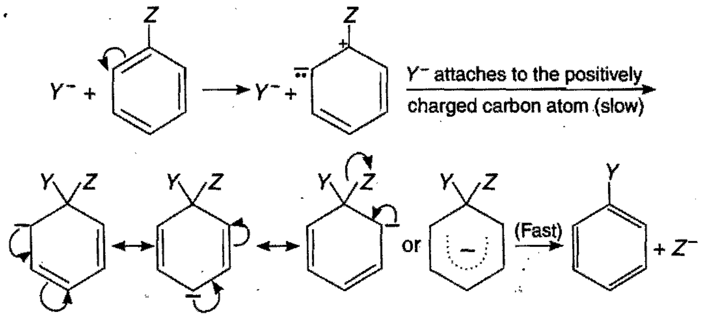
1. Electrophilic aromatic substitution : It is believed to proceed by a bimolecular (S_{E2}) mechanism involving the formation of an intermediate carbocation (σ-complex) which is a rate determining step. Examples are halogenation, nitration, sulphonation and Friedel-Crafts reaction, etc., (Details in **Section 16.5**)

2. Nucleophilic aromatic substitution : The replacement of hydrogen or any other substituent by a nucleophilic reagent is termed *nucleophilic substitution.* This replacement of hydrogen by a nucleophile does not occur in benzene itself under ordinary conditions, but the presence of an electron withdrawing group ($—NO_2$, —CN, $—SO_3H$, —COOH, —CHO or diazo $—N_2^+$, etc.) is sufficient to activate the *o*- and *p*-position. In general, there are three types of mechanism : *unimolecular* Ar $S_{N}1$, *bimolecular* Ar $S_{N}2$ and the *elimination-addition mechanism via Benzynes* (*Arynes*).

(i) Unimolecular mechanism : This mechanism is most uncommon in aromatic substitution. There is only one example and that is the decomposition of aryl diazonium cations in aqueous solution to yield phenol or aryl halides (in presence of nucleophilic halide ions).

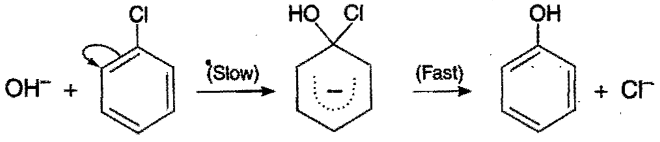


(ii) Bimolecular mechanism : Nucleophilic aromatic substitutions are commonly bimolecular and proceeds through a negative ion intermediate, *i.e.,* cyclohexadienyl anion, *e.g.,*



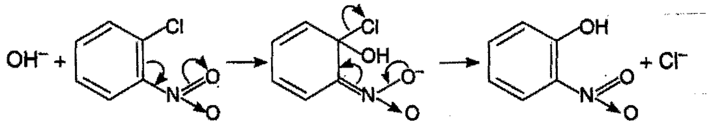
(Resonating structure of the hexadienyl anion)

Aryl halides undergo nucleophilic substitution only in vigorous conditions. Thus, the reaction between chlorobenzene and aqueous alkali at 300°C to form phenol may be represented as follows:



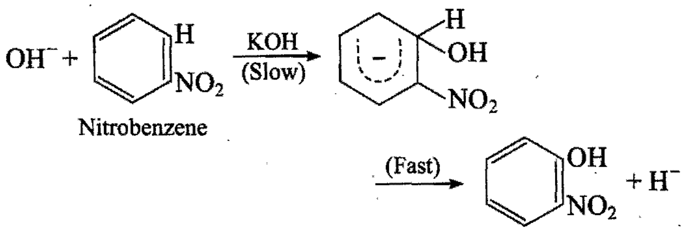
Chlorobenzene Phenol

This replacement when facilitated by the presence of an electron withdrawing group (*meta*-directing groups) in the *o*- and/or the *p*-position, is termed activated nucleophilic aromatic substitution and an example is the conversion of *o*-chloronitro benzene into *o*-nitrophenol when heated with aq. alkali at 200°C.



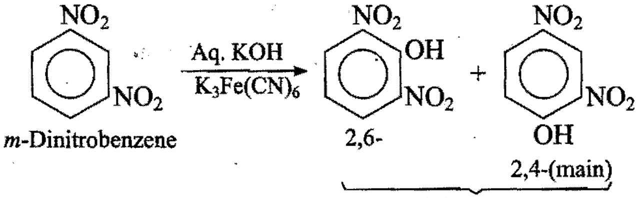
Because of the electron withdrawing effect of the nitro group, the carbon atom of the C—Cl group acquires a positive charge, so the negatively charged OH⁻ attacks the positively charged carbon atom of the C—Cl group.

This explains why benzene itself does not undergo nucleophilic substitution and replacement of hydrogen by a nucleophile can occur in presence of one nitro group to activate the *o*- and *p*-positions.



Nitrobenzene

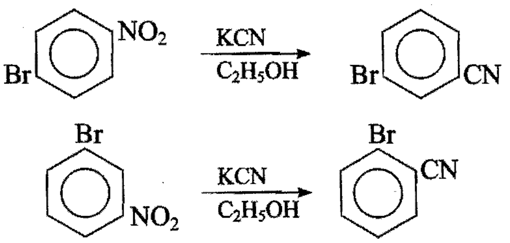
o-Nitrophenol



m-Dinitrobenzene

Dinitrophenol

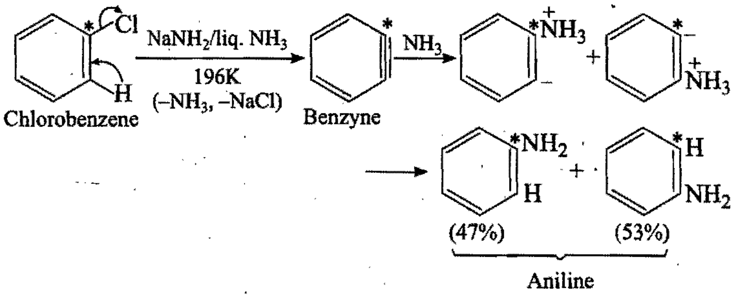
When halogeno nitro benzene is heated with ethanolic KCN at 150°C, the nitro group is expelled and a cyano group enters the ring *ortho* to the position occupied by the former ($—NO_2$ group). This another example of nucleophilic substitution with rearrangement is called **Von Richter reaction.**



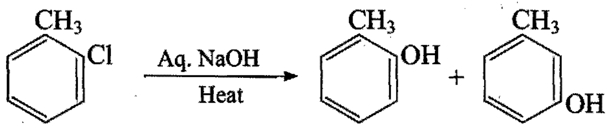
(iii) Elimination-addition (Benzyne or aryne) mechanism: In a number of cases of nucleophilic aromatic substitution, the entering group does not occupy the position vacated by the expelled group. Reactions of this type have been called **cine-substitutions.** This mechanism involves two steps: (a) formation of a benzyne (1,2-dehydrobenzene) intermediate by a stepwise elimination, followed by (b) stepwise addition to benzyne to form the product in which position of the nucleophile may be different.

When chlorobenzene with C—Cl carbon atom labelled with ^{14}C is treated with potassium in liquid ammonia at 196 K the reaction occurs through the intermediate **benzyne**

formation and aniline is formed and the amino group enters partly at the labelled carbon atom and partly at the *ortho*-carbon atom.



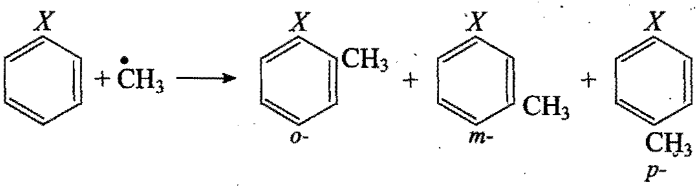
Experimentally both products are formed, hence, elimination-addition mechanism is followed. This can be exemplified by the fact that *o*-chlorotoluene on heating with aq. NaOH gives a mixture of 2- and 3-methyl phenol.



3. Free radical aromatic substitution : The aromatic substitution reactions which follow free radical mechanisms are very few and have limited synthetic value. A typical example of these reactions is the methylation of aromatic compound by tertiary butyl peroxide which gives methyl radicals through the various intermediates. The methyl radical may now get substituted at the *o*-, *m*- or *p*-positions. Among these, the *ortho* product always predominates.

$$\underset{\textit{Tert. butyl peroxide}}{(CH_3)_3CO\cdot OC(CH_3)_3} \xrightarrow{\text{Heat}} \underset{\substack{\textit{Tert. butoxyl}\\ \text{radical}}}{2(CH_3)_3\dot{C}O}$$

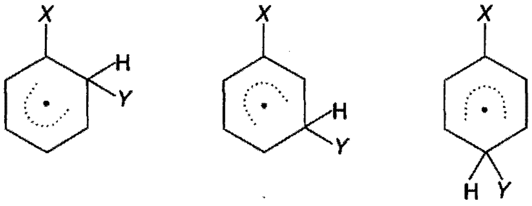
$$\longrightarrow \underset{\text{Acetone}}{2(CH_3)_2CO} + \underset{\substack{\text{Methyl}\\ \text{radical}}}{2\dot{C}H_3}$$



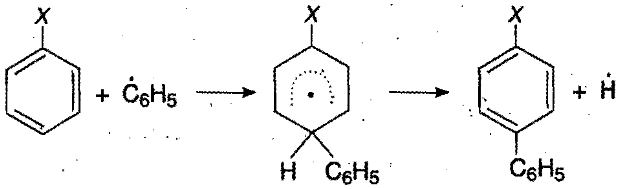
where $X = —Cl, —OCH_3, —NO_2, —CH_3$, etc.

In the case of free radical aromatic substitution, it has been found that the *ortho* and *para* product predominate even in presence of some *meta*-directing group in the aromatic nucleus.

The structures of *o*-, *m*- and *p*-intermediates may be written as follows:



By the substitution of an aromatic compound with an aryl radical to form bi aryl may be shown as follows :



$$(\dot{C}_6H_5 + \dot{H} \longrightarrow C_6H_6)$$

The mechanism of chlorination of benzene at high temperature is similar to that of the free radical aliphatic substitution.

(i) $Cl_2 \longrightarrow \dot{C}l + \dot{C}l$ (chain initiation)

(ii) $C_6H_6 + \dot{C}l \longrightarrow \dot{C}_6H_5 + HCl$ (H-abstraction)

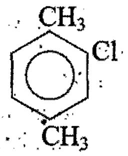
(iii) $\dot{C}_6H_5 + Cl_2 \longrightarrow C_6H_5Cl + \dot{C}l$ (chain propagation)

Problem 5. *Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.*

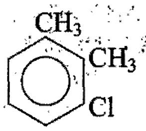
Solution : Anhydrous $FeCl_3$, BF_3, $SnCl_4$, etc.

Problem 6. *Which xylene gives (a) one, (b) two and (c) three, monochloro derivatives? Give their structures and names.*

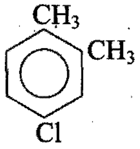
Solution : (a) Monochlorination of *p*-xylene gives one monochloro derivative because all the four available positions are equivalent. The product is 2-chloro-1,4-dimethylbenzene.



(b) *o*-Xylene has two types of equivalent positions, leading to two isomeric products :

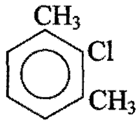
(i)


1-Chloro-2,3-dimethylbenzene

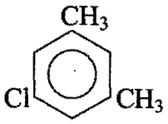
(ii)


4-Chloro-1,2-dimethylbenzene

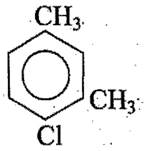
(c) *m*-Xylene has three types of positions giving three different derivatives:

(i)


2-Chloro-1,3-dimethylbenzene

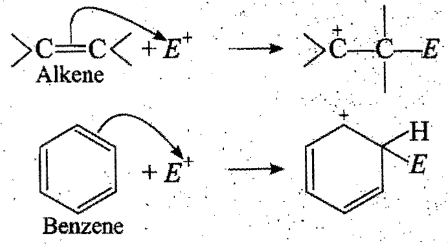
(ii)


1-Chloro-3,5-dimethylbenzene

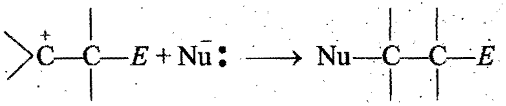
(iii)  1-Chloro-2,4-dimethylbenzene

Problem 7. *Explain why benzene undergoes electrophilic substitution reactions whereas alkenes undergo addition reactions?*

Solution : Both benzene and alkenes react with electrophiles because of their exposed π-electrons and form carbocations.

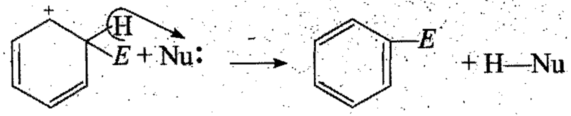


- The carbocation formed by alkene combines with the nucleophile to form the addition product.



Addition product

If this happened to benzene, the product would lose the aromatic character. Thus, the nucleophile removes a proton from benzene carbocation to form substitution product as to maintain the aromatic character.



Substitution product

Problem 8. *Explain : n-propylbenzene is best prepared by acylation followed by reduction of the carbonyl group with zinc amalgam and* HCl *rather than by direct alkylation of benzene with n-propylchloride.*

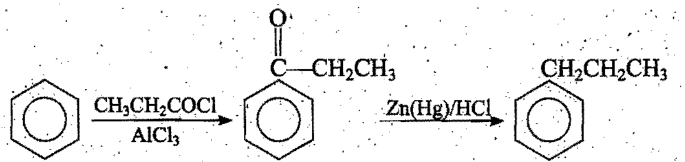
Solution : The direct alkylation of benzene with *n*-propylchloride by Friedel-Crafts reaction gives isopropylbenzene and not *n*-propylbenzene as the primary carbocation $(CH_3CH_2\overset{+}{C}H_2)$ rearranges to a more stable secondary carbocation $(CH_3\overset{+}{C}HCH_3)$.

$$CH_3CH_2CH_2Cl + AlCl_3 \longrightarrow CH_3CH_2\overset{+}{C}H_2 + Al\bar{C}l_4$$

$$CH_3CH_2\overset{+}{C}H_2 \longrightarrow CH_3\overset{+}{C}HCH_3$$

$$C_6H_6 + CH_3\overset{+}{C}HCH_3 \longrightarrow \underset{\text{Isopropylbenzene}}{C_6H_5CH(CH_3)_2}$$

Acylation gives keto compound which on reduction forms alkylbenzene.



n-Propylbenzene

Problem 9. *Explain the following with proper reasoning:*

(*a*) *Although benzene is highly unsaturated, it does not undergo addition reactions.*

(*b*) *Benzene though unsaturated, undergoes substitution reactions easily rather than addition.*

(*c*) *All m-directors are deactivating.*

(*d*) *The halogens, as exceptions, are o-, p-directors but are deactivating.*

(*e*) *Most o-,p-directing substituents are activating.*

Solution : (a) π-electrons of benzene ring are delocalized throughout the molecule. This makes the molecule very stable. The addition reactions would result in the breaking of this delocalization, *i.e.*, the stability of the molecule which is resisted.

(b) Resonance is present in benzene molecule. This makes the benzene molecule stable. As the substitution reactions do not disturb the resonance stabilization or aromatic character, these occur easily. Addition reactions disturb the resonance stabilization or aromatic character, thus, these reactions are resisted.

(c) The *meta*-directing substituents withdraw electrons from the benzene ring and thus, deactivate the benzene ring for further substitution.

(d) In the case of halogens, two opposing effects operate simultaneously. A halogen substituent releases electrons due to resonance but withdraws electrons also due to high electronegativity, *i.e.*, –*I* (inductive) effect. The inductive effect is more pronounced than the resonance effect and the net result is that the benzene ring is rendered electron deficient and thus deactivated for further substitution.

(e) The *o-,p*-directing substituents release electrons into the benzene ring and thus, activate the benzene ring for further substitution.

Problem 10. (*a*) *Show the formation of the electrophile in the following reactions :*

(*i*) $Cl_2 + AlCl_3$, (*ii*) $HNO_3 + H_2SO_4$, (*iii*) Br_2 + Fe, (*iv*) H_2SO_4 *and* (*v*) $H_2S_2O_7$, *fuming sulphuric acid.*

(*b*) *How do substituents groups on an aromatic ring influence the course of electrophilic aromatic substitution? Classify them by their effects.*

Solution :

(a) (i) $Cl_2 + AlCl_3 \longrightarrow \mathbf{Cl^+} + AlCl_4^-$

(ii) $HONO_2 + HOSO_3H \longrightarrow H_2O + \mathbf{NO_2^+} + HSO_4^-$

(iii) $2Fe + 3Br_2 \longrightarrow 2FeBr_3$

$FeBr_3 + Br_2 \longrightarrow \mathbf{Br^+} + FeBr_4^-$

(iv) $2H_2SO_4 \longrightarrow H_3O^+ + HSO_4^- + \mathbf{SO}$

(v) $H_2S_2O_7 \longrightarrow H^+ + HSO_4^- + \mathbf{SO_3}$

(b) The substituents on an aromatic ring affect the electrophilic substitution in two ways :

1. Reactivity : The compound is more reactive than benzene, the groups present are **activating.** In case, the compound is less reactive than benzene, the groups present are **deactivating.**

2. Orientation : Whether electrophile (E) enters *ortho*, *para* or *meta*. There are three classes of substituent groups:

(i) All activating groups direct E to *ortho* or *para*-positions.

(ii) Most deactivating groups direct E to *meta*-positions.

(iii) A few deactivating groups, *e.g.*, halogens direct E to *ortho* or *para*-positions.

Problem 11. *Give the principal monosubstitution products from the following reactions and indicate whether each reaction is faster or slower than with benzene.*

(*a*) *Nitration of* $PhNHCOCH_3$

(*b*) *Bromination of* $PhCBr_3$

(*c*) *Chlorination of* $PhC(CH_3)_3$

(*d*) *Nitration of* Ph–Ph

(*e*) *Nitration of* $PhCOOCH_3$

(*f*) *Sulphonation of* $PhCH(CH_3)_2$

(*g*) *Nitration of* $PhC{\equiv}N$

(*h*) *Bromination of* PhI

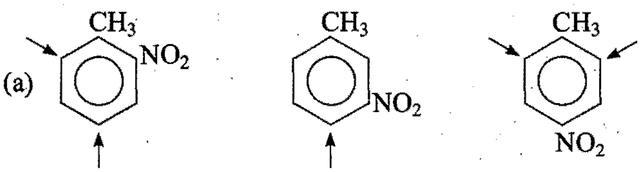
Solution :

	Principal products	**Nature of reaction in comparison to benzene**
(a)	$p\text{-}O_2NC_6H_4NHCOCH_3$	Faster
(b)	$m\text{-}BrC_6H_4CBr_3$	Slower
(c)	$p\text{-}ClC_6H_4C(CH_3)_3$	Faster
(d)	$p\text{-}O_2NC_6H_4Ph$ (Ph is *o*-, *p*-directing and activating)	Faster
(e)	$m\text{-}O_2NC_6H_4COOCH_3$	Slower
(f)	$p\text{-}HSO_3\cdot C_6H_4CH(CH_3)_2$	Faster
(g)	$m\text{-}O_2NC_6H_4CN$	Slower
(h)	$p\text{-}BrC_6H_4I$	Slower

Problem 12. *Show by an arrow the preferred product of reaction with* E^+ *of each of the three isomeric, (a) nitrotoluenes, (b) methoxy toluenes and (c) methoxy acetanilides. Explain your choices in each case.*

Solution :

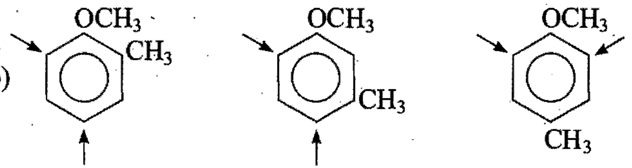
(a)



ortho (*A*) *meta* (*B*) *para* (*C*)

In (A), CH_3 directs E^+ to *ortho* and *para*-positions which are also *meta* to NO_2, *i.e.*, substituents reinforce each other. In (B), the orientation is in opposition. The *o*-,*p*-director controls the orientation, *i.e.*, E^+ enters *para* to CH_3 and *ortho* to NO_2. In (C), both groups are reinforcing, *i.e.*, *ortho* to CH_3 and *meta* to NO_2.

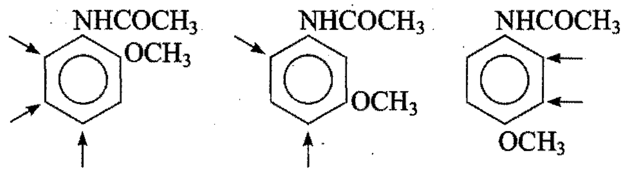
(b)



ortho (*A*) *meta* (*B*) *para* (*C*)

Both groups are *o*-,*p*-directing. In (B), the substituents reinforce each other, very little substitution occurs between the groups due to steric hindrance. In (A) and (C), the two groups are in opposition. The more strongly activating $—OCH_3$ controls the orientation.

(c)



ortho (*A*) *meta* (*B*) *para* (*C*)

Both the substituents are *o*-,*p*-directing and equally moderate strong activators. In (B), both the groups are reinforcing and a mixture of two isomers is obtained. In (A) and (C), two groups are in opposition. In (A), substantial amounts of all isomers are obtained while in (C), substitution occurs *ortho* to both the groups.

Problem 13. *Explain the following percentages of meta electrophilic substitutions.*

(*a*) $\underset{4.4\%}{C_6H_5CH_3}$, $\underset{15.5\%}{C_6H_5CH_2Cl}$, $\underset{33.8\%}{C_6H_5CHCl_2}$, $\underset{64.6\%}{C_6H_5CCl_3}$

(*b*) $\underset{100\%}{C_6H_5\overset{+}{N}(CH_3)_3}$, $\underset{88\%}{C_6H_5CH_2\overset{+}{N}(CH_3)_3}$,

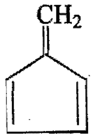
$\underset{19\%}{C_6H_5CH_2CH_2\overset{+}{N}(CH_3)_3}$

Solution : (a) Successive replacement of hydrogen atoms in electron releasing group ($—CH_3$) by electronegative chlorine atoms makes the group increasingly electron attracting and *meta*-directing.

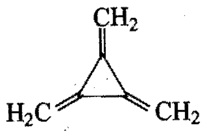
(b) The +ve charge on N makes the substituent electron attracting and *meta*-directing. The positive charge decreases successively by inserting electron releasing $—CH_2$ groups and thus *o*-,*p*-orientation dominates in $C_6H_5CH_2CH_2\overset{+}{N}(CH_3)_3$.

Example : Which of the following isomeric compounds give only one C_6H_5Br isomer?

(a)

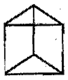


(b)



(c)

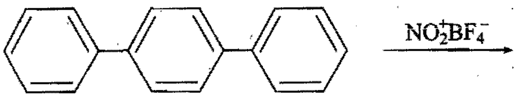
(d)



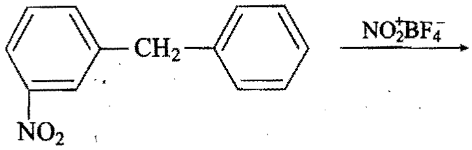
Ans. (b) In this molecule, all the methylene groups are identical hence only one monobromo derivative is formed.

Problem 14. *Give the monosubstitution product in the following reactions*:

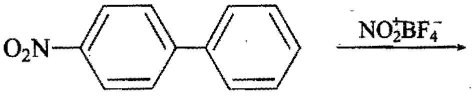
(*i*)



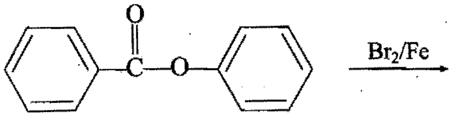
(*ii*)



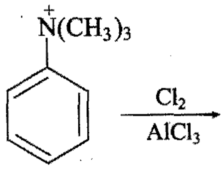
(*iii*)



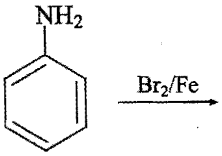
(*iv*)



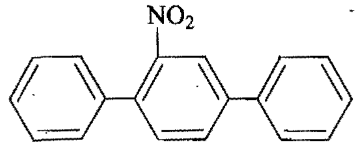
(*v*)



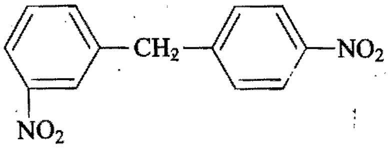
(*vi*)



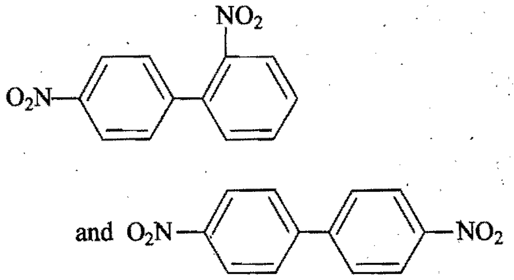
Solution: (i)



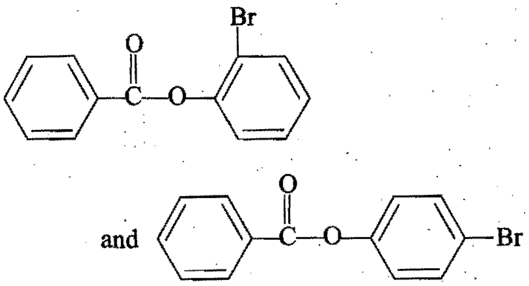
(ii)



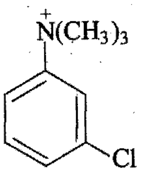
(iii)



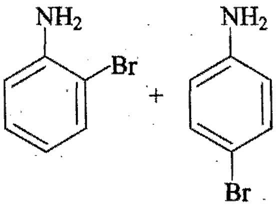
(iv)



(v)



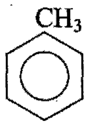
(vi)



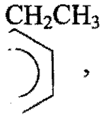
16.9 AROMATIC HYDROCARBONS (ARENES)

The term *arene* is used to designate aromatic hydrocarbons derived by replacement of one or more hydrogen atoms of the benzene ring by hydrocarbon substituents such as alkyl, alkenyl, alkynyl or aryl groups. They can be divided into two categories:

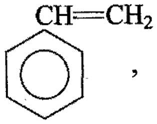
(i) Arenes containing one benzene ring and (ii) arenes containing more than one benzene rings either linked directly with each other or through one or more carbon atoms. Some of the common examples of both the categories are:



Toluene

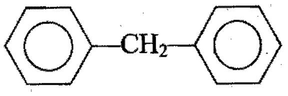


enzene

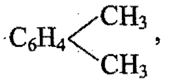


Styrene

Bi-pheny



Diphenylmethane

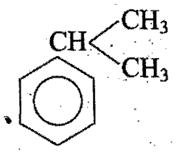


$C_6H_4(CH_3)_2$

o-, *m*- or *p*-Xylene

$C_6H_3(CH_3)_3$,

Adj-, unsym- or sym-trimethylbenzene

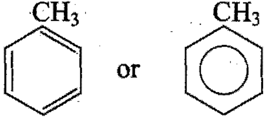


Isopropylbenzene (Cumene)

HOMOLOGOUS OF BENZENE

[A] Toluene or Methyl benzene or Phenylmethane

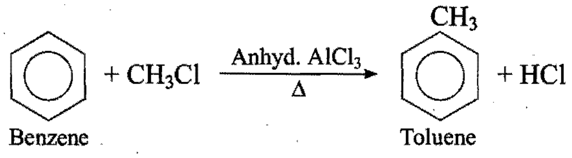
$C_6H_5CH_3$ or



Toluene is the simplest homologue of benzene. It was first obtained by dry distillation of **Tolubalsam** and hence its name toluene. It is present in coal-tar. Toluene is commercially known as toluol.

Methods of Preparation

1. From benzene (Friedel-Crafts reaction): Benzene reacts with methyl chloride in presence of anhydrous aluminium chloride to form toluene.



[The formation occurs through electrophilic substitution.

$$CH_3Cl + AlCl_3 \longrightarrow \underset{\text{Electrophile}}{CH_3^+} + AlCl_4^-$$

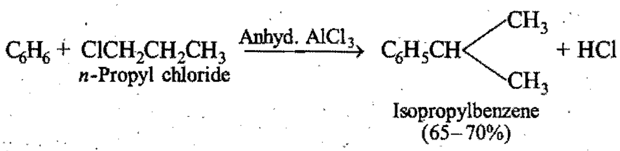
$$C_6H_5H + CH_3^+ + AlCl_4^- \longrightarrow C_6H_5CH_3 + HCl + AlCl_3]$$

Note : (i) The reaction is not very useful as the monoalkyl derivative first formed readily undergoes further alkylation at a still greater speed to produce polysubstituted products.

$$C_6H_6 + 2CH_3Cl \longrightarrow C_6H_4(CH_3)_2 + 2HCl$$

$$C_6H_6 + 3CH_3Cl \longrightarrow C_6H_3(CH_3)_3 + 3HCl$$

(ii) Alkyl halide employed may undergo an isomeric change.



$$C_6H_6 + \underset{n\text{-Propyl chloride}}{ClCH_2CH_2CH_3} \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\substack{\text{Isopropylbenzene}\\(65-70\%)}}{C_6H_5CH(CH_3)_2} + HCl$$

Inspite of the above two difficulties, Friedel-Crafts reaction is extensively used in the preparation of aromatic hydrocarbons. The following catalysts can be used in place of anhydrous $AlCl_3$ to moderate the speed of the reaction.

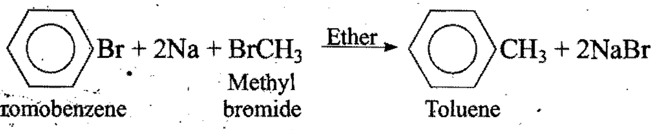
$$AlCl_3 > SbCl_3 > SnCl_4 > BF_3 > ZnCl_2 > HgCl_2$$

Alcohols and olefins can be used in place of alkyl halides.

$$C_6H_5H + HOCH_3 \xrightarrow{\text{Anhyd. AlCl}_3} C_6H_5CH_3 + H_2O$$

$$C_6H_5H + C_2H_4 \longrightarrow C_6H_5C_2H_5$$

2. From bromobenzene (Wurtz-Fittig reaction): When metal sodium reacts with a mixture of bromobenzene and methyl bromide in dry ethereal solution, toluene is obtained as a main product.



This reaction is an extension of Wurtz reaction. It follows free radical mechanism.

$$C_6H_5Br + Na \longrightarrow C_6\dot{H}_5 + NaBr$$

$$CH_3Br + Na \longrightarrow C\dot{H}_3 + NaBr$$

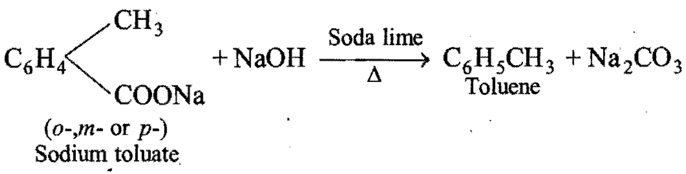
$$C_6\dot{H}_5 + C\dot{H}_3 \longrightarrow C_6H_5CH_3 \text{ (Toluene)}$$

Diphenyl and ethane are obtained as byproducts.

$$C_6\dot{H}_5 + C_6\dot{H}_5 \longrightarrow \underset{\text{(Diphenyl)}}{C_6H_5—C_6H_5}$$

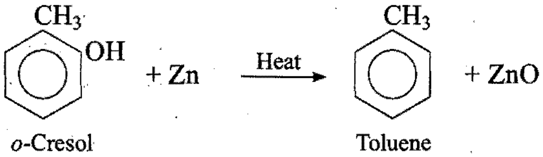
$$C\dot{H}_3 + C\dot{H}_3 \longrightarrow \underset{\text{(Ethane)}}{CH_3—CH_3}$$

3. From toluic acid (Decarboxylation): The sodium salt of (*o*-,*m*- or *p*-) toluic acid when heated with soda lime, toluene is formed.

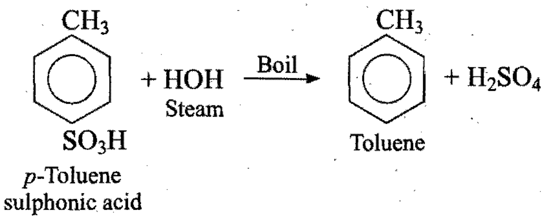


$$\underset{\substack{(o\text{-},m\text{- or }p\text{-})\\\text{Sodium toluate}}}{C_6H_4(CH_3)(COONa)} + NaOH \xrightarrow[\Delta]{\text{Soda lime}} \underset{\text{Toluene}}{C_6H_5CH_3} + Na_2CO_3$$

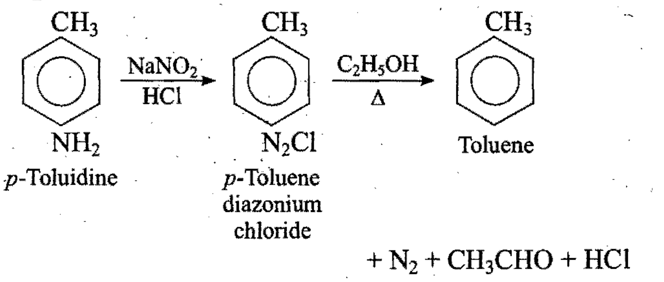
4. From cresol: When cresol (*o*-,*m*- or *p*-) is distilled with zinc dust, toluene is obtained.



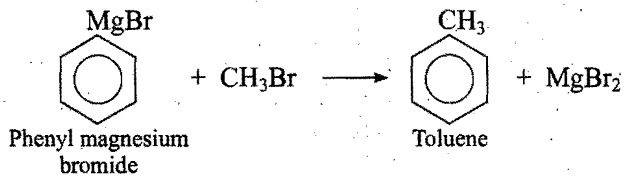
5. From toluene sulphonic acid: When (*o*-, *m*- or *p*-) toluene sulphonic acid is boiled with HCl or treated with super-heated steam, toluene is formed.



6. From toluidine: Toluidine is first diazotised with sodium nitrite and HCl at low temperature. The diazonium compound when heated with alkaline stannous chloride ($SnCl_2$) or absolute alcohol gives toluene.



7. From Grignard reagent: Toluene is formed when phenyl magnesium bromide is treated with methyl bromide.



8. From aromatic ketones : Mixed aliphatic aromatic ketone is obtained by condensation of acid chloride with aromatic hydrocarbon in presence of anhydrous $AlCl_3$ (Friedel-Crafts synthesis).

$$C_6H_5H + ClCOCH_3 \xrightarrow[\Delta]{\text{Anhyd. } AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

The ketone thus formed is then reduced by amalgamated zinc and concentrated hydrochloric acid.

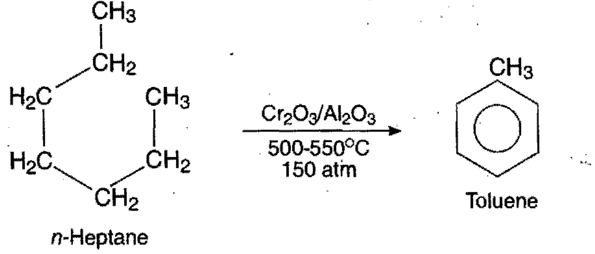
$$C_6H_5COCH_3 + 4[H] \xrightarrow{Zn(Hg)/HCl} \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3} + H_2O$$

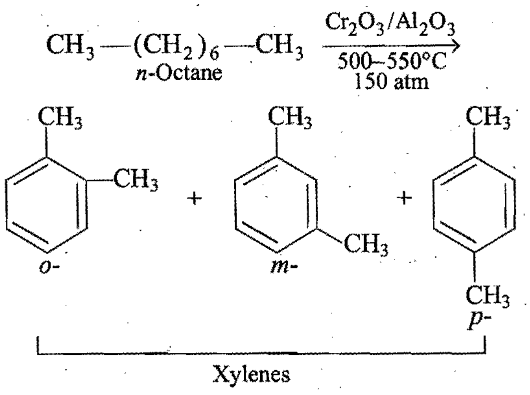
This method is used for the preparation of alkylbenzenes other than toluene.

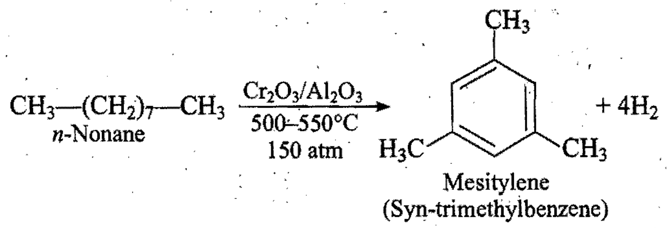
Commercial Preparation

1. From coal-tar : The main source of commercial production of toluene is the light oil fraction of coal-tar. The light oil fraction is washed with conc. H_2SO_4 to remove the bases, then with NaOH to remove acidic substances and finally with water. It is subjected to fractional distillation. The vapours collected between 80–110°C is 90% benzol which contains 70–80% benzene and 14–24% toluene. 90% benzol is again distilled and the portion distilling between 108–110°C is collected. It is toluene.

2. From *n*-heptane and methyl cyclohexane : Large quantities of commercial toluene are obtained by catalytic dehydrogenation of *n*-heptane or methyl cyclohexane (petroleum products).







Physical properties : (i) It is a colourless mobile liquid having characteristic aromatic odour.

(ii) It is lighter than water (sp. gr. 0.867 at 20°C).

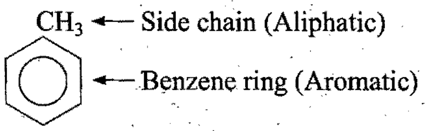
(iii) It is insoluble in water but miscible with alcohol and ether in all proportions.

(iv) Its vapours are inflammable. It boils at 110°C and freezes at −96°C.

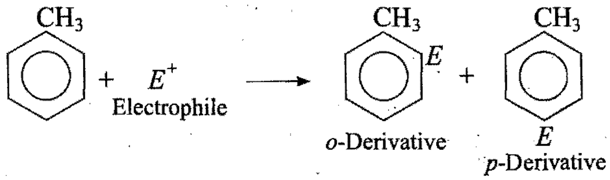
(v) It is a good solvent for many organic compounds.

(vi) It is a weak polar compound having dipole moment 0.4 D.

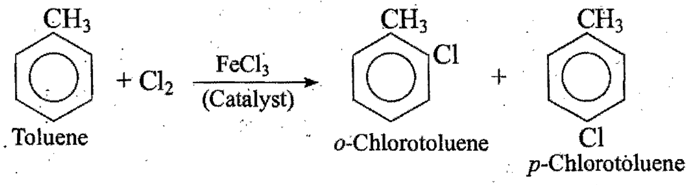
Chemical properties : Since, the molecule of toluene is made of benzene ring and methyl group, it shows behaviour of both.



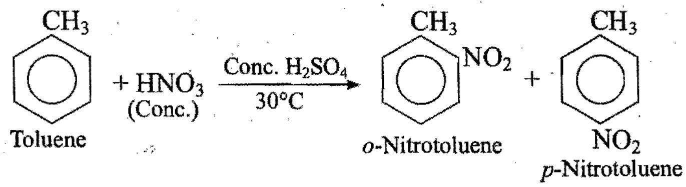
Electrophilic substitution reactions : The methyl group in toluene is electron releasing group (+Inductive effect) and thus, it activates the benzene nucleus and gives electrophilic substitution reactions more readily than benzene. It is an *ortho* and *para*-directing group, *i.e.*, on substitution forms always a mixture of *ortho*- and *para*-derivatives.



(i) Halogenation : Toluene reacts with chlorine or bromine in the presence of $FeCl_3$ or $AlCl_3$ to form a mixture of *o*- and *p*-derivatives.

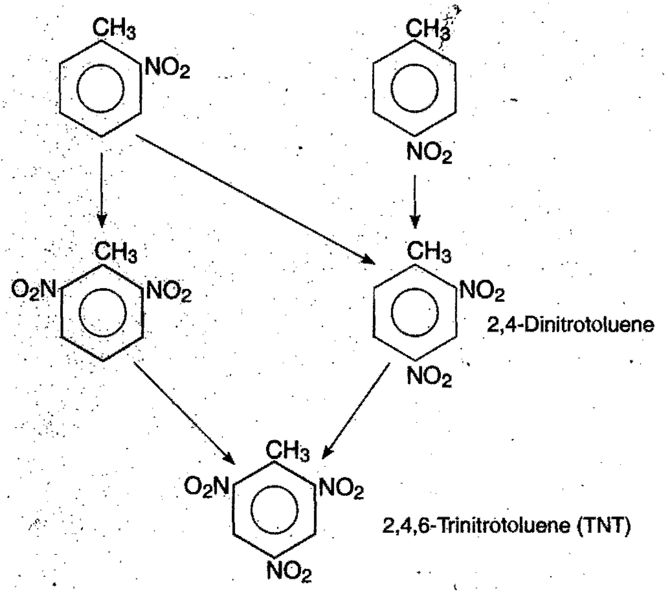


(ii) Nitration : Toluene forms a mixture of *ortho*- and *para*-nitrotoluenes when treated with a mixture of conc. HNO_3 and conc. H_2SO_4.



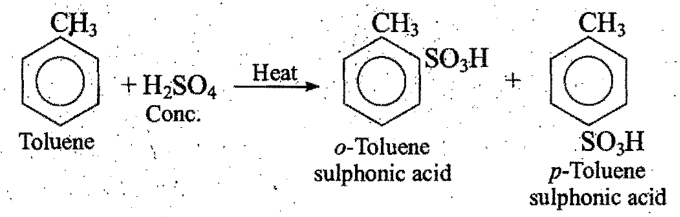
Nitration of toluene is 25 times more reactive than benzene and —CH_3 group is an activating group.

On further nitration (using fuming nitric acid), dinitrotoluene and trinitrotoluene are formed.



2,4,6-Trinitrotoluene (TNT) is a powerful explosive material.

(iii) Sulphonation : Toluene on heating with conc. H_2SO_4 forms a mixture of *ortho* and *para*-toluene sulphonic acids.

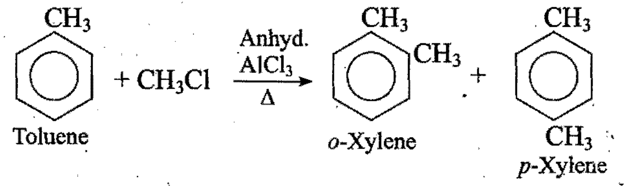


Sulphonation of toluene is approximately ten times more reactive than sulphonation of benzene.

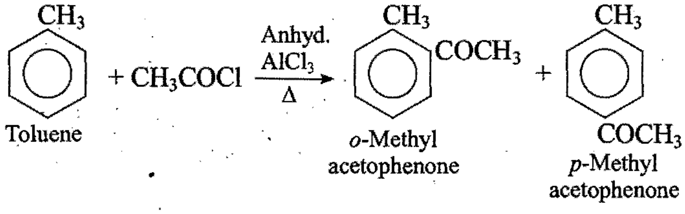
The same products are formed when fuming sulphuric acid is used at 0°C.

(iv) Friedel-Crafts reaction : It readily undergoes Friedel-Crafts reaction.

(a) Toluene reacts with methyl chloride in presence of anhydrous aluminium chloride to form a mixture of *ortho* and *para*-xylenes.

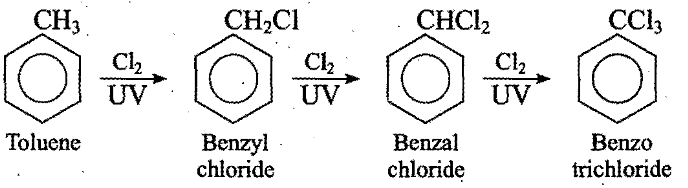


(b) Toluene reacts with acetyl chloride in presence of aluminium chloride to give a mixture of *o*- and *p*-methyl acetophenone.



Reactions of Side-chain

1. Side-chain halogenation : When chlorine is passed through boiling toluene in presence of ultraviolet light, side-chain substitution occurs forming benzyl chloride, benzal chloride and benzo trichloride.



Note : (i) Benzyl chloride on hydrolysis with aqueous caustic soda forms benzyl alcohol.

$$\underset{\text{(Phenyl methyl chloride)}}{C_6H_5CH_2Cl} + NaOH \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + NaCl$$

(ii) Benzal chloride on hydrolysis forms benzaldehyde.

$$\underset{\text{(Benzylidene chloride)}}{C_6H_5CHCl_2} + 2NaOH \longrightarrow C_6H_5CH(OH)_2 + 2NaCl$$

$$\downarrow$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + H_2O$$

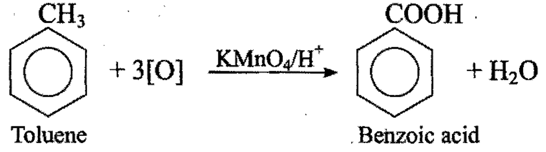
(iii) Benzo trichloride on hydrolysis forms benzoic acid.

$$\underset{\text{(Benzylidyne chloride)}}{C_6H_5CCl_3} + 3NaOH \longrightarrow C_6H_5C(OH)_3 + 3NaCl$$

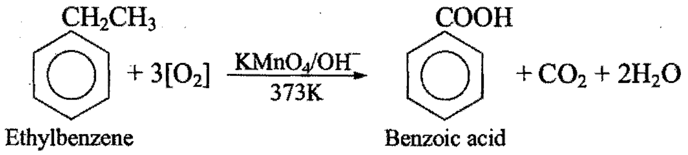
$$\downarrow$$

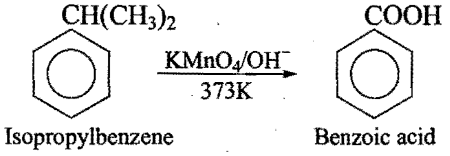
$$\underset{\text{Benzoic acid}}{C_6H_5COOH + H_2O}$$

2. Oxidation : (a) With hot acidic $KMnO_4$, $Na_2Cr_2O_7$ or conc. HNO_3, methyl group is oxidised to —COOH group, *i.e.*, toluene is converted into benzoic acid and all other homologues of benzene are oxidised to —COOH group **irrespective of the length of side-chain.**

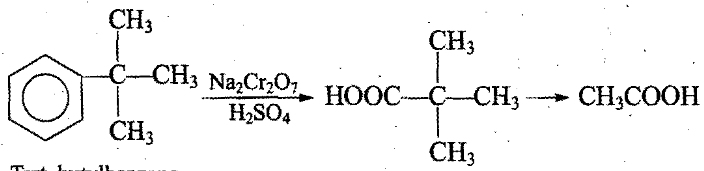


Even when oxidised with alkaline $KMnO_4$ or acidic $Na_2Cr_2O_7$, the entire side-chain with atleast one H at α-carbon, regardless of length is oxidised to —COOH.



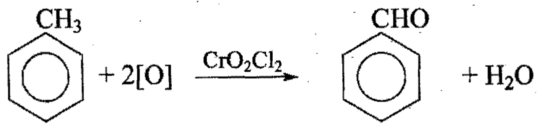


But if the side-chain has no C—H bond at the α-carbon (with respect to benzene nucleus), then benzene ring is broken during oxidation.



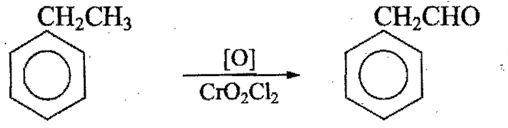
Tert. butylbenzene

(b) With acidic manganese dioxide or chromyl chloride, in CCl_4 solution, toluene and all other homologues of benzene are oxidised to terminal carbon atom giving aldehydes.

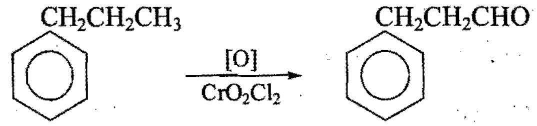


Toluene Benzaldehyde

$$[C_6H_5CH_3 + 2CrO_2Cl_2 \xrightarrow{CCl_4} \underset{\text{Complex}}{C_6H_5CH_3 \cdot 2CrO_2Cl_2} \xrightarrow{3H_2O} C_6H_5CHO + 2H_2CrO_4 + 4HCl]$$



Ethylbenzene Phenylacetaldehyde

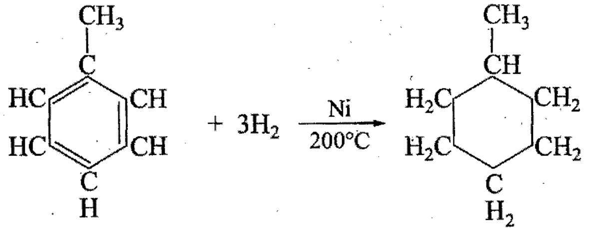


Propylbenzene 3-Phenylpropanal

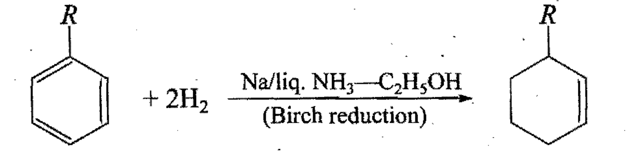
This is **Etard's reaction.**

Note : All alkyl benzenes, on oxidation with hot acidic $KMnO_4$ or $Na_2Cr_2O_7$ form benzoic acid. The length of the side-chain does not matter.

3. Addition reaction (Hydrogenation) : The mixture of toluene vapour and hydrogen when heated at 200°C in presence of nickel or Pt as catalyst methyl cyclohexane is formed.



Methylbenzene Methyl cyclohexane

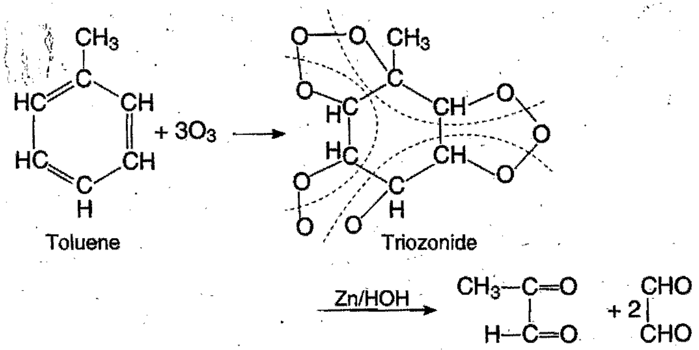


Alkylbenzene Alkyl cyclohexene

4. Combustion : Toluene burns with smoky flame in air or oxygen.

$$C_6H_5CH_3 + 9O_2 \xrightarrow{\text{Burn}} 7CO_2 + 4H_2O$$

5. Ozonolysis :



Toluene Triozonide

Methyl glyoxal Glyoxal

Uses : Toluene is used,

(i) in the manufacture of benzyl chloride, benzal chloride, benzyl alcohol, benzaldehyde, benzoic acid, saccharin, etc.

(ii) in the manufacture of trinitrotoluene (TNT), a highly explosive substance.

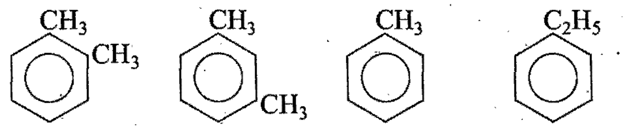
(iii) as an industrial solvent and in dry-cleaning.

(iv) as a petrol substitute.

(v) in the manufacture of certain dyes and drugs.

[B] Xylenes (Dimethylbenzene), $C_6H_4(CH_3)_2$

The molecular formula, C_8H_{10} represents four isomers.

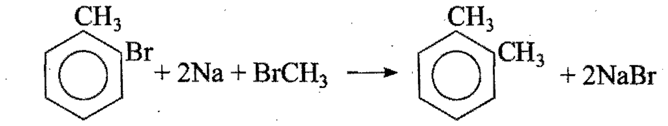


o-Xylene m-Xylene p-Xylene Ethylbenzene

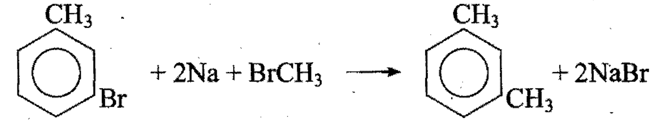
These are produced along with benzene, toluene and ethylbenzene when aromatisation of C_6—C_8 fraction of petroleum naphtha is done. The xylenes are isolated from the resulting mixture (BTX) by fractional distillation.

Preparations

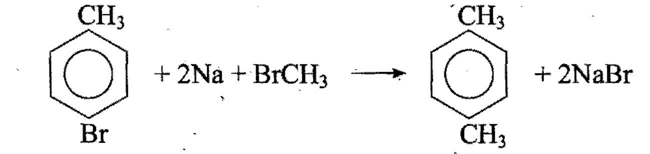
These can be prepared by Wurtz-Fittig reaction. A mixture of bromotoluene and methylbromide is treated with sodium in dry ethereal solution to form the desired xylene.



o-Bromotoluene o-Xylene

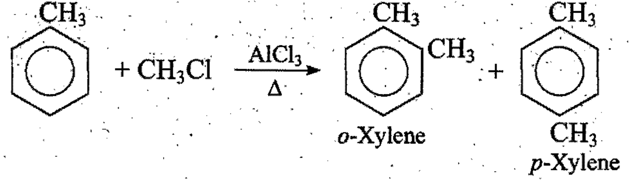


m-Bromotoluene m-Xylene

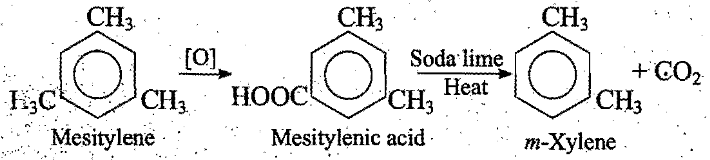


p-Bromotoluene p-Xylene

These can also be obtained by Friedel-Crafts synthesis,



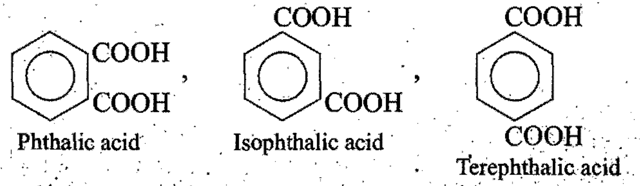
m-Xylene can be obtained from mesitylene.



Properties : Xylenes are colourless liquids having characteristic odour. The boiling points of three isomers are:

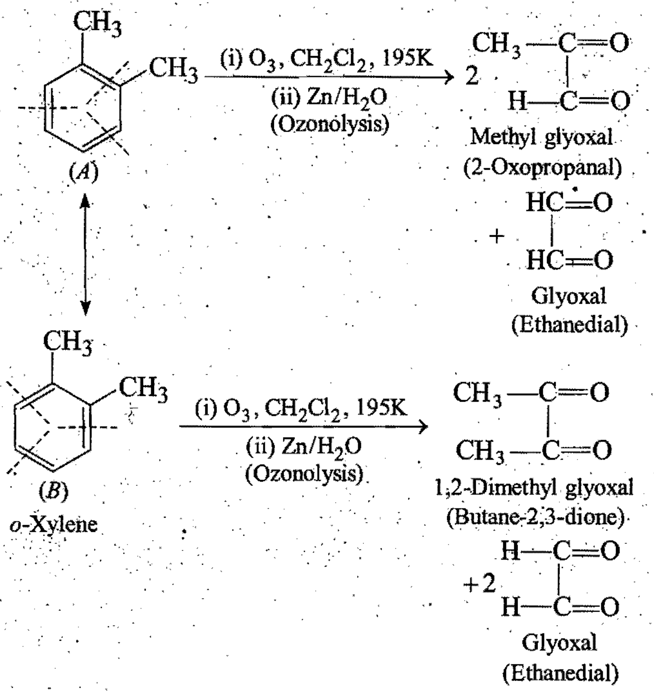
o-Xylene = 144°C; m-Xylene = 139°C; p-Xylene = 138°C.

Xylenes undergo electrophilic substitution reactions in the same manner as toluene. Upon oxidation with $KMnO_4$ or $K_2Cr_2O_7$, xylenes form corresponding dicarboxylic acids.



Ozonolysis

o-Xylene may be regarded as a resonance hybrid of the following two Kekule's structures (A) and (B). Ozonolysis of each one of these gives two products. For example,



Thus, all three products are obtained by the ozonolysis of o-xylene (*i.e.*, glyoxal, methyl glyoxal and dimethyl glyoxal). Since, all the three products cannot be obtained from any one of the two Kekule's structures (A) and (B), this shows that o-xylene is a resonance hybrid of the two Kekule's structures (A) and (B).

Xylenes are used in the manufacture of lacquers and as solvent for rubber. o-Xylene is used for the manufacture of phthalic anhydride.

[C] Ethylbenzene, $C_6H_5C_2H_5$

Preparations

It can be prepared by the following reactions:

(i) By Wurtz-Fittig reaction.

$$\underset{\text{Bromo-benzene}}{C_6H_5Br} + 2Na + \underset{\text{Bromoethane}}{BrC_2H_5} \longrightarrow \underset{\text{Ethyl-benzene}}{C_6H_5C_2H_5} + 2NaBr$$

(ii) By Friedel-Crafts reaction.

$$\underset{\text{Benzene}}{C_6H_5H} + BrC_2H_5 \xrightarrow{\text{Anhyd. AlCl}_3} C_6H_5C_2H_5 + HBr$$

(iii) By catalytic reduction of styrene (Vinylbenzene).

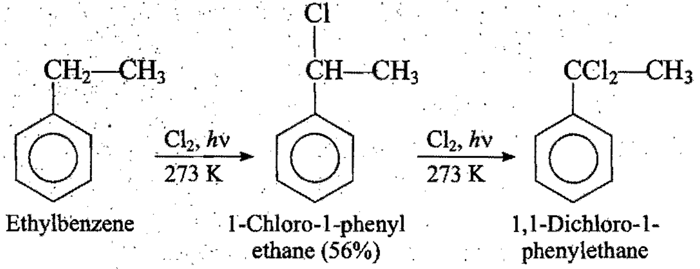
$$\underset{\text{Vinylbenzene}}{C_6H_5CH{=}CH_2} + H_2 \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3}$$

(iv) By alkylbenzene synthesis.

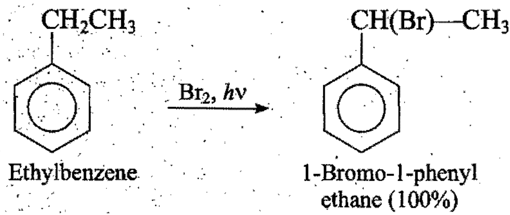
$$C_6H_5H + \underset{\text{Ethene}}{H_2C{=}CH_2} \xrightarrow[\text{or } H_3PO_4\ 95°C,\ \text{Pressure}]{\text{Anhyd. AlCl}_3,\ HCl} C_6H_5CH_2CH_3$$

Properties : It is a colourless liquid, boiling point 136°C.

1. Halogenation : Side-chain halogenation mainly takes place at benzylic carbon (*i.e.*, carbon atom next to benzene ring). This is because, the reaction intermediate in this particular case is benzyl free radical which is stabilized by resonance due to the presence of benzene ring.



Bromine radicals are not as reactive as chlorine radicals, and bromination is selective than chlorination. Bromine reacts exclusively at the benzylic position.



Thus, side-chain halogenation undergo free radical halogenation more easily than alkanes.

Further, it undergoes electrophilic substitution reaction in the same way as toluene. Ethyl group is an o- and p-directing group, *i.e.*, on substitution forms always a mixture of *o*- and *p*-derivatives.

2. Oxidation : When oxidised with dil. HNO_3 or alkaline $KMnO_4$ or chromic acid it forms benzoic acid.

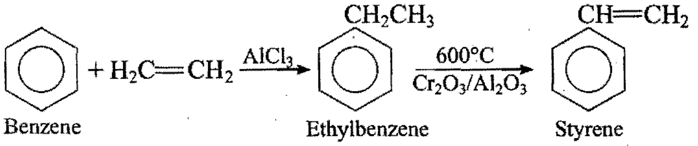
$$C_6H_5C_2H_5 \xrightarrow{[O]} C_6H_5COOH$$

[D] Styrene (Vinylbenzene), $C_6H_5CH{=}CH_2$

It is present in storax balsam and in coal-tar in traces.

Preparations

1. Dehydrogenation of side-chain of ethylbenzene : Dehydrogenation of side-chain is affected by heating ethylbenzene to high temperature in presence of a catalyst.



2. Decarboxylation of cinnamic acid : This is the laboratory preparation. It involves heating of cinnamic acid with a small amount of quinol.

$$C_6H_5CH{=}CHCOOH \xrightarrow{\text{Quinol}} C_6H_5CH{=}CH_2 + CO_2$$

3. Dehydration of 1-phenylethanol with H_2SO_4 :

$$C_6H_5CHOHCH_3 \xrightarrow[-H_2O]{H_2SO_4} C_6H_5CH{=}CH_2$$

4. Dehydration of 2-phenylethanol with $ZnCl_2$:

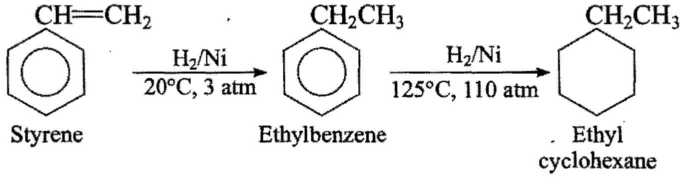
$$C_6H_5CH_2CH_2OH \xrightarrow[-H_2O]{ZnCl_2,\ \text{Heat}} C_6H_5CH{=}CH_2$$

5. Dehydrohalogenation of 1-phenyl-1-chloroethane: On heating with alcoholic potassium hydroxide, a molecule of hydrogen chloride is eliminated by the chloroderivative.

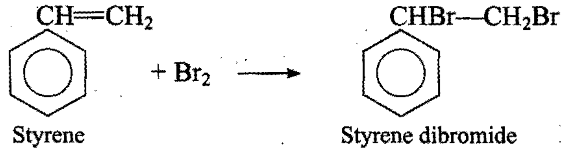
$$C_6H_5CHClCH_3 \xrightarrow[\text{Heat}]{\text{Alc. KOH}} C_6H_5CH{=}CH_2$$

Properties : It is a colourless liquid, boiling point 145°C. On keeping, it gradually changes into a solid polymer called a ***meta*-styrene.** The polymerization is rapid in sunlight or when treated with sodium. It shows properties of benzene ring (electrophilic substitution) and unsaturated side-chain (electrophilic addition). However, the side-chain double bond is more susceptible to electrophilic attack as compared to benzene ring.

At lower temperature and pressure, it reacts with hydrogen to produce ethylbenzene and at higher temperature and pressure, it is converted into ethyl cyclohexane.



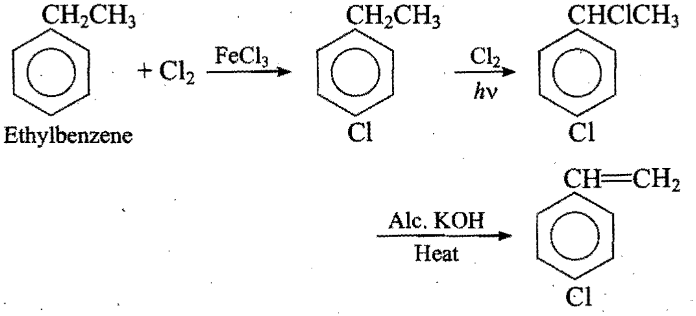
With bromine, it gives the dibromide.



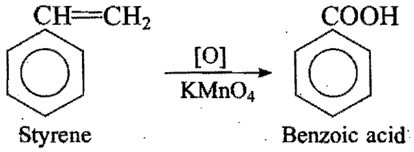
Halogen acids add to the side-chain.

$$C_6H_5CH{=}CH_2 + HX \longrightarrow C_6H_5CHXCH_3$$

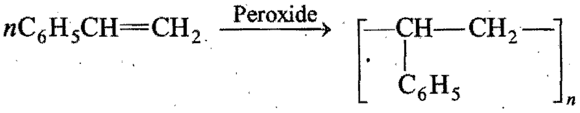
Preparation of ring substituted styrenes is not done by direct halogenation but through indirect route.



When oxidised under drastic conditions, the side-chain is completely oxidised to a carboxyl group.



In presence of peroxides, styrene undergoes free radical polymerization resulting in the formation of polystyrene—an industrially important plastic.



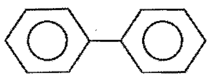
$$nC_6H_5CH{=}CH_2 \xrightarrow{\text{Peroxide}} \left[\begin{array}{l} -CH-CH_2- \\ \quad | \\ \quad C_6H_5 \end{array} \right]_n$$

Co-polymers of styrene with butadiene and other substances are also important since many of them are industrially useful products such as SBR (a rubber substitute).

POLYNUCLEAR HYDROCARBONS

Compounds having more than one aromatic ring are known as polynuclear hydrocarbons and their main source is coal-tar. These are of two types.

1. Isolated polynuclear hydrocarbons : These are the compounds containing more than one benzene ring which are isolated from each other or through one or more carbon atoms. They are also called as **polyphenyl compounds.** For example,



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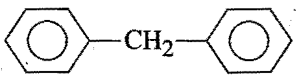
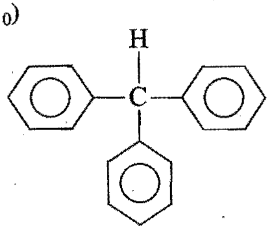


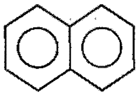
Diphenyl (Biphenyl) ($C_{12}H_{10}$)

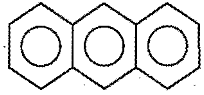
Diphenylmethane

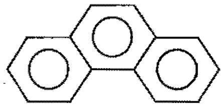


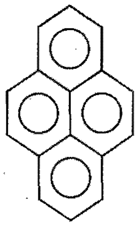
Triphenylmethane

2. Condensed (fused) polynuclear hydrocarbons : These are the compounds containing two or more benzene rings fused together in the *ortho* position. For example,


Naphthalene ($C_{10}H_8$)


Anthracene ($C_{14}H_{10}$)

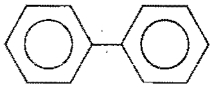

Phenanthrene ($C_{14}H_{10}$)


Pyrene ($C_{18}H_{12}$)

(Anthracene and phenanthrene are isomers.)

Naphthalene is the simplest and the most important member of fused-ring hydrocarbons. It is the largest single constituent (6-10%) of coal-tar, obtained by cooling the middle oil fraction (b.pt. 443-503 K). In naphthalene all carbon atoms are sp^2-hybridized and as the sp^2-orbitals are planar, all carbon and hydrogen atoms lie in one plane.

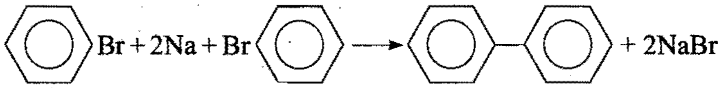
Anthracene is a tricyclic aromatic hydrocarbon and is obtained from green oil fraction (b.pt. 543–633K) of coal-tar. Like naphthalene, all carbon atoms in anthracene are also sp^2-hybridized.

[A] Biphenyl, C_6H_5—C_6H_5, 

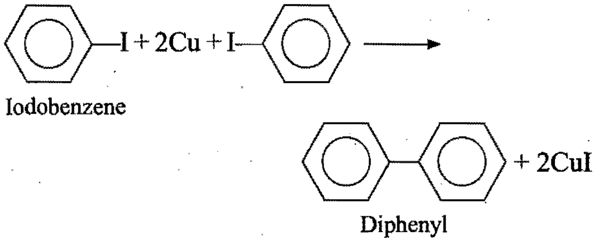
It occurs in coal-tar. It is the simplest example of an aromatic hydrocarbon in which two benzene rings are directly linked to each other.

Methods of Formation

1. Fittig reaction : It consists heating of an ethereal solution of bromobenzene with metallic sodium.



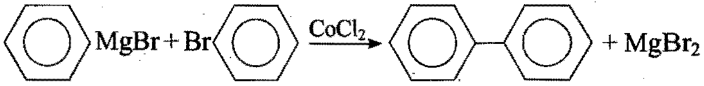
2. Ulmann biaryl synthesis : Iodobenzene, on heating with copper at 200°C in a sealed tube, forms biphenyl. The reaction is facilitated if a strong electron withdrawing group is present in *ortho* or *para*-position.



Comparison of Aromatic and Aliphatic Hydrocarbons

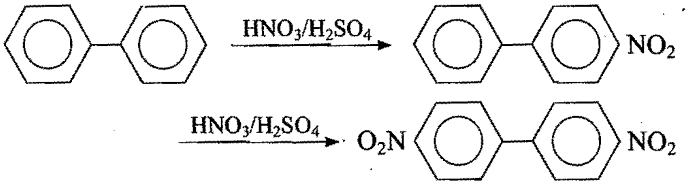
Characteristic	Benzene and its homologues	Aliphatic hydrocarbons
1. Composition	These are closed ring compounds. These are represented by general formula C_nH_{2n-6}.	These are open-chain compounds. These are represented by general formulae; C_nH_{2n+2} (alkanes), C_nH_{2n} (alkenes) and C_nH_{2n-2} (alkynes).
2. Carbon percentage	These contain high percentage of carbon. In benzene C_6H_6, the carbon percentage is 92.3.	These have low percentage of carbon in comparison to aromatic hydrocarbons. In hexane, C_6H_{14}, the carbon percentage is 83.7.
3. Combustion	These burn with smoky flame.	These burn with non-smoky flame.
4. Nature	These have high unsaturation. For example, benzene molecule consists three double bonds.	These are saturated as well as unsaturated.
5. Physical state	These are colourless liquids or solids. They have characteristic odour (aromatic).	A few lower members are colourless gases while higher members are liquids or solids. Generally no characteristic odour exists.
6. Addition reactions	Inspite of the fact that these are unsaturated, generally resist addition reactions. These do not react with HCl, HBr, HI or HClO.	The unsaturated hydrocarbons show addition reactions.
7. Substitution reactions	Generally exhibit substitution (electrophilic) reactions such as halogenation, nitration, sulphonation, Friedel-Crafts reaction, etc.	The saturated hydrocarbons show substitution reactions such as halogenation. The unsaturated hydrocarbons resist substitution reactions. Nitration and sulphonation occur with difficulty in higher alkanes. Friedel-Crafts reaction is not shown by aliphatic hydrocarbons.
8. Stability	Highly stable.	The unsaturated hydrocarbons are less stable.
9. $(4n+2)$ rule	Follow $(4n+2)$ rule, *i.e.*, contain $(4n+2)\pi$ electrons where $n = 0, 1, 2, 3, \ldots$	$(4n+2)$ rule does not apply to aliphatic unsaturated hydrocarbons.
10. Oxidation	Except benzene, all oxidise easily.	Alkanes do not oxidise easily while unsaturated hydrocarbons oxidise easily.

3. Grignard reaction : Phenyl magnesium bromide reacts with bromobenzene in presence of $CoCl_2$.

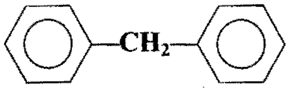


Properties : It is a colourless solid, melting point 71°C. It undergoes usual electrophilic substitution reactions. Since, aryl groups are electron withdrawing, they should have deactivating and *m*-orientating effect. But, it has been experimentally shown that presence of one benzene ring activates the other for electrophilic substitution and directs the incoming group to *o*- and *p*-positions. It has been shown that monosubstitution in the biphenyl results in the formation of *para* isomer as the major product.

Another special feature of the biphenyl is the behaviour towards second substitution in a monosubstituted biphenyl. The second substituent invariably enters the unsubstituted ring in the *ortho* and *para*-position no matter what is the nature of substituent already present.



Oxidation of biphenyl with chromic acid gives benzoic acid in small amounts.

[B] Diphenyl methane, 

Preparations

It can be prepared by following methods :

1. Friedel-Crafts reaction :

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + \underset{\text{Benzene}}{C_6H_6} \xrightarrow[\Delta]{\text{Anhyd. AlCl}_3} \underset{\text{Diphenyl methane}}{C_6H_5CH_2C_6H_5} + HCl$$

$$\text{or} \quad 2C_6H_6 + \underset{\text{Dichloromethane}}{CH_2Cl_2} \xrightarrow[\Delta]{\text{Anhyd. AlCl}_3} C_6H_5CH_2C_6H_5 + 2HCl$$

2. By action of formaldehyde on benzene in presence of conc. sulphuric acid :

$$2C_6H_6 + O{=}CH_2 \xrightarrow{\text{Conc. H}_2\text{SO}_4} C_6H_5CH_2C_6H_5 + H_2O$$

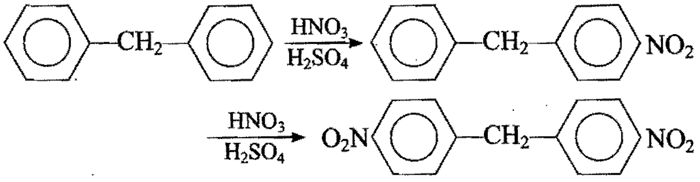
3. By Grignard reaction : Phenyl magnesium bromide reacts with benzyl bromide to form diphenyl methane.

$$C_6H_5MgBr + BrCH_2C_6H_5 \longrightarrow C_6H_5CH_2C_6H_5 + MgBr_2$$

4. By reduction of benzophenone : Reduction can be done with $LiAlH_4$ or P and HI.

$$C_6H_5COC_6H_5 \xrightarrow{4[H]} C_6H_5CH_2C_6H_5 + H_2O$$

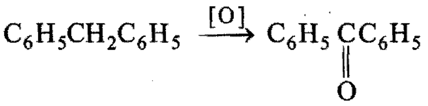
Properties : It is a colourless solid, melting point 26°C. Like biphenyl, it also easily undergoes electrophilic substitution reactions.



The methylene hydrogens of diphenylmethane are situated on carbon atom linked by two electron attracting benzene rings. Thus, these are somewhat acidic in nature.

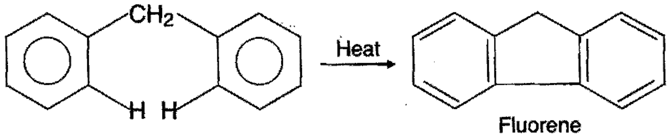
$$C_6H_5CH_2C_6H_5 + Br_2 \longrightarrow C_6H_5CHBrC_6H_5 + HBr$$

When oxidised with $K_2Cr_2O_7/H_2SO_4$ mixture, it forms benzophenone.



$$C_6H_5CH_2C_6H_5 \xrightarrow{[O]} C_6H_5\underset{\underset{O}{\|}}{C}C_6H_5$$

It forms fluorene when its vapours are passed through a red hot tube.



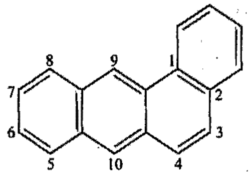
Carcinogenicity and Toxicity of Polynuclear Hydrocarbons

The most dreadful disease, cancer, developed by tar is due to the presence of some higher boiling polynuclear hydrocarbons called **carcinogenic hydrocarbons.** Cancer is a collection of diseases characterised by malignant cells (or cancerous cells) which reproduce by themselves in an uncontrolled manner. The difference between a normal cell and a cancerous cell is that the normal cell replicates only when it is required and the cancerous cell divides abnormally giving rise to a tumour which disturbs the normal function of vital organs of the body and therefore ultimately may lead to death.

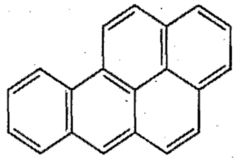
Generally, in the skin the transference of a normal cell into cancerous growth takes place in two distinct stages known as **initiation** and **promotion.** The first step initiation is an irreversible change caused only by carcinogenic compounds and it transfers a normal cell into dormant (sleeping) tumour cells which are stimulated to activity either by additional treatment with a carcinogen or with a promoting agent, such as iodoacetic acid, phenols, detergents and even mechanical tissue injury. Hence, these agents accelerate the development of tumours.

The normal cell may be converted into a cancerous cell either by environmental effects or by genetic factors. When a child feeds from his mother, a substance is transferred to him. The outer environment is mainly responsible in developing cancer. Radiations, chemical and physical irritations, coal-tar (due to the presence of certain polynuclear hydrocarbons), hormones and certain viruses can be the cause of cancer. Out of these, polynuclear hydrocarbons are among the most common agents which cause cancer and hence such hydrocarbons are known as **Carcinogenic polynuclear hydrocarbons.** These hydrocarbons are mainly formed on incomplete combustion of organic materials like coal-tar, tobacco tar, shoot, shale oil and petroleum etc. Azo dyes, aromatic amines and carbamates are also carcinogenic.

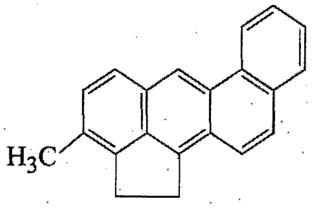
Examples of some polynuclear hydrocarbons having carcinogenic activity are:



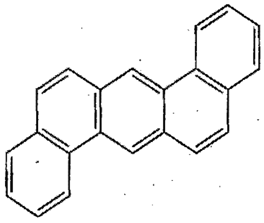
1,2-Benzanthracene



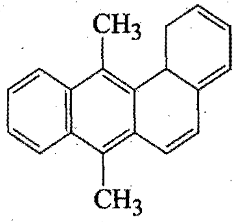
1,2-Benzpyrene



20-Methyl cholanthrene



1,2,5,6-Dibenzanthracene



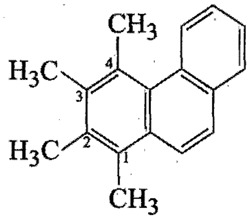
9,10-Dimethyl-1,2-benzanthracene

The reactivities of these carcinogenic hydrocarbons are as below:

20-Methyl cholanthrene > 1,2-Benzpyrene > 1,2-Benzanthracene

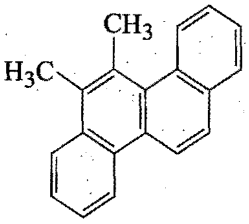
The degree of potency of producing cancerous hydrocarbons varies with the number and position of certain substituents like $—CH_3$, —OH, —CN and $—OCH_3$ group, etc.

Effect of $—CH_3$ group : 1,2-Benzanthracene is found to be the parent compound of almost all the important carcinogenic hydrocarbons. The addition of methyl groups and their position in these compounds influence their activity, *e.g.*, phenanthrene is inactive, while its methyl derivatives are active and the order follows as shown below:



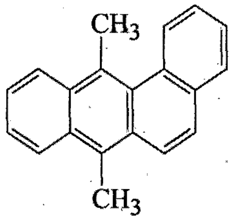
1,2,3,4-Tetramethyl phenanthrene

<



1,2-Dimethylchrysene

<



9,10-Dimethyl 1,2-benzanthracene

Methyl derivatives are very potent to cancer. In the same manner anthracene is found to be inactive but its methyl derivatives, *viz*, 6-methyl and 2,6-dimethyl are potent in the increasing order.

However, it has also been observed that the presence of methyl group may reduce carcinogenic activity, *e.g.*, 3,4,8,9 and 3,4,9,10-dibenzpyrenes are active while their methyl derivatives are less reactive.

It is believed that when these polynuclear hydrocarbons (PNH) enter into human body, they undergo various biochemical reactions (conversion into their oxides called epoxides and dihydroxy epoxides) and finally damage DNA causing mutations and ultimately lead to cancer.

Problem 15. *The Wurtz-Fittig reaction may be employed to unite aryl and alkyl radicals although it is impractical for the union of unlike aliphatic radicals. Explain.*

Solution : Dialkyls, diaryls and aryl-alkyls formed by Wurtz-Fittig reaction differ in their boiling points. Diaryls have high boiling points, aryl-alkyls have moderate boiling points and the dialkyls have low boiling points. Hence, it is easy to separate these products by fractional distillation. Union of two unlike alkyl radicals produce three different alkanes and their separation into individual members is very difficult.

Problem 16. *Predict the product (s) and outline the mechanism for the process when benzene is treated with,*

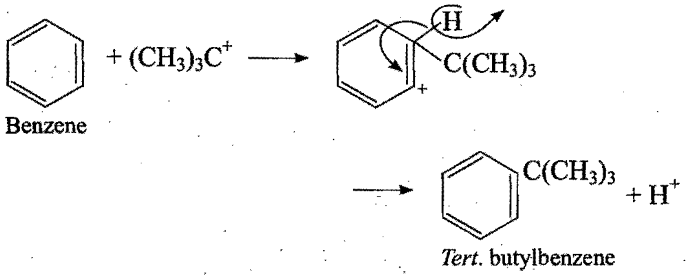
(*i*) $(CH_3)_3CCl$ *in presence of* $AlCl_3$

(*ii*) $(CH_3)_2C{=}CH_2$ *in presence of* H_2SO_4

(*iii*) $(CH_3)_2CHCH_2Cl$ *in presence of* $AlCl_3$

(*iv*) $(CH_3)_3COH$ *in presence of* H_2SO_4.

Solution : In all the four cases, the same product *t*-butylbenzene is formed by electrophilic substitution, *i.e.*, same electrophile $(CH_3)_3C^+$ attacks benzene in each case.



$$\text{(i)}\ (CH_3)_3CCl + AlCl_3 \longrightarrow (CH_3)_3C^+ + AlCl_4^-$$

$$\text{(ii)}\ (CH_3)_2C{=}CH_2 + H^+ \longrightarrow (CH_3)_3C^+$$

$$\text{(iii)}\ (CH_3)_2CHCH_2Cl + AlCl_3 \longrightarrow (CH_3)_2\underset{\displaystyle\downarrow \atop \displaystyle (CH_3)_3C^+}{C}HCH_2^+ + AlCl_4^-$$

$$\text{(iv)}\ (CH_3)_3C\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}H + H^+ \longrightarrow (CH_3)_3C\overset{H}{\overset{\bullet\bullet\,+}{\underset{\bullet\bullet}{O}}}H \longrightarrow (CH_3)_3C^+ + H_2O$$

Problem 17. *Sketch the following transformations :*

(*i*) $C_6H_5CH_2CH_2CH_3 \longrightarrow p\text{-}ClC_6H_4CH{=}CHCH_3$
Propylbenzene → *1-(p-Chlorophenyl) propene*

(*ii*) $C_6H_5CH{=}CHCOOH \longrightarrow C_6H_5CH{=}CH_2$
Cinnamic acid → *Styrene*

(*iii*) $C_6H_6 \longrightarrow C_6H_5CH{=}CH_2$

(*iv*) $p\text{-}CH_3{-}C_6H_4COOH \longrightarrow C_6H_5{-}CH_3$

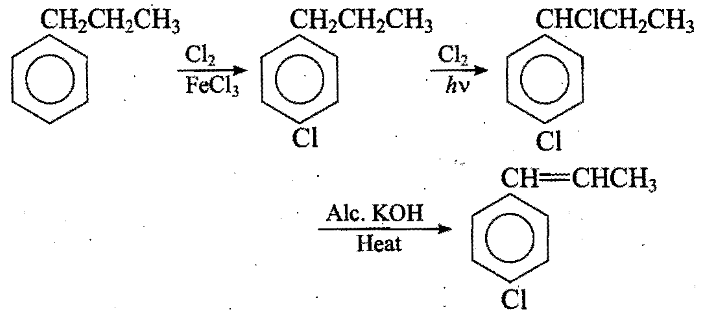
(*v*) $C_6H_5CH{=}CH_2 \longrightarrow C_6H_5C{\equiv}CH$
Phenyl acetylene

(*vi*) $C_6H_5CH_3 \longrightarrow C_6H_6$

(*vii*) $CH_3{-}C{\equiv}CH \longrightarrow$ *Sym*-$C_6H_3(CH_3)_3$

(*viii*) $C_6H_6 \longrightarrow C_6H_5CH(CH_3)_2$

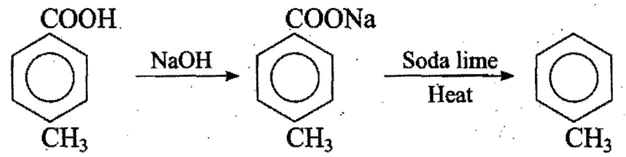
Solution :

(i)


(ii) $C_6H_5CH{=}CHCOOH \xrightarrow{\text{Heat}} C_6H_5CH{=}CH_2 + CO_2$

(iii) $C_6H_6 + ClCH_2CH_3 \xrightarrow{AlCl_3} C_6H_5CH_2CH_3$

$\xrightarrow[h\nu]{Cl_2} C_6H_5CHClCH_3 \xrightarrow[\text{Heat}]{\text{Alc. KOH}} C_6H_5CH{=}CH_2$

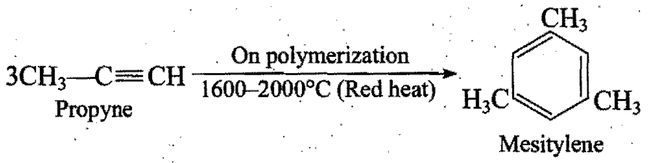
(iv)


(v) $C_6H_5CH{=}CH_2 \xrightarrow[\text{in } CCl_4]{Br_2} C_6H_5CHBr{-}CH_2Br$

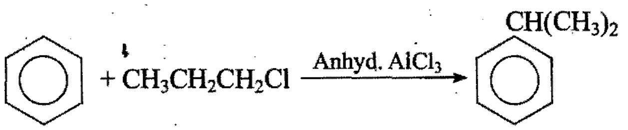
$\xrightarrow{\text{Alc. KOH}} C_6H_5C{\equiv}CH$

(vi) $C_6H_5CH_3 \xrightarrow[\text{[O]}]{KMnO_4} C_6H_5COOH$

$\xrightarrow{\text{Decarboxylation}} C_6H_6$

(vii)


Mesitylene

(viii)


Problem 18. *How will you distinguish between :*

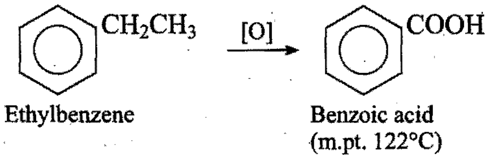
(*i*) *Ethylbenzene and o-xylene?*

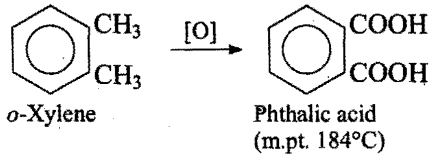
(*ii*) *Ethylbenzene and styrene?*

(*iii*) *Phenyl acetylene and styrene?*

(*iv*) *Benzene and toluene?*

Solution : (i) Ethylbenzene gives benzoic acid on oxidation with $KMnO_4$ while *o*-xylene gives phthalic acid.

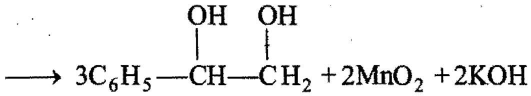




(ii) Styrene, having a double bond in the side-chain, gives the following two tests :

(a) It decolourises purple colour of dilute cold $KMnO_4$ solution. Brown precipitate of MnO_2 is formed. This test is not given by ethylbenzene.

$3C_6H_5CH{=}CH_2 + 2KMnO_4 + 4H_2O$



$$\longrightarrow 3C_6H_5{-}\underset{}{\overset{\overset{\displaystyle OH}{|}}{C}H}{-}\overset{\overset{\displaystyle OH}{|}}{C}H_2 + 2MnO_2 + 2KOH$$

(b) Styrene rapidly decolourises red colour of bromine in CCl_4. Ethylbenzene does not decolourise under this condition.

$C_6H_5CH{=}CH_2 + Br_2 \longrightarrow \underset{\text{Colourless}}{C_6H_5CHBrCH_2Br}$

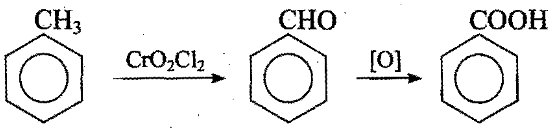
However, ethylbenzene reacts with bromine at high temperature or in presence of UV light.

(iii) Phenyl acetylene gives a precipitate with ammoniacal silver nitrate solution. Styrene does not react.

$C_6H_5C{\equiv}CH + AgNO_3 + NH_4OH \longrightarrow \underset{\text{ppt.}}{C_6H_5C{\equiv}C\cdot Ag}$

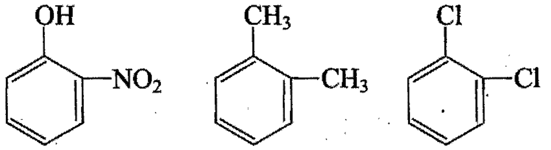
$+ NH_4NO_3 + H_2O$

(iv) Toluene is easily oxidised to benzaldehyde with CrO_2Cl_2 or benzoic acid with $KMnO_4$.

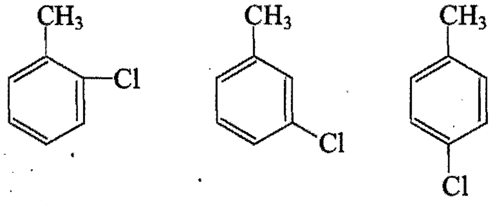


Benzene is quite stable and does not undergo oxidation with CrO_2Cl_2 or $KMnO_4$.

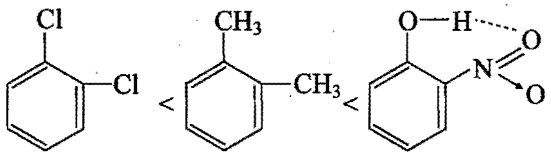
Problem 19. *Arrange the following in increasing order of dipole moment.*

(*a*)


(*b*)



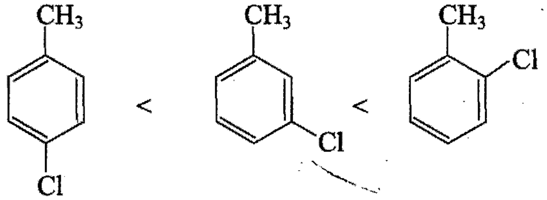
Ans. (a)



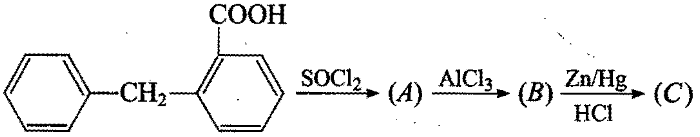
In *ortho*-dichlorobenzene, dipole-dipole repulsion of two halogens increases the bond angle (more than 60°) and hence, dipole moment is lowered.

In *ortho*-nitrophenol, intramolecular H-bond decreases the bond angle and hence, dipole moment is increased.

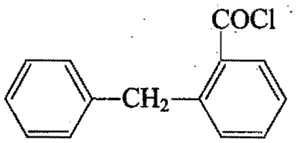
(*b*)



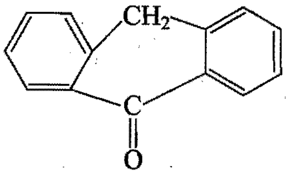
Problem 20. *What are (A), (B) and (C) in the following scheme of reactions?*



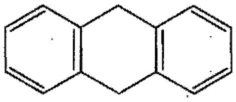
Ans. (A)



(B)



(C)



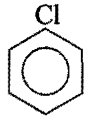
16.10 AROMATIC HALOGEN COMPOUNDS

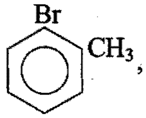
Benzene and its homologous react with halogens to produce either **addition** or **substitution** products.

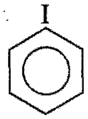
1. Addition compounds : These compounds are obtained by exposing the mixture of aromatic hydrocarbons and the halogens to direct sunlight, *e.g.*, benzene hexachloride (BHC), $C_6H_6Cl_6$; benzene hexabromide, $C_6H_6Br_6$, etc.

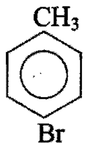
2. Substitution products : Two types of halogen substituted products are known.

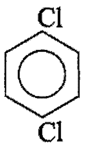
(i) Nuclear halogen substitution products (Aryl halides) or Haloarenes : In these products, the halogen is linked directly to the carbon of the benzene nucleus. These products are generally called aryl halides.


Chlorobenzene

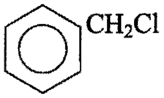

2-Bromotoluene

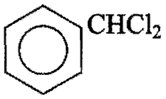

Iodobenzene

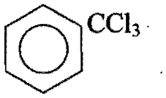

4-Bromotoluene
(*p*-Bromotoluene)


1,4-Dichlorobenzene
(*p*-Dichlorobenzene)

(ii) Side-chain halogen substitution products (Aralkyl halides) : In these products, the halogen is linked to the carbon atom of the side-chain.

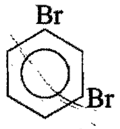

1-Chloro-1-phenylmethane
(Benzyl chloride)

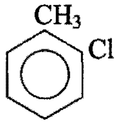

1,1-Dichloro-1-phenylmethane
(Benzal dichloride)

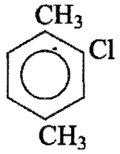

1,1,1-Trichloro-1-phenylmethane
(Benzotrichloride)

These are also called side-chain aryl halides. They have properties similar to alkyl halides.

Aryl halides : According to IUPAC system, aryl halides are named as **Haloarenes.** If more than one halogen is present, their positions in the ring are indicated by numbers or appropriate prefixes, *ortho, meta* and *para.*


1,3-Dibromobenzene or
(*m*-Dibromobenzene)

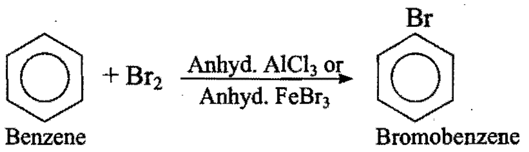

2-Chlorotoluene or
(*o*-Chlorotoluene)


2-Chloro-1,4-dimethylbenzene

General Methods of Preparation

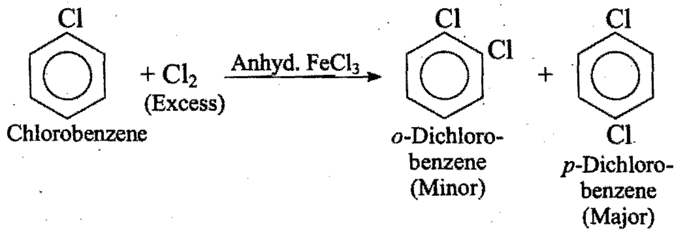
1. By direct halogenation of aromatic hydrocarbons : This method is used for the preparation of chloro and bromo derivatives. Halogens react with aromatic hydrocarbons in presence of catalysts or halogen carriers such as iron, iodine or anhydrous ferric or aluminium chloride (Lewis acid) at room temperature in absence of direct sunlight.

$$\underset{\text{Benzene}}{C_6H_6} + Cl_2 \xrightarrow[\text{Anhyd. FeCl}_3]{\text{Anhyd. AlCl}_3\text{ or}} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl$$



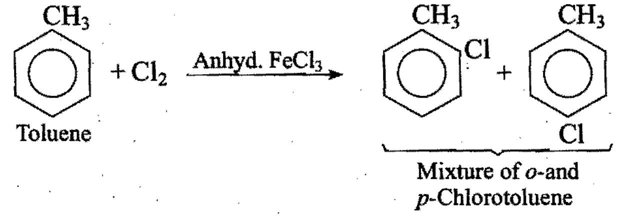
$(2Fe + 3Cl_2 \longrightarrow 2FeCl_3)$

For further halogenation, more halogen is used,



The function of the Lewis acid is to carry the halogens to the aromatic hydrocarbon.

Toluene in presence of Fe or $FeCl_3$ reacts with Cl_2 or Br_2 to form a mixture of *o*- (minor) and *p*- (major) chloro or bromotoluenes, respectively.



The *ortho* and *para* isomers can be easily separated due to large difference in their melting points.

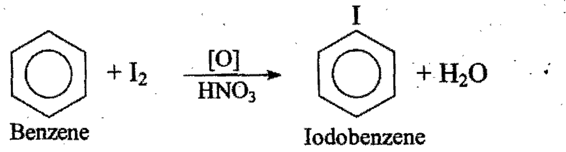
Iodo derivatives cannot be obtained by direct reaction with iodine as the reaction is reversible.

$$C_6H_6 + I_2 \rightleftharpoons C_6H_5I + HI$$

Iodo derivatives can be obtained if the reaction is carried out in presence of an oxidising agent, *e.g.*, iodic acid, or nitric acid, etc. The oxidising agent oxidises HI to iodine and thus, the reaction moves to proceed to the right.

$$(2HI + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + I_2)$$

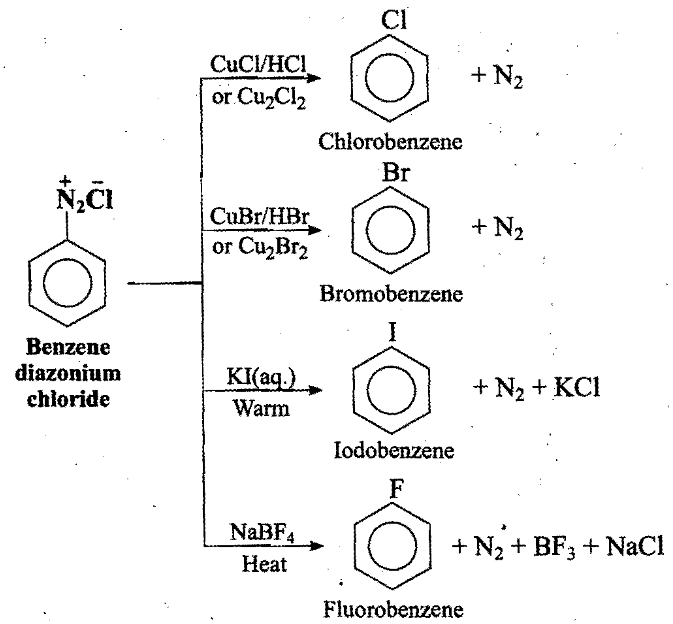
$$(5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O)$$



Aryl fluorides (fluoroarenes), however, cannot be prepared by direct fluorination of aromatic hydrocarbons because of the high affinity of fluorine for hydrogen and the reaction is very violent.

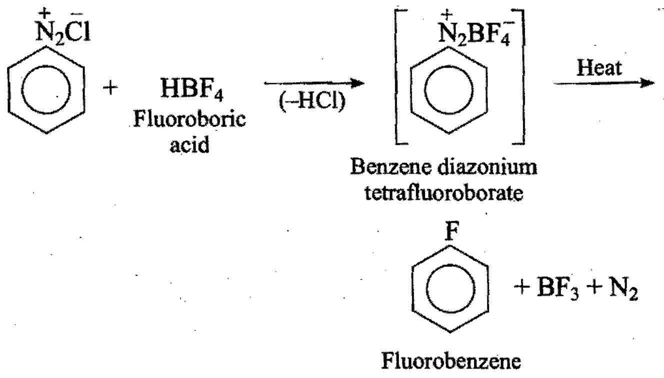
For mechanism of halogenation (see Section 16.5).

2. From diazonium salts : Aryl halides can be obtained most satisfactorily by the decomposition of aryl diazonium salts in presence of copper halide solution dissolved in the corresponding halogen acid, the diazo group is replaced by a halogen atom **(Sandmeyer's reaction).** In this reaction, it is the halogen atom attached to copper which enters the benzene ring.



Iodo compounds may be obtained by boiling the diazonium salt solution with aqueous potassium iodide.

Aryl fluorides are prepared by the reaction of corresponding diazonium salt with fluoroboric acid. This reaction produces diazonium fluoroborates which on heating produces fluorobenzene.



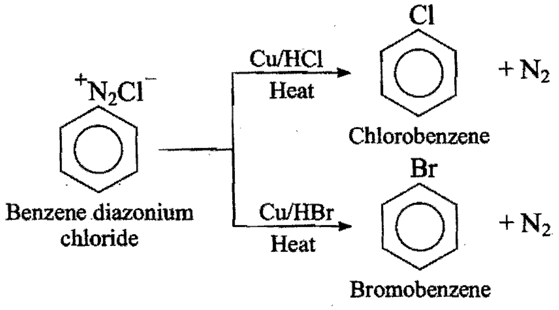
This reaction is called **Balz-Schiemann's reaction.**

In **Gattermann's reaction,** the catalyst finely divided copper is used to form chlorobenzene or bromobenzene.

$$C_6H_5N_2Cl \xrightarrow[\text{Heat}]{\text{Cu}} C_6H_5Cl + N_2$$

$$C_6H_5N_2Br \xrightarrow[\text{Heat}]{\text{Cu}} C_6H_5Br + N_2$$

or the catalyst copper powder in presence of corresponding halogen acid (HCl or HBr) is used in place of cuprous halide.

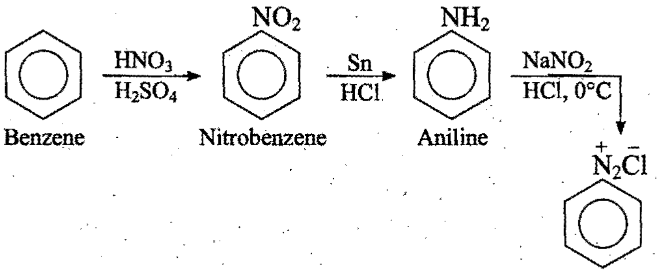


Further benzene diazonium chloride solution on treatment with cuprous cyanide dissolved in aqueous potassium cyanide, $K_3Cu(CN)_4$ or with aqueous potassium cyanide in the presence of copper powder, gives phenyl cyanide (benzonitrile). This is a special case of Sandmeyer's and Gattermann's reactions.

$$C_6H_5N_2Cl + KCN \xrightarrow{K_3Cu(CN)_4} C_6H_5CN + N_2 + KCl$$

$$C_6H_5N_2Cl + KCN \xrightarrow{Cu} C_6H_5CN + N_2 + KCl$$

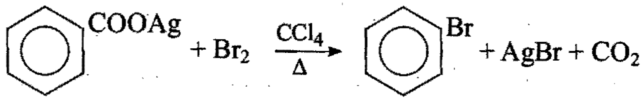
Benzene diazonium chloride is obtained from benzene, nitrobenzene or aniline as follows:



Benzene Nitrobenzene Aniline

Benzene diazonium chloride

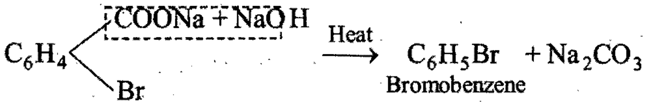
3. Hunsdiecker's reaction : Aryl bromides are obtained by heating the silver salts of aromatic acids (in CCl_4 or xylene) with bromine.



Silver benzoate Bromobenzene

Note : The decomposition of the acid is accelerated if a $—NO_2$ group is present in the nucleus.

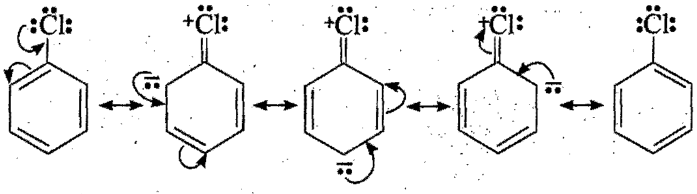
4. Decarboxylation of halogenated acids : Sodium salts of halogenated acid when heated with soda lime produce aryl halides.



$$C_6H_4(COONa)(Br) + NaOH \xrightarrow{Heat} \underset{\text{Bromobenzene}}{C_6H_5Br} + Na_2CO_3$$

Properties : Aryl halides are colourless stable liquids with pleasant odour. These are insoluble in water but readily miscible with organic solvents. Most of them are steam volatile, heavier than water. Their boiling points are higher than corresponding alkyl halides. The boiling points rise gradually from fluoro to iodo compounds.

(i) Low reactivity for S_N reaction : Aryl halides are unreactive as compared to alkyl halides as the halogen atom in these compounds is firmly attached and cannot be replaced by nucleophiles such as $—OH^-$, NH_2^-, CN^-, etc. In chlorobenzene, the electron pair of chlorine atom is in conjugation with π-electrons of benzene ring. Thus, chlorobenzene is a resonance hybrid of the following structures:



I II III IV V

Low reactivity or **inertness** of aryl halides has been attributed to two different factors:

(a) Delocalization of electrons by resonance : The contributing structures II, III and IV indicate that the C—Cl bond in chlorobenzene has partial double bond character. This makes the bond stronger and shorter than pure single bond (*i.e.*, in alkyl halide). The shortening of bond length imparts stability to alkyl halides and as a result the C—Cl bond cleavage becomes difficult which makes aryl halides less reactive than alkyl halides towards nucleophilic substitution. So, aryl halides are stabilized by resonance but alkyl halides are not.

Like aryl halides, the vinyl halides show resonance as follows:

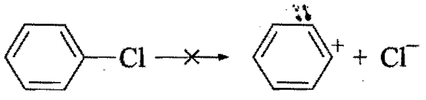
$$H_2C{=}CH{-}\ddot{\underset{..}{Cl}}: \longleftrightarrow H_2\overset{-}{\ddot{C}}{-}CH{=}\overset{+}{\underset{..}{Cl}}:$$

As a result, C—*X* bond in vinyl halides like aryl halides is little more stronger than in alkyl halides and hence can not be easily broken.

(b) Bond energies due to difference in hybridization : In alkyl halides, the carbon holding halogen is sp^3-hybridized. In aryl halides, carbon is sp^2-hybridized; the carbon-halogen bond is shorter and stronger and the molecule is more stable. This has also been confirmed by the X-ray analysis which shows that the C—Cl bond in chlorobenzene is 1.69 Å, whereas in methyl chloride it is 1.77 Å (177 pm).

(c) Polarity of carbon-halogen bond : Another reason for the low reactivity of aryl halides over alkyl halides is their lesser polar character and C—Cl bond in aryl halides is less polar than in alkyl halides. This is supported by the fact that the dipole moment of chlorobenzene is 1.73 D as compared to the dipole moment of haloalkane in the range 1.94–2.22 D.

(d) Instability of phenyl (or vinyl) cation : In haloarenes and vinyl halides, the phenyl cation or vinyl cation is not stabilized by resonance (as a result of self ionization) because the sp^2-hybridized orbital of carbon having the positive charge is perpendicular to the *p*-orbitals of the phenyl ring or the vinyl group. Therefore, these cations are not formed hence, haloarenes and vinyl halides do not undergo S_N1 reactions.



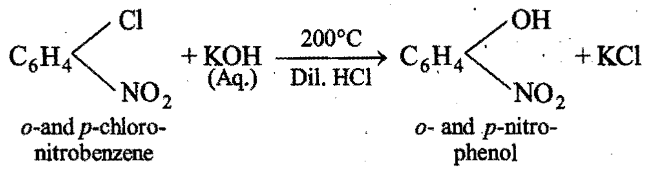
Chlorobenzene Phenylcation

$$\underset{\text{Vinyl chloride}}{H_2C{=}CH{-}Cl} \not\longrightarrow \underset{\text{Vinyl cation}}{H_2C{=}\overset{+}{C}H} + Cl^-$$

Thus, aryl halides are much less reactive towards nucleophilic substitution reactions than haloalkanes.

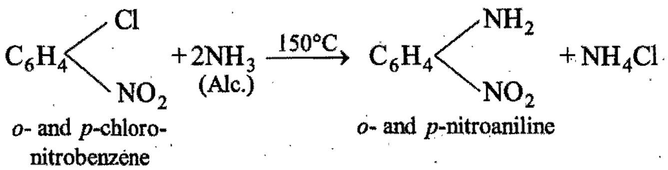
However, under drastic conditions, such as high temperature or pressure, etc., the aryl halides can undergo substitution reactions.

Activation of halogen atom : When a powerful electron withdrawing group (*e.g.*, $—NO_2$, —CN, $—SO_3H$ or —COOH) is present in the *o*- or *p*-position to the halogen atom, the replacement of halogen atom by nucleophile (OH^- or NH_2^-) is now facilitated. For example,



$$C_6H_4\begin{matrix}Cl\\NO_2\end{matrix} + \underset{(Aq.)}{KOH} \xrightarrow[\text{Dil. HCl}]{200°C} C_6H_4\begin{matrix}OH\\NO_2\end{matrix} + KCl$$

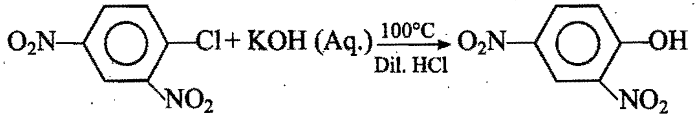
o-and *p*-chloronitrobenzene *o*- and *p*-nitrophenol



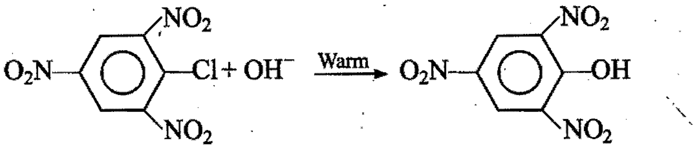
$$C_6H_4\begin{matrix}Cl\\NO_2\end{matrix} + \underset{(Alc.)}{2NH_3} \xrightarrow{150°C} C_6H_4\begin{matrix}NH_2\\NO_2\end{matrix} + NH_4Cl$$

o- and *p*-chloronitrobenzene *o*- and *p*-nitroaniline

The greater the number of electron withdrawing substituents in benzene nucleus, the easier it will be to carry out the nucleophilic substitution (S_N) reactions.



2,4-Dinitro chlorobenzene 2,4-Dinitro phenol



2,4,6-Trinitro chlorobenzene 2,4,6-Trinitro phenol (Picric acid)

Further, greater the number of such groups at *o*- and *p*-positions w.r. to the halogen atom, more is the reactivity of aryl halides.

It may be noted that nitro group at the *meta*-position w.r. to halogen atom has no effect on the reactivity.

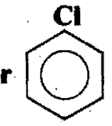
These are the examples of activated nucleophilic substitution (Mechanism in **Sec. 16.8**).

(ii) Ullmann reaction : When iodobenzene is heated with copper powder at 200°C in a sealed tube, biphenyl is formed.

$$\underset{\text{Iodobenzene}}{C_6H_5I} + 2Cu + IC_6H_5 \xrightarrow[\text{Sealed tube}]{\text{Heat}} \underset{\text{Diphenyl}}{C_6H_5—C_6H_5} + Cu_2I_2$$

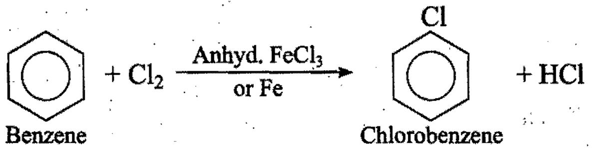
Aryl chlorides and bromides usually do not give this reaction unless the halogen is activated by suitable substituents ($—NO_2$) in the *ortho* or *para*-position.

Chlorobenzene, C_6H_5Cl or



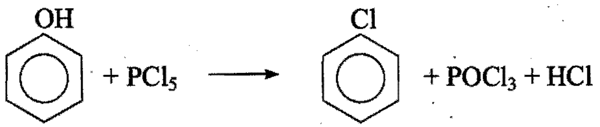
Methods of Preparation

1. From benzene (By chlorination) : Chlorobenzene is prepared by passing chlorine through benzene containing iron turnings. The rate of bubbling chlorine is so adjusted that the temperature is maintained at 40°C. In place of iron turnings, a halogen carrier like I_2 or anhydrous $FeCl_3$ or $AlCl_3$, etc., can also be used.



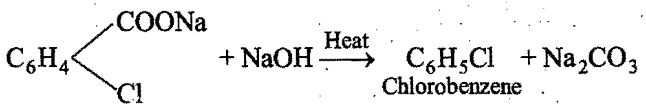
Benzene Chlorobenzene

2. From phenol : Chlorobenzene can be prepared by the action of phosphorus pentachloride on phenol. The yield, is however, very poor because of side reactions giving triphenyl phosphate (TPP). To get better yield a little of TPP is added in reaction mixture.



Phenol Chlorobenzene

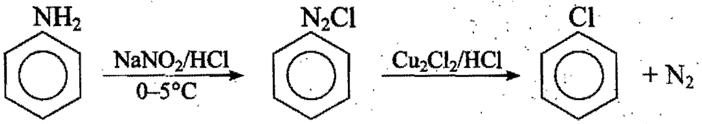
3. From chlorobenzoic acids : When the sodium salt of chlorobenzoic acid is heated with soda lime, decarboxylation occurs and chlorobenzene is formed.



$$C_6H_4\begin{matrix}COONa\\Cl\end{matrix} + NaOH \xrightarrow{\text{Heat}} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + Na_2CO_3$$

(*o*-, *m*- or *p*-) Chlorobenzoic acid

4. Laboratory method (Sandmeyer's reaction) : The most convenient method of preparing chlorobenzene in laboratory is by Sandmeyer's reaction, in which benzene diazonium chloride obtained from aniline is heated with cuprous chloride in presence of hydrochloric acid.



Aniline Benzene diazonium chloride Chlorobenzene

Manufacture (Raschig method) : The vapours of benzene, air and hydrogen chloride are passed over cupric chloride at about 230°C when chlorobenzene is obtained in sufficient yield.

$$2C_6H_6 + 2HCl + O_2 \xrightarrow[\text{Heat}]{Cu_2Cl_2} 2C_6H_5Cl + 2H_2O$$

The method is used in Germany. The exact nature and composition of the catalyst is still a trade secret.

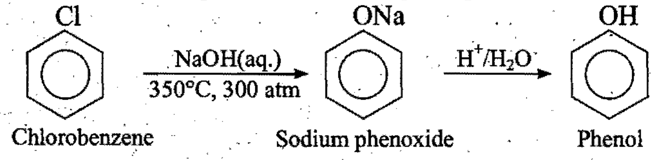
Physical properties : It is a colourless mobile liquid having a pleasant aromatic odour. It boils at 132°C. It is heavier than water (sp. gr. 1.128). It is insoluble in water but soluble in alcohol and ether. It is steam volatile.

Chemical properties : The important reactions of chlorobenzene are:

Nucleophilic substitution reactions

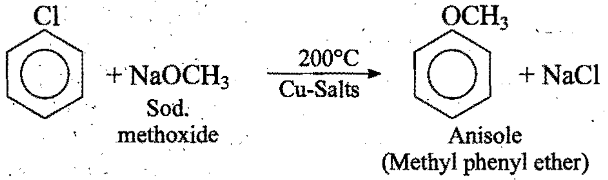
(i) Reactions of the chlorine atom : The chlorine atom in chlorobenzene is firmly attached to benzene nucleus due to resonance and cannot be readily replaced by groups like hydroxy, amino, nitrile, etc. However, by using drastic conditions, replacement of chlorine atom by nucleophiles can be done.

(a) Replacement of —Cl by —OH : When chlorobenzene is heated with aqueous solution of sodium hydroxide at 350°C under 300 atmosphere pressure, sodium phenoxide is first formed which upon acidification gives phenol.



This reaction is known as **DOW process** for the manufacture of phenol.

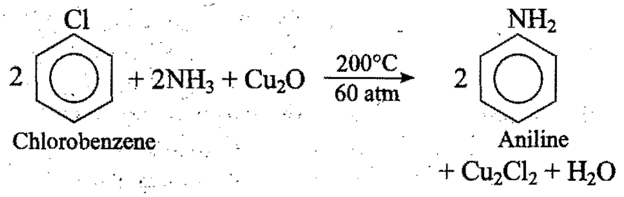
(b) Replacement by methoxy group : Ether is formed when chlorobenzene is heated with sodium methoxide at 200°C in presence of copper salts.



But on treatment with alcohol in presence of $Ni(CN)_4$, an ester is formed.

$$\underset{\text{Iodobenzene}}{C_6H_5I} + C_2H_5OH \xrightarrow[\text{Warm}]{Ni(CN)_4} \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5}$$

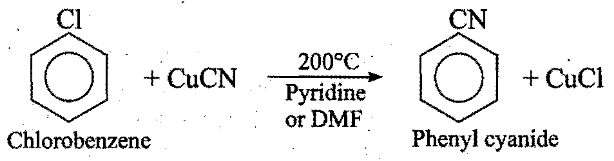
(c) Replacement by amino group : When chlorobenzene is treated with aqueous ammonia at 200°C under a pressure of 60 atmospheres in presence of cuprous oxide or cuprous chloride, aniline is formed.



Aniline can also be prepared by treating chlorobenzene with $NaNH_2/KNH_2$ in liquid ammonia at room temperature.

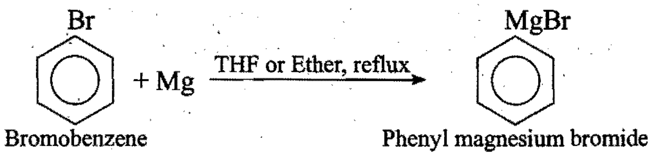
$$C_6H_5Cl + KNH_2 \xrightarrow{\text{Liquid } NH_3} C_6H_5NH_2 + KCl$$

(d) Replacement by —CN group : When chlorobenzene is treated with cuprous cyanide in pyridine or DMF at 200°C, phenyl cyanide is formed.



Phenyl cyanide (benzonitrile) can be converted into many other useful compounds like benzylamine, benzoic acid, benzaldehyde and benzamide, etc. (see **sec. 16.11**).

(ii) Reaction of magnesium : Grignard reagent is formed. Tetrahydrofuran (THF) or dry ether is used as solvent.

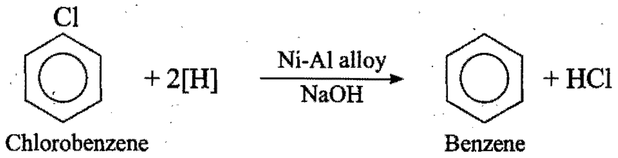


The order of reactivity is: Ar-I > Ar-Br > Ar-Cl

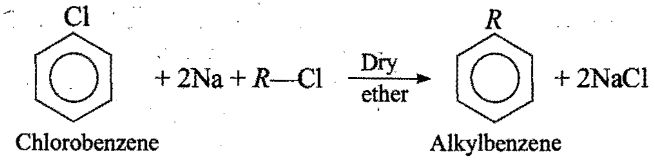
Aryl bromides react with lithium metal in ether and form aryl lithium.

$$C_6H_5Br + 2Li \xrightarrow{\text{Dry ether}} \underset{\text{Phenyl Lithium}}{C_6H_5Li} + LiBr$$

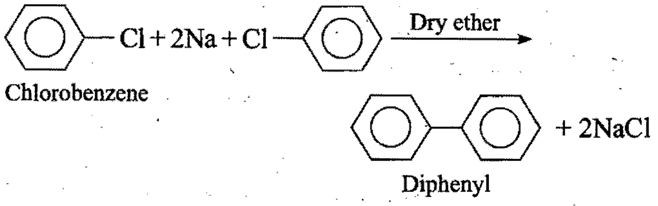
(iii) Reduction : Chlorobenzene undergoes reduction with $LiAlH_4$ or Ni—Al alloy in NaOH solution or Na—Mg/H_2O to give benzene.



(iv) Wurtz-Fittig reaction : Alkyl benzenes are formed when chlorobenzene is treated with alkyl halides and sodium metal in dry ether.



But chlorobenzene reacts with sodium in presence of dry ether to give diphenyl.



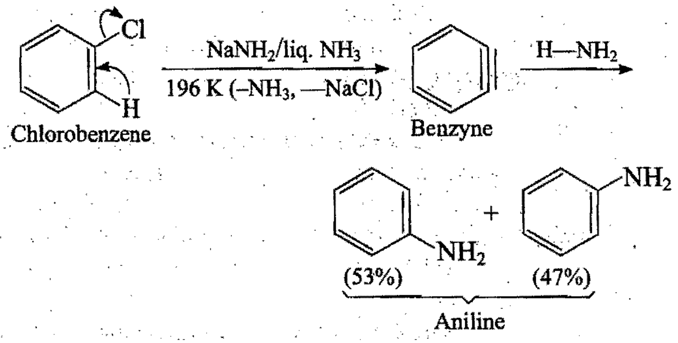
This is known as **Fittig reaction.**

(v) Replacement by —SH group : When chlorobenzene is treated with aqueous potassium hydrogen sulphide in presence of copper salt at 220°C, phenyl thiophenol is formed.

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + KSH(aq.) \xrightarrow[\text{(Cu-Salt)}]{220°C} \underset{\text{Thiophenol}}{C_6H_5SH} + KBr$$

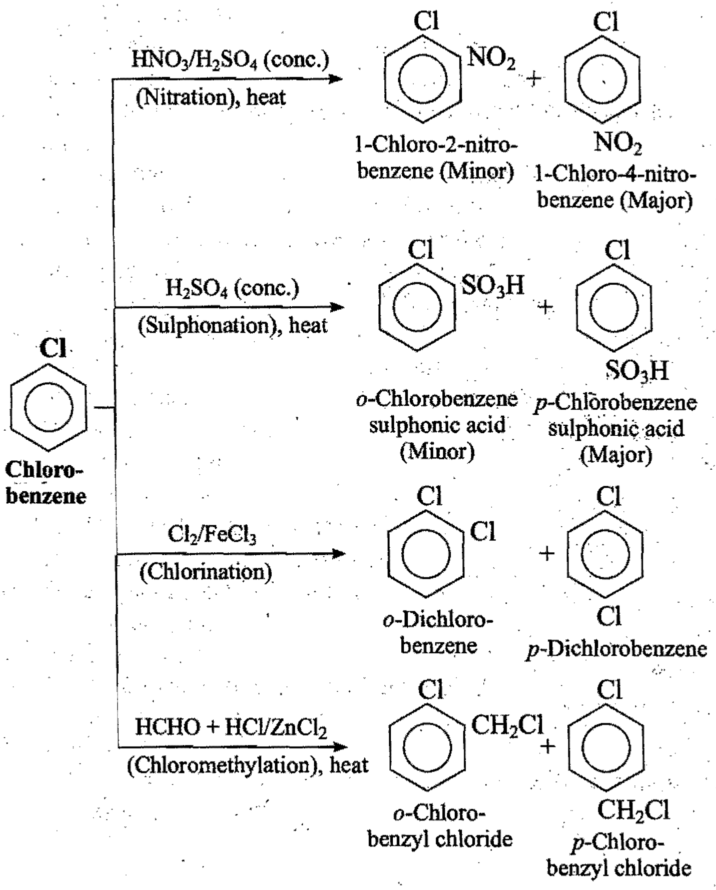
(vi) Reaction with sodamide in liquid ammonia (Formation of aniline): In a number of cases of nucleophilic aromatic substitution, the entering group does not occupy the position vacated by the expelled group. Reactions of this type have been called cine-substitution. This mechanism involves two steps:

(a) Formation of benzyne (1,2-dehydrobenzene) intermediate by a stepwise elimination followed by (b) stepwise addition to benzyne to form the product in which position of the nucleophile may be different.

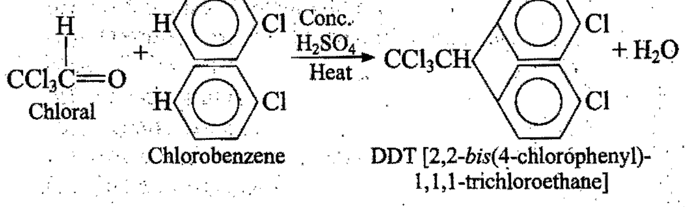


When chlorobenzene is treated with sodamide in liquid ammonia at 196 K, the reaction occurs through the intermediate benzyne formation and finally gives aniline.

(vii) Reactions of benzene ring: The —Cl group in chlorobenzene is *o-,p*-director and deactivating. However, because of steric hindrance at the *o*-position, the *p*-product usually predominates over the *o*-product. The benzene ring undergoes halogenation, nitration and sulphonation **(Electrophilic substitution)** reactions. The rate of reactions is bit slower in comparison to benzene, *e.g.*, the nitration of chlorobenzene is 33 times slower than that of benzene.



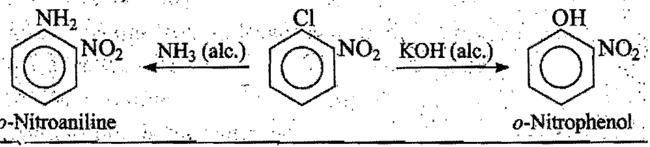
(viii) Reaction with chloral: When chlorobenzene is heated with chloral (trichloroacetaldehyde) in the presence of conc. H_2SO_4, a powerful insecticide, DDT **(*p, p'*-dichlorodiphenyltrichloroethane)** is formed.



DDT is an effective insecticide for mosquitoes, flies and crop pests. However, it is highly toxic to fish and was also an important antimalarial since it destroys anopheles mosquitoes. It is non-biodegradable in nature and gets deposited on the tissues. Therefore, its use has been recently banned in several countries.

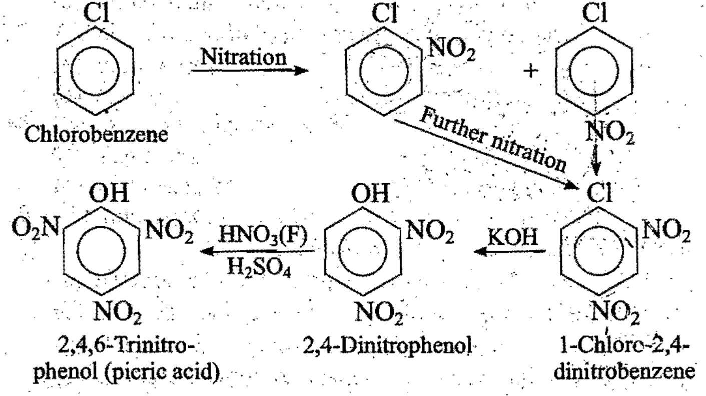
Note: (i) Chlorobenzene does not react with aqueous NaOH, alcoholic ammonia and KCN at room temperature while benzyl chloride, $C_6H_5CH_2Cl$, reacts with these reagents (nucleophilic substitution like alkyl halides).

(ii) In chlorobenzene with negative (electron withdrawing) group like $—NO_2$, —CN or —COOH is present in *ortho* or *para* position, the replacement of Cl-atom by OH⁻ or $—NH_2$ group is easily achieved (activation of halogen atom).



Uses: Chlorobenzene is used for the manufacture of aniline, phenol, picric acid and DDT.

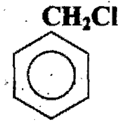
Manufacture of picric acid:



Side-chain Aryl Halides (Aralkyl Halides)

Side-chain aryl halides or aralkyl halides are prepared by methods similar to those used for the preparation of aliphatic halides. These halides are active compounds like alkyl halides. These exhibit nucleophilic substitution reactions and electrophilic aromatic substitution reactions. Benzyl chloride is the simplest side-chain aryl halide.

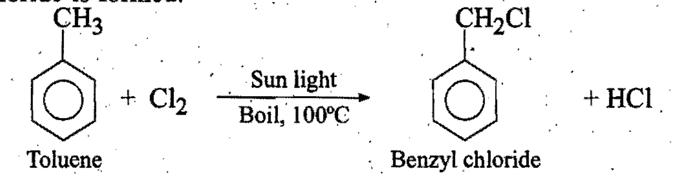
Benzyl Chloride, $C_6H_5CH_2Cl$,



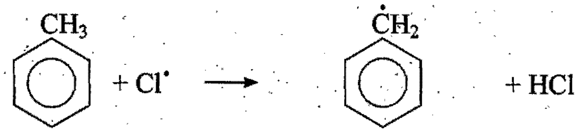
(Phenyl methyl chloride or Chlorophenylmethane)

Methods of Preparation

1. By passing chlorine into boiling toluene in the presence of sunlight and absence of halogen carrier, benzyl chloride is formed.

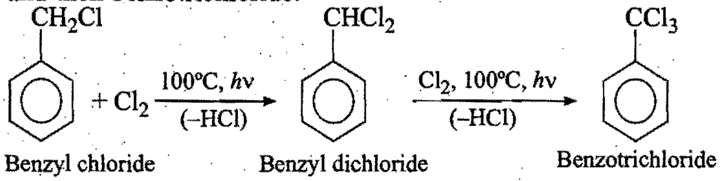


Side-chain halogenation involves free radical mechanism due to lower bond energy of the benzyl C—H bond.



(Stable) benzyl free radical

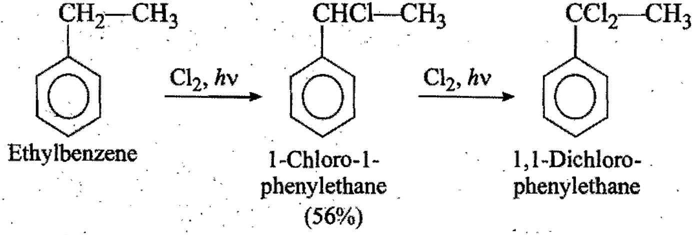
If Cl_2 is passed for a longer time, the initially formed benzyl chloride reacts further to form first benzal dichloride and then benzotrichloride.



Instead of Cl_2, sulphuryl chloride (SO_2Cl_2) at 200°C in presence of light and traces of peroxide can also be used for side-chain halogenation of toluene.

$$\underset{\text{Toluene}}{C_6H_5CH_3} + SO_2Cl_2 \xrightarrow[\text{(Peroxide)}]{200^\circ\text{C},\ h\nu} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

When the side-chain (*R*—) is larger than a methyl group, side-chain halogenation preferentially occurs at room temperature on the benzylic carbon (*i.e.*, carbon atom next to the benzene ring). For example,



2. By the action of PCl_5 on benzyl alcohol. $SOCl_2$ (thionyl chloride) can be used in place of PCl_5.

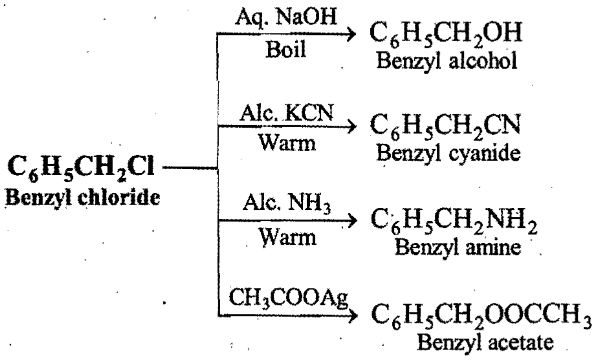
$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + PCl_5 \longrightarrow \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + POCl_3 + HCl$$

3. By heating benzene with formaldehyde solution and HCl in presence of anhydrous zinc chloride, benzyl chloride is formed and this reaction is called **chloromethylation** or **Blance reaction.**

$$C_6H_6 + \underset{\text{Formaldehyde}}{HCHO} + HCl \xrightarrow[60^\circ\text{C}]{ZnCl_2} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + H_2O$$

Properties : It is a lachrymatory colourless bad smelling liquid. It boils at 179°C. Its vapours bring tears from eyes and are irritating. It is insoluble in water but soluble in organic solvents.

(i) Nucleophilic substitution reactions :



(ii) Wurtz reaction :

$$\underset{\text{Benzyl chloride}}{2C_6H_5CH_2Cl} + 2Na \xrightarrow{\text{Ether}} \underset{\text{Dibenzyl}}{C_6H_5CH_2—CH_2C_6H_5} + 2NaCl$$

(iii) Wurtz-Fittig reaction :

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + 2Na + ClC_6H_5 \longrightarrow \underset{\text{Diphenylmethane}}{C_6H_5CH_2C_6H_5} + 2NaCl$$

(iv) Formation of Grignard reagent :

$$C_6H_5CH_2Cl + \underset{\text{(Dry)}}{Mg} \xrightarrow{\text{Ether}} \underset{\substack{\text{Benzyl magnesium}\\ \text{chloride}}}{C_6H_5CH_2MgCl}$$

(v) Oxidation : When oxidised with 60% HNO_3, benzoic acid is formed. Oxidation by $KMnO_4$ also yields benzoic acid.

$$C_6H_5CH_2Cl + 2[O] \xrightarrow{\text{Conc. } HNO_3} C_6H_5COOH + HCl$$

When boiled with cupric nitrate or lead nitrate, it is oxidised to benzaldehyde.

(vi) Reduction : When reduced with Zn–Cu couple, it forms toluene.

$$C_6H_5CH_2Cl + 2[H] \longrightarrow C_6H_5CH_3 + HCl$$

(vii) Electrophilic aromatic substitution : It gives usual electrophilic substitution reactions. $—CH_2Cl$ is *ortho, para*-director.

Distinction between Chlorobenzene and Benzyl Chloride

In chlorobenzene (Nuclear halogen compounds), the halogen atom is inert and cannot be replaced by —OH,

—NH_2, —CN, etc. under ordinary conditions, while in benzyl chloride (side-chain halogen compounds), the halogen atom is very reactive and hence can be easily replaced by —OH, —NH_2, —CN, etc.

(i) Reaction with alcoholic $AgNO_3$: Benzyl chloride gives a white precipitate with alcoholic $AgNO_3$ solution while chlorobenzene does not react.

$$C_6H_5CH_2Cl + AgNO_3\ (\text{Alc.}) \longrightarrow \text{White ppt. of AgCl}$$

$$C_6H_5Cl + AgNO_3\ (\text{Alc.}) \longrightarrow \text{No reaction}$$

(ii) Reaction with alkaline $KMnO_4$: Benzyl chloride is oxidised to benzoic acid with alk. $KMnO_4$, *i.e.*, decolourisation occurs and whole side-chain gives —COOH group. The halogen atom is thus, eliminated. Chlorobenzene does not react, *i.e.*, no decolourisation takes place, and the halogen atom is not affected by oxidation.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + 2[O] \xrightarrow{\text{Alk. } KMnO_4} C_6H_5COOH + HCl$$

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} \xrightarrow{\text{Alk. } KMnO_4} \text{No reaction}$$

(iii) Hydrolysis : Chlorobenzene cannot be easily hydrolysed while benzyl chloride and other side-chain derivatives can easily be hydrolysed.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + KOH\ (\text{Aq.}) \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + KCl$$

$$\underset{\text{Benzylidene chloride}}{C_6H_5CHCl_2} + Ca(OH)_2 \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + CaCl_2 + H_2O$$

$$\underset{\text{Benzylidyne chloride}}{C_6H_5CCl_3} + 3HOH \xrightarrow{Ca(OH)_2} \underset{\text{Benzoic acid}}{C_6H_5COOH} + 3HCl$$

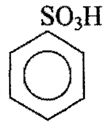
(iv) Odour : Chlorobenzene has agreeable odour while benzyl chloride is lachrymatory having irritating odour.

(v) Friedel-Crafts reaction : Chlorobenzene do not give Friedel-Crafts reaction with benzene or toluene, while benzyl chloride gives Friedel-Crafts reaction with benzene in presence of anhydrous $AlCl_3$ and forms diphenylmethane.

$$\underset{\text{Benzene}}{C_6H_5H} + \underset{\text{Benzyl chloride}}{ClCH_2C_6H_5} \xrightarrow[\text{(Anhyd.)}]{AlCl_3} \underset{\text{Diphenylmethane}}{C_6H_5CH_2C_6H_5} + HCl$$

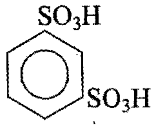
16.11 AROMATIC SULPHONIC ACIDS

They are derivatives of aromatic hydrocarbons in which one or more hydrogen atoms of the benzene nucleus have been replaced by sulphonic acid (—SO_3H) groups or their derivatives. Examples are:

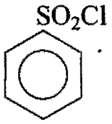


Benzene sulphonic acid

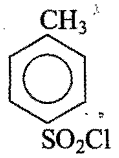
p-Toluene sulphonic acid



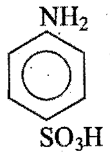
m-Benzene disulphonic acid



Benzene sulphonyl chloride (Hinsberg's reagent)

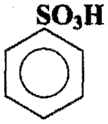


p-Toluene sulphonyl chloride (TsCl) (Tosyl chloride)



p-Aminobenzene sulphonic acid (Sulphanilic acid)

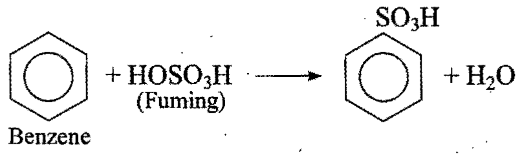
Benzene Sulphonic Acid, $C_6H_5SO_3H$, or



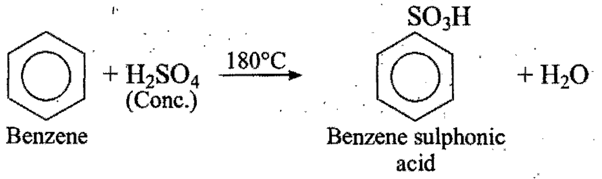
Methods of Preparation

1. Laboratory method : Benzene sulphonic acid is prepared by heating benzene with concentrated sulphuric acid at 180°C. The reaction may be carried at room temperature by using fuming sulphuric acid.

$$\underset{\text{Benzene}}{C_6H_5H} + \underset{\text{(Conc.)}}{HOSO_3H} \rightleftharpoons C_6H_5SO_3H + H_2O$$



$$(SO_3 + H_2O \longrightarrow H_2SO_4)$$



During sulphonation, a small amount of diphenyl sulphone is produced as a byproduct.

$$2C_6H_6 + H_2SO_4 \longrightarrow (C_6H_5)_2SO_2 + 2H_2O$$

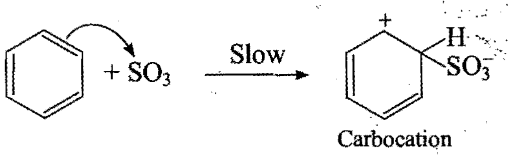
$$C_6H_5SO_3H + \underset{\text{Benzene}}{HC_6H_5} \longrightarrow \underset{\text{Diphenyl sulphone}}{C_6H_5SO_2C_6H_5} + H_2O$$

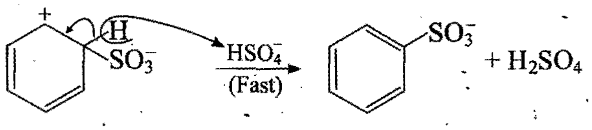
Mechanism (See Section 16.5)

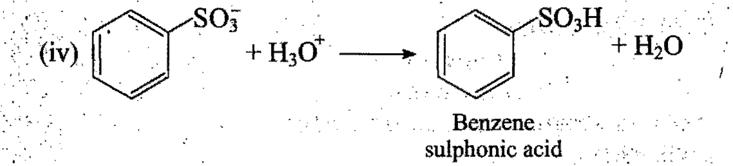
In sulphonation, the electrophile is, either $\mathbf{SO_3}$, (neutral) or $\overset{+}{\mathbf{SO_3H}}$, which is produced as follows :

(i) $$2H_2SO_4 \rightleftharpoons \underset{\text{Sulphurtrioxide}}{SO_3} + H_3O^+ + HSO_4^-$$

or $$3H_2SO_4 \rightleftharpoons \overset{+}{SO_3}H + H_3O^+ + 2HSO_4^-$$

(ii)


(iii)


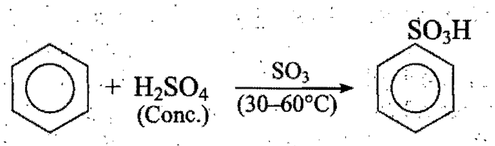


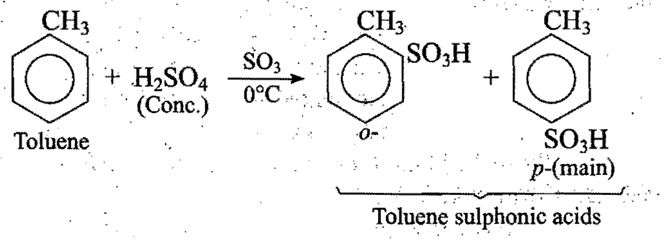
Benzene sulphonic acid

Thus, various possibilities exist for sulphonation with concentrated sulphuric acid are :

$$H_2SO_4 + SO_3 \rightleftharpoons H_2SO_4(SO_3) \text{ or } H_2S_2O_7$$

$$3H_2SO_4 \rightleftharpoons SO_3H^+ + H_3O^+ + 2HSO_4^-$$





Toluene

Toluene sulphonic acids

Low temperature (below 100°C) favours the formation of *ortho* isomer, and high temperature (above 100°C), the *para* isomer.

2 Benzene sulphonic acid is obtained when benzene (1 mole) is treated with chlorosulphonic acid (1 mole), while excess of the reagent results in the formation of benzene sulphonyl chloride (Hinsberg's reagent).

$$C_6H_6 + ClSO_3H \xrightarrow{CCl_4} C_6H_5SO_3H + HCl$$

$$C_6H_5SO_2OH + ClSO_3H \longrightarrow C_6H_5SO_2Cl + H_2SO_4$$

Benzene sulphonyl chloride can also be prepared by treating benzene with sulphuryl chloride in presence of pyridine or anhydrous $AlCl_3$.

$$\underset{\text{Benzene}}{C_6H_5H} + Cl—SO_2—Cl \xrightarrow{\text{Pyridine}} \underset{\text{Benzene sulphonyl chloride}}{C_6H_5SO_2Cl} + HCl$$

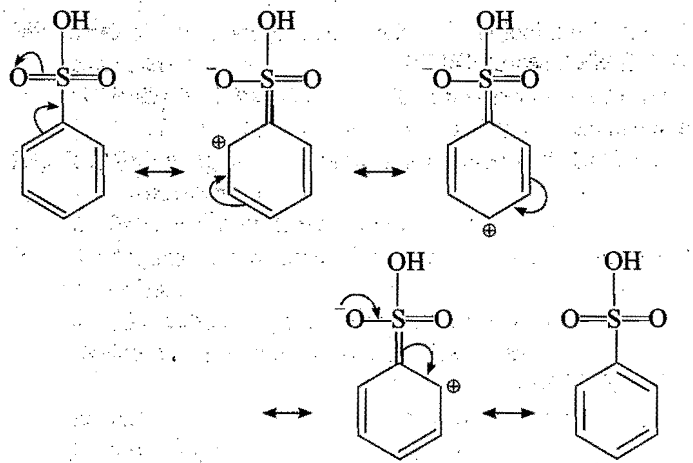
3. By oxidation of thiophenol :

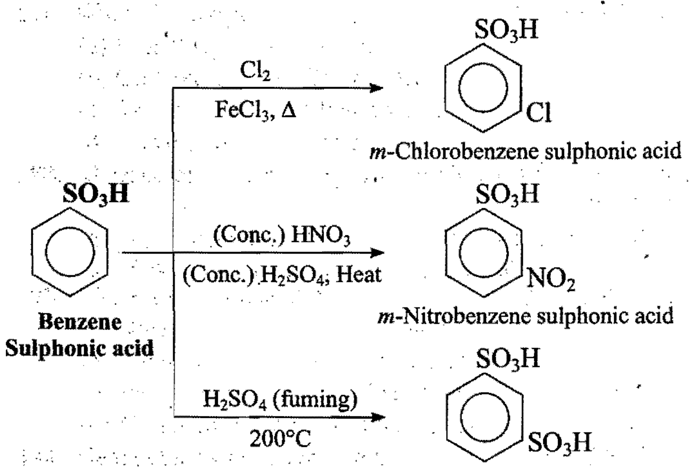
$$\underset{\text{Thiophenol}}{C_6H_5SH} + 3[O] \xrightarrow{KMnO_4} \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H}$$

Physical properties : It is a colourless crystalline compound. Its melting point is 46°C. It is deliquescent and easily soluble in water and the solution is strongly acidic in nature (about as strong as sulphuric acid). It is also soluble in alcohol.

Chemical properties

1. Reactions of benzene nucleus (Electrophilic substitution) : Benzene sulphonic acid undergoes normal chlorination, nitration and sulphonation. **The —SO_3H group is a *meta* directing and deactivating group.**





Benzene Sulphonic acid

m-Chlorobenzene sulphonic acid

m-Nitrobenzene sulphonic acid

m-Benzene disulphonic acid

2. Reaction of —SO_3H group :

They are stronger acid than carboxylic acid

(K_a = Very large) ($K_a = 6.5 \times 10^{-5}$)

(i) Salt formation (Acidic nature) : It is a strong acid (more stronger than benzoic acid) and completely ionises in water.

$$C_6H_5SO_3H \longrightarrow H^+ + C_6H_5SO_3^-$$

$$(C_6H_5SO_3H + H_2O \rightleftharpoons C_6H_5SO_3^- + H_3O^+)$$

It combines with alkalies and metal carbonates to form salts.

$$\underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H} + NaOH \longrightarrow \underset{\text{Sodium benzene Sulphonate}}{C_6H_5SO_3Na} + H_2O$$

$$C_6H_5SO_3H + NaHCO_3 \longrightarrow C_6H_5SO_3Na + CO_2 + H_2O$$

$$2C_6H_5SO_3H + Na_2CO_3 \longrightarrow 2C_6H_5SO_3Na + CO_2 + H_2O$$

(ii) Reaction with PCl_5 : Benzene sulphonyl chloride is formed when benzene sulphonic acid or its sodium salt is heated with PCl_5.

$$\underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H} + PCl_5 \xrightarrow{\text{Heat}} \underset{\text{Benzene sulphonyl chloride}}{C_6H_5SO_2Cl} + POCl_3 + HCl$$

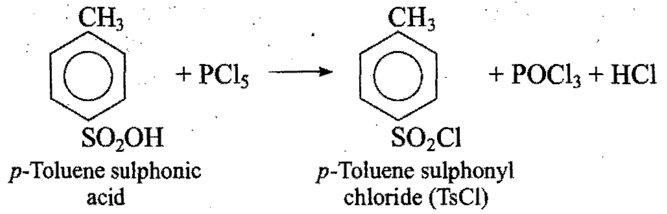
[It has many important applications :

$$\underset{\text{Benzene sulphonyl chloride}}{\mathbf{C_6H_5SO_2Cl}} \xrightarrow{HOH} \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H}$$

$$\underset{\text{Benzene sulphonyl chloride}}{\mathbf{C_6H_5SO_2Cl}} \xrightarrow[(NaOH)]{ROH} \underset{\text{Alkyl benzene sulphonate}}{C_6H_5SO_3R}$$

$$\underset{\text{Benzene sulphonyl chloride}}{\mathbf{C_6H_5SO_2Cl}} \xrightarrow{2NH_3(conc.)} \underset{\text{Benzene sulphonamide}}{C_6H_5SO_2NH_2}\ ]$$

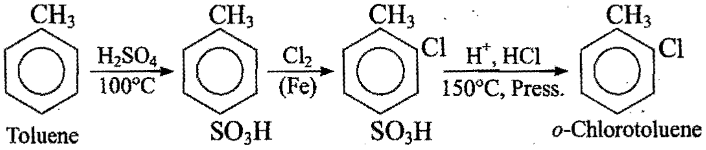
p-Toluene sulphonic acid forms tosyl chloride which can also be used to protect —NH_2 or —OH groups, susceptible to oxidation.



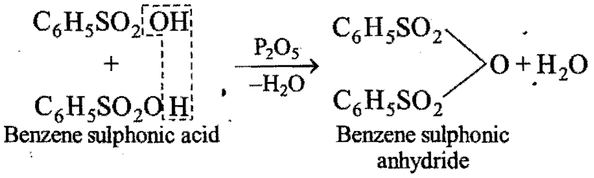
(iii) Desulphonation : When benzene sulphonic acid is heated with dil. HCl or dil. H_2SO_4 or superheated steam under pressure, benzene is formed.

$$C_6H_5SO_3H + H_2O \xrightarrow[150°C]{H^+} \underset{\text{Benzene}}{C_6H_6} + H_2SO_4$$

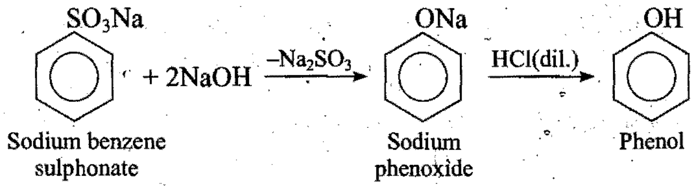
The desulphonation is very useful for preparing certain isomers which are otherwise not obtained in pure state, *e.g.*, *o*-chlorotoluene may be prepared as follows :



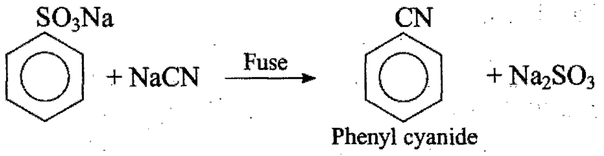
(iv) Dehydration : When benzene sulphonic acid is heated with excess of phosphorus pentoxide, benzene sulphonic anhydride is formed with elimination of water molecule.



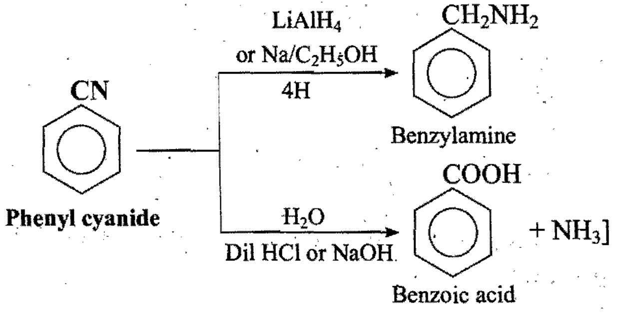
(v) Replacement of —SO_3H by —OH (Formation of phenol) : On fusing sodium salt with sodium hydroxide, sodium phenoxide is formed which on treatment with dil. HCl gives phenol.



(vi) Replacement of —SO_3H by —CN : Sodium benzene sulphonate is fused with sodium cyanide when phenyl cyanide is formed.

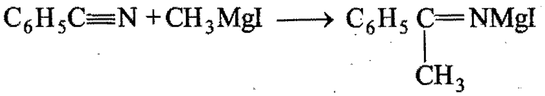


[Phenyl cyanide on reduction forms benzylamine and on hydrolysis gives benzoic acid.



Other important applications of benzonitrile (C_6H_5CN) are as follows :

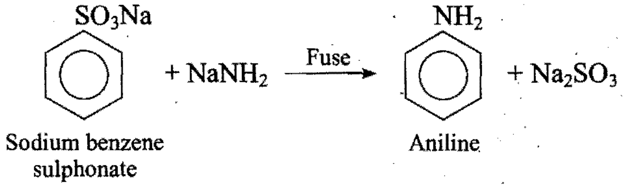
$$\underset{\text{Benzonitrile}}{C_6H_5C{\equiv}N} + 2[H] \xrightarrow[\text{Stephen's reaction}]{SnCl_2/HCl\ (Conc.)} \underset{\text{Benzal imine hydrochloride}}{C_6H_5CH{=}NH\cdot HCl} \xrightarrow[H^+]{H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$



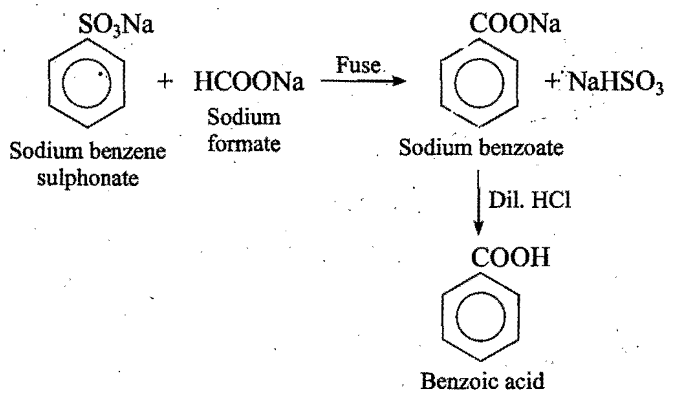
$$C_6H_5C{\equiv}N + CH_3MgI \longrightarrow C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NMgI \xrightarrow[HCl\ (dil.)]{2H_2O} \underset{\text{Acetophenone}}{C_6H_5COCH_3}$$

$$\underset{\text{Benzonitrile}}{C_6H_5C{\equiv}N} \xrightarrow[\substack{\text{or alk. } H_2O_2\\ \text{(Partial hydrolysis)}}]{\text{Conc. HCl}} \underset{\text{Benzamide}}{C_6H_5CONH_2}$$

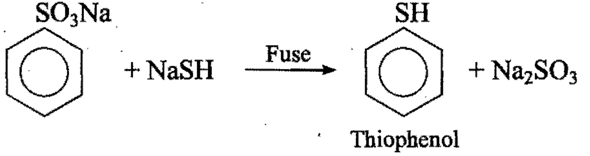
(vii) Replacement of —SO_3H by —NH_2 (Formation of aniline) : Sodium benzene sulphonate is fused with sodamide, $NaNH_2$, when aniline is formed.



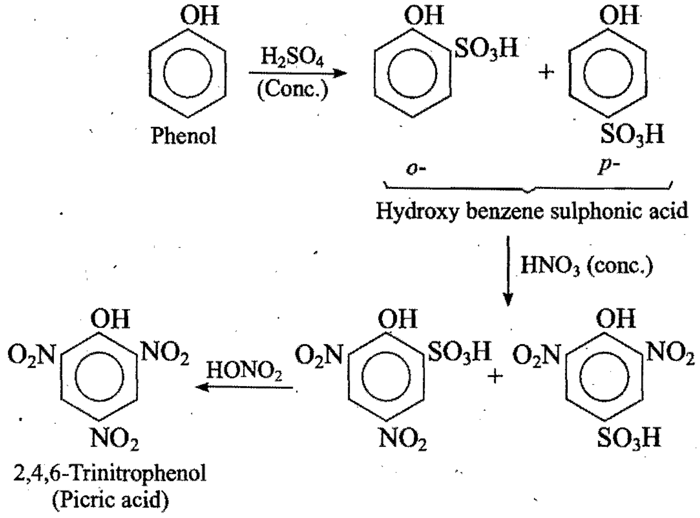
(viii) Replacement of —SO_3H by —COOH (Formation of benzoic acid) : When sodium benzene sulphonate is fused with sodium formate, sodium benzoate is formed which on treatment with HCl yields benzoic acid.



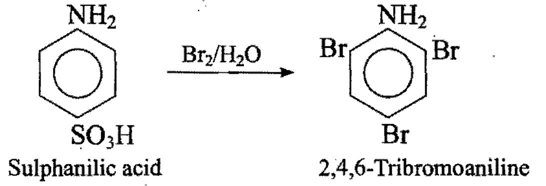
(ix) Replacement of $-SO_3H$ by $-SH$: Sodium benzene sulphonate is fused with sodium hydrogen sulphide, NaSH, when thiophenol is formed.



(x) Replacement of $-SO_3H$ by $-NO_2$ (Formation of picric acid) : Since phenol or aniline are easily oxidised by nitric acid, so they are first sulphonated and then nitrated.



(xi) Replacement of $-SO_3H$ by halogen atom : Sulphonic acid group present on the *o*- and *p*-positions with respect to $-NH_2$ or $-OH$ group can be easily replaced by a halogen atom (or other groups).



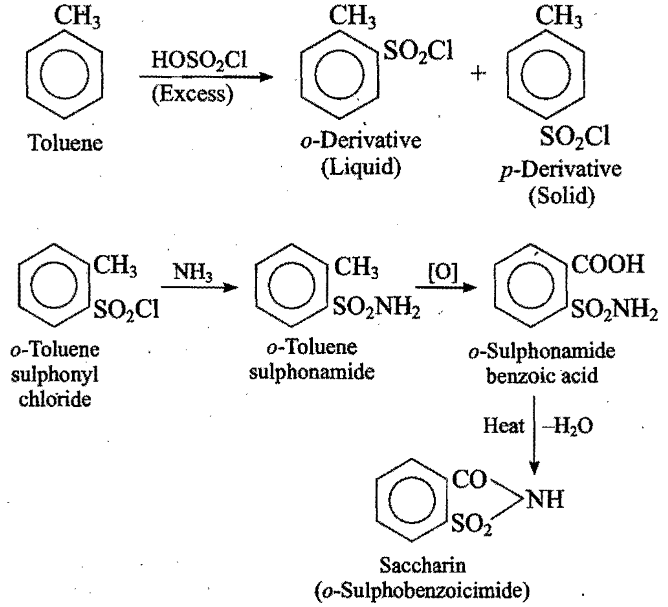
Uses : (i) Benzene sulphonic acid is a synthetic reagent. It is used to prepare phenol, aniline, phenyl cyanide, benzoic acid, etc.

(ii) It is used as dehydrating agent in esterification where sulphuric acid cannot be used due to side reactions.

(iii) The presence of $-SO_3H$ group in nucleus makes the compound soluble in water, so sulphonation is an important process in the manufacture of dyes and drugs.

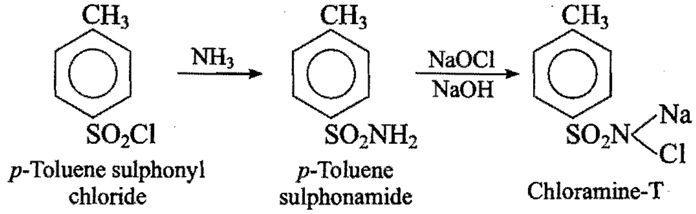
Important Derivatives of Toluene; Saccharin and Chloramine-T

(i) Saccharin (*o*-Sulphobenzoicimide)

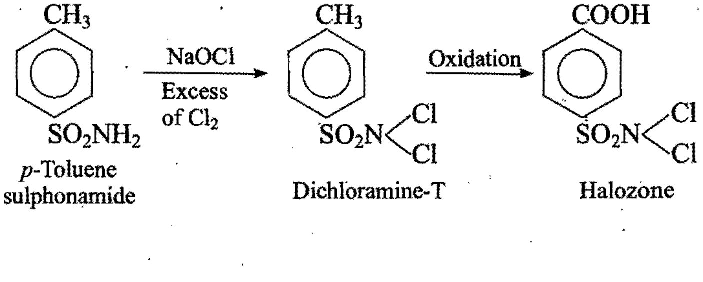


Saccharin is a crystalline solid, m.pt. 224°C and about 600 times sweeter than cane sugar. It has no food value and is excreted unchanged in urine. It is also used as sweetening agent in cheap drinks and by diabetic patients in the form of sodium salt which is soluble in water.

(ii) Chloramine-T (Sodium salt of *N*-chloro-*p*-toluene sulphonamide)

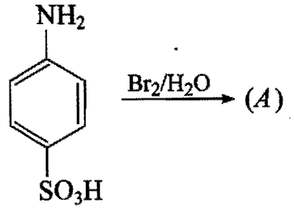


Chloramine-T is an important antiseptic. Its antiseptic property is due to the formation of hypochlorite in-situ. Its 1–2% solution is used for mouth wash and for washing wounds. (Dichloramine-T is *N,N*-dichloro-*p*-toluene sulphonamide).



Halozone is used for sterilizing drinking water.

Example. Give the products in following reactions.

(i)


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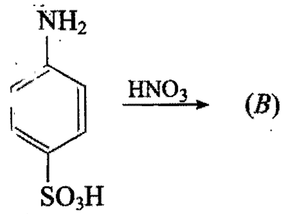

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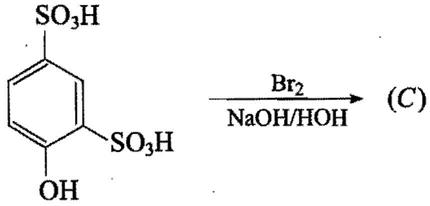

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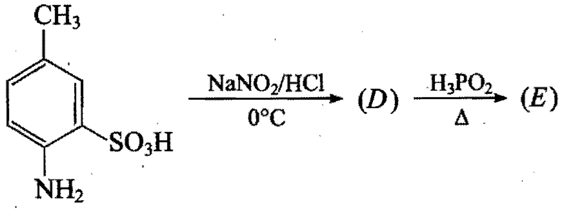

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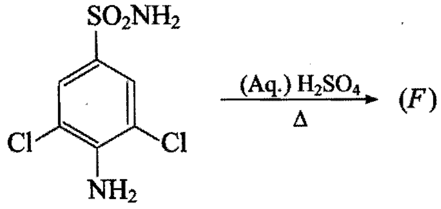

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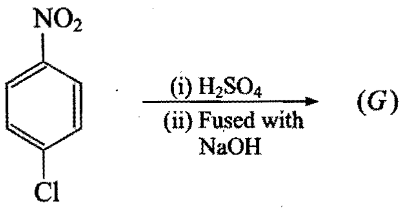

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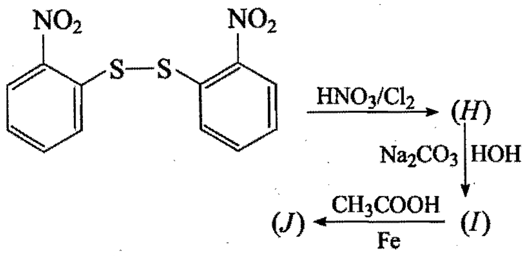

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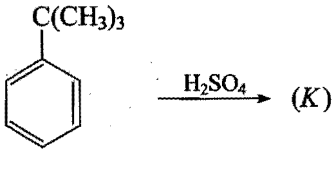

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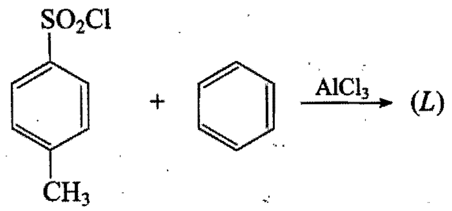

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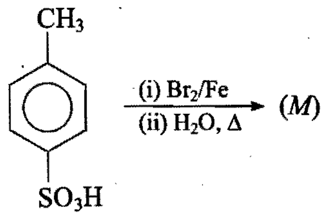

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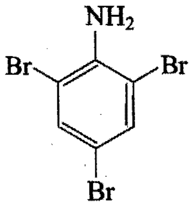

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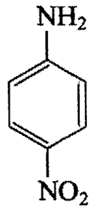

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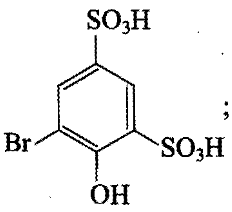

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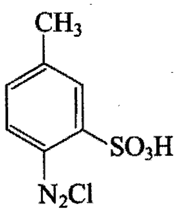

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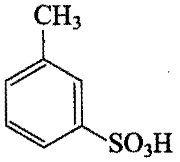

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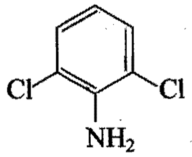

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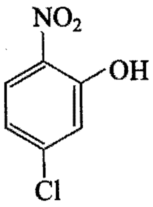

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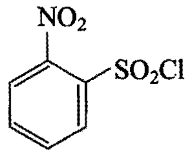

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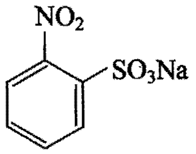
(I)


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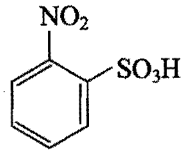

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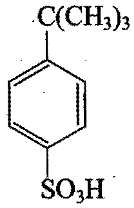
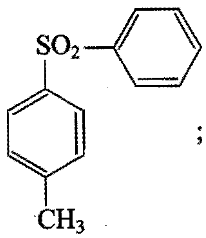


; (L)


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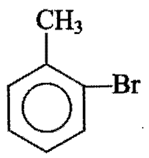
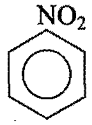
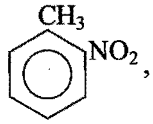
(M)


16.12 AROMATIC NITRO COMPOUNDS

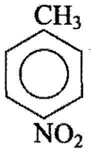
The aromatic nitro compounds are the substitution products of aromatic hydrocarbons in which one or more hydrogen atoms have been replaced by nitro ($—NO_2$) group. Examples are:



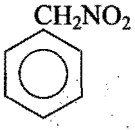
Nitrobenzene



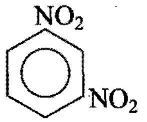
o-Nitrotoluene



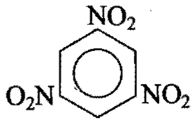
p-Nitrotoluene



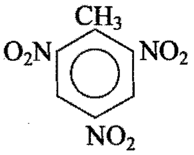
Phenyl-nitromethane



m-Dinitrobenzene

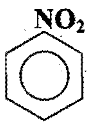


1,3,5-Trinitrobenzene (TNB)



2,4,6-Trinitrotoluene (TNT)

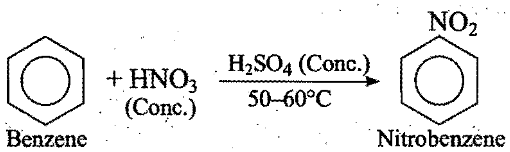
Nitrobenzene (Oil of Mirabane), $C_6H_5NO_2$ or

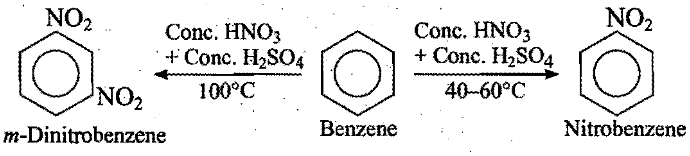


Nitrobenzene is sometimes called as artificial oil of bitter almonds or oil of mirabane as its odour is like that of bitter almonds.

Methods of Preparation

1. Laboratory preparation : In the laboratory, it is prepared by nitration of benzene with a mixture of concentrated nitric acid and concentrated sulphuric acid at temperature below 60°C. The temperature should not increase otherwise *m*-dinitrobenzene is formed. So nitration of benzene depends upon (i) temperature (ii) nature of the nitrating agent used.





Various nitrating agents used are :

(i) Concentrated HNO_3 (sp. gr. about 1.5)

(ii) Fuming HNO_3 (Conc. $HNO_3 + NO_2$)

(iii) Nitrating mixture :

(a) Conc. HNO_3 + Conc. H_2SO_4

(b) fuming HNO_3 + Conc. H_2SO_4

(c) fuming HNO_3 + fuming H_2SO_4

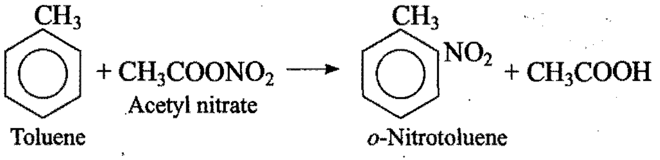
(d) conc. HNO_3 in glacial CH_3COOH or $(CH_3CO)_2O$

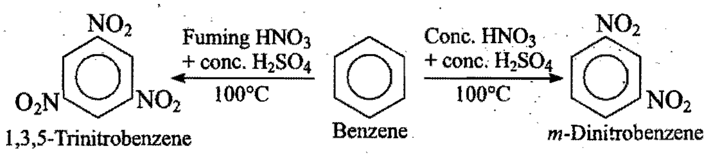
(e) conc. HNO_3 in presence of BF_3
or nitronium tetrafluoroborate ($NO_2^+BF_4^-$)

(f) N_2O_5 in CCl_4

(g) nitronium perchlorate ($NO_2^+ClO_4^-$)

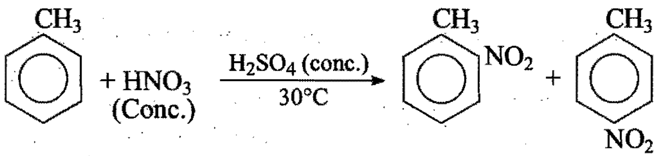
(iv) Acetyl nitrate (N_2O_5 in Ac_2O) : Used to introduce only one nitro group at the *ortho*-position.





$—NO_2$ is deactivating group, hence, further nitration takes place with fuming HNO_3 and H_2SO_4 mixture.

Similarly, toluene on nitration gives *o*- and *p*-nitrotoluene.

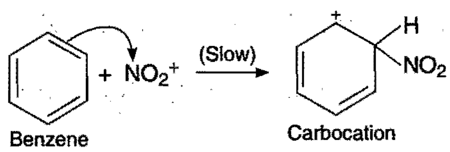


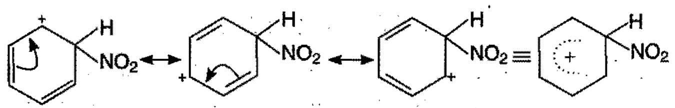
Nitration of toluene is easier than that of benzene, because $—CH_3$ group is an electron releasing (activating group) and makes the π ring system electron rich.

The **Mechanism** of nitration remains the same as for benzene and the electrophile is **nitronium ion (NO_2^+)** which attacks the benzene ring to give an intermediate carbonium ion (σ-complex) stabilized by resonance and then removal of proton gives nitrobenzene.

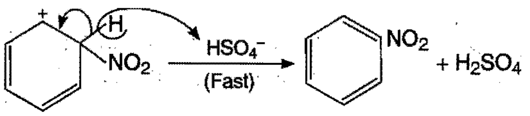
Step (i) $HNO_3 + 2H_2SO_4 \rightleftharpoons \underset{\text{Nitronium ion}}{NO_2^+} + H_3O^+ + 2HSO_4^-$

Step (ii)





Step (iii)



The nitration of benzene, (C_6H_6) and hexadeutero benzene, (C_6D_6) proceeds at the same rate.

$$\underset{\substack{\text{Hexadeutero}\\\text{benzene}}}{C_6D_5—D} \xrightarrow{\text{Nitration}} \underset{\text{Pentadeutero nitrobenzene}}{C_6D_5—NO_2}$$

Industrial preparation (Manufacturing) of nitrobenzene is **similar** to the laboratory method with the difference that nitration is carried out in big cast iron retorts.

2. From benzene diazonium salt (or from aniline) : Nitrobenzene can be prepared by carrying out diazotization of aniline and then, reacting with nitrous acid, HNO_2 ($NaNO_2$ + HCl) in the presence of cuprous oxide.

$$\underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} + HNO_2 \xrightarrow{Cu_2O} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + N_2 + HCl$$

$$\text{or } C_6H_5N_2Cl \xrightarrow{HBF_4} C_6H_5N_2BF_4 \xrightarrow[Cu/\Delta]{NaNO_2} C_6H_5NO_2$$

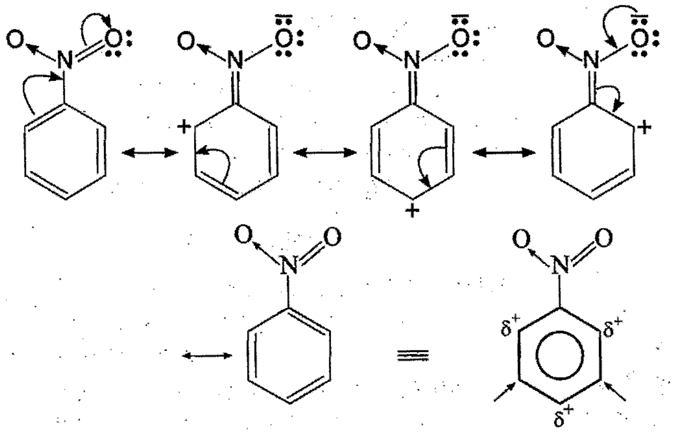
3. From oxidation of aniline by trifluoro acetic acid:

$$C_6H_5NH_2 + 3[O] \xrightarrow{CF_3COOH} C_6H_5NO_2 + H_2O$$

4. By the action of acetyl nitrate on benzene:

$$C_6H_5H + CH_3COONO_2 \longrightarrow C_6H_5NO_2 + CH_3COOH$$

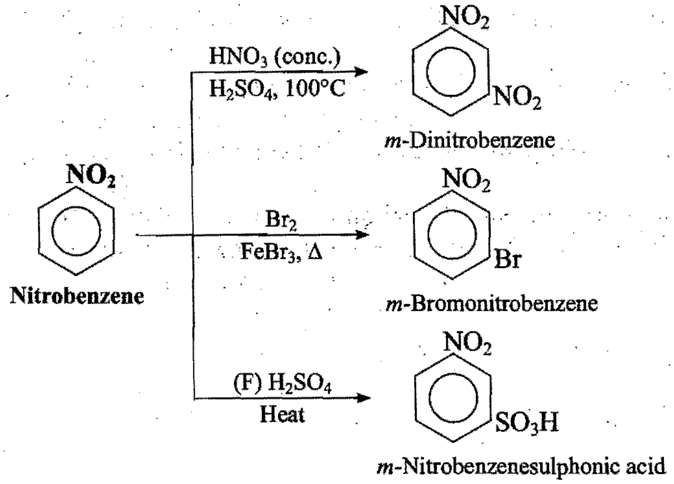
Physical properties : It is a lemon (pale) yellow oily liquid. Its boiling point is 210°C. It is heavier than water (sp. gr. 1.208). It has a smell of bitter almonds. It is insoluble in water but soluble in alcohol, benzene and ether. It is steam volatile. Its vapours are poisonous in nature.



So, electrophile attacks at the *meta*-position, where it gets least repulsion.

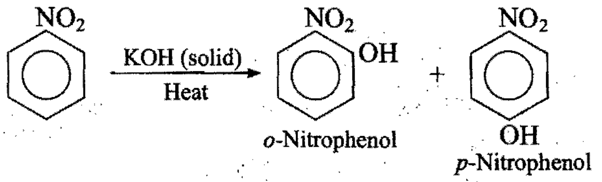
Chemical properties : The nitro group is very firmly linked to the benzene nucleus and shows partial double bond character due to resonance which makes it inert and hence, nitrobenzene does not undergo any displacement reaction.

1. The nitro group deactivates the benzene nucleus and thus, **electrophilic substitution** (nitration, halogenation, sulphonation, but not Friedel-Crafts reaction) occurs only under vigorous conditions. The —NO_2 group is a *meta*-directing.

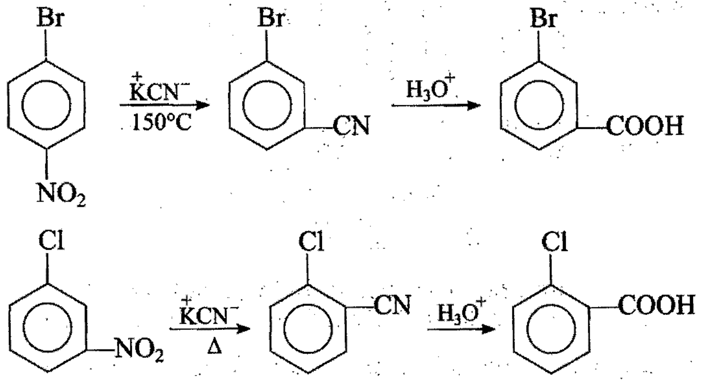


(Nitrobenzene is often used as a solvent in Friedel-Crafts alkylation).

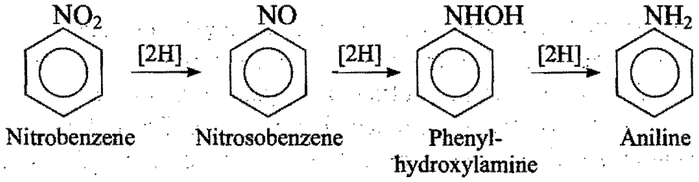
2. Reaction with KOH : On heating with solid KOH, nitrobenzene yields a mixture of *o*- and *p*-nitrophenols along with some azoxybenzene. **It is an example of nucleophilic substitution,** (Mechanism in **Section 16.8**), where the presence of one nitro group is sufficient to activate the benzene nucleus for nucleophilic substitution at *o*- and *p*-positions.



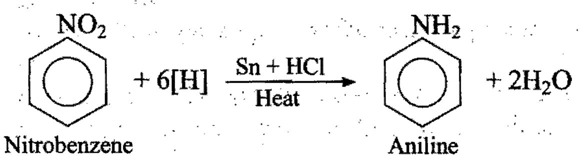
3. Von Richter reaction : When halonitrobenzene is heated with KCN at 150°C, the —NO_2 group is expelled and a cyano (or —COOH) group enters the ring at *ortho*-position with respect to nitro group.



4. Reduction : Nitrobenzene may be reduced to a variety of compounds depending on the nature of reducing agent and pH. The reduction of nitrobenzene probably proceeds through the following route:

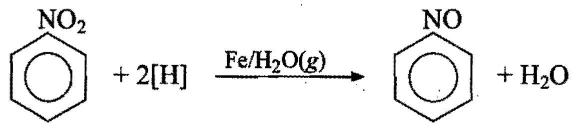


(a) Reduction in acidic medium : Reduction of nitrobenzene in presence of tin and hydrochloric acid (Sn + HCl) or iron and hydrochloric acid (Fe + HCl) yields only the final product aniline and intermediate products, nitrosobenzene and phenylhydroxylamine do not appear at all.



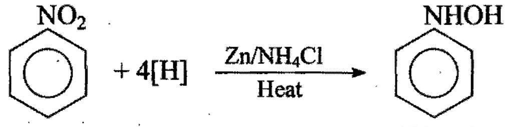
(b) Reduction in neutral medium :

(i) With iron and steam, nitrobenzene is reduced to nitrosobenzene.



Nitrosobenzene

(ii) Zinc and ammonium chloride or zinc and calcium chloride or aluminium mercury couple reduce nitrobenzene to phenylhydroxylamine.



Nitrobenzene *N*-Phenylhydroxylamine

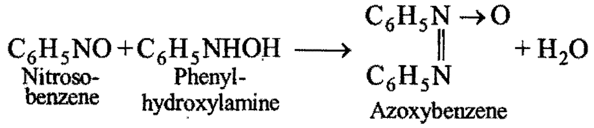
Nitrosobenzene cannot be isolated.

Hydroxylamine on warming with ammoniacal silver nitrate solution (Tollens' reagent) are easily oxidised back to the corresponding nitroso compounds and thus reduce the Tollens' reagent to metallic silver. This reaction is used as a test for nitro compounds and is also known as **Baker-Mulliken's test.**

$$C_6H_5NHOH + \underset{\text{Tollens' reagent}}{Ag_2O} \longrightarrow \underset{\text{Nitrosobenzene}}{C_6H_5NO} + H_2O + 2Ag\downarrow$$

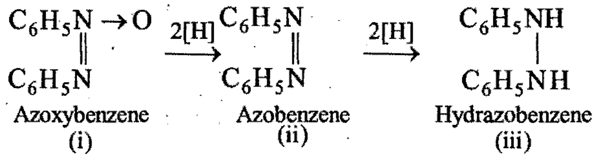
(c) Reduction in alkaline medium: When nitrobenzene is reduced in alkaline medium with zinc and alkali, the, mononuclear intermediate products formed interact to produce dinuclear products.

$$C_6H_5NO_2 \xrightarrow[-H_2O]{2[H]} C_6H_5NO \xrightarrow{2[H]} C_6H_5NHOH$$



$$\underset{\substack{\text{Nitroso-}\\\text{benzene}}}{C_6H_5NO} + \underset{\substack{\text{Phenyl-}\\\text{hydroxylamine}}}{C_6H_5NHOH} \longrightarrow \underset{\text{Azoxybenzene}}{\begin{array}{c} C_6H_5N \rightarrow O \\ \| \\ C_6H_5N \end{array}} + H_2O$$

Azoxybenzene undergoes further reduction forming azobenzene and hydrazobenzene.



$$\underset{\substack{\text{Azoxybenzene}\\\text{(i)}}}{\begin{array}{c} C_6H_5N \rightarrow O \\ \| \\ C_6H_5N \end{array}} \xrightarrow{2[H]} \underset{\substack{\text{Azobenzene}\\\text{(ii)}}}{\begin{array}{c} C_6H_5N \\ \| \\ C_6H_5N \end{array}} \xrightarrow{2[H]} \underset{\substack{\text{Hydrazobenzene}\\\text{(iii)}}}{\begin{array}{c} C_6H_5NH \\ | \\ C_6H_5NH \end{array}}$$

By selecting a suitable alkaline reducing agent, any of the three reduction products (i), (ii) and (iii) can be isolated. For example,

(i) Azoxybenzene is formed in presence of alkaline sodium arsenite (Na_3AsO_3 + NaOH) or glucose/NaOH.

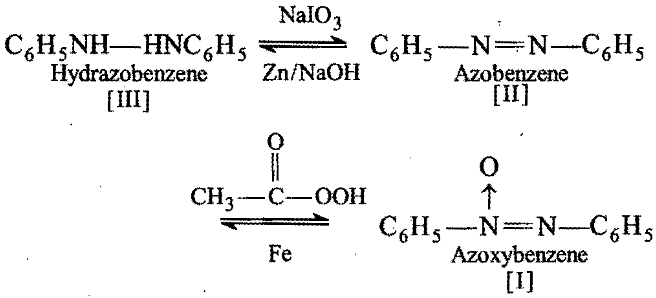
(ii) Azobenzene is obtained by using sodium amalgam, zinc dust and caustic soda in methanol or with alkaline sodium stannite.

(iii) Hydrazobenzene is obtained when reduction is carried out with zinc dust and aqueous sodium hydroxide.

$$\text{or } [\underset{\text{Nitrobenzene}}{2C_6H_5NO_2} + 8[H] \xrightarrow[(CH_3OH)]{Zn + NaOH} \underset{\text{Azobenzene [II]}}{C_6H_5N{=}N{-}C_6H_5} + 4H_2O]$$

$$[\underset{\text{Nitrobenzene}}{2C_6H_5NO_2} + 10[H] \xrightarrow[NaOH\ (aq.)]{Zn} \underset{\text{Hydrazobenzene [III]}}{C_6H_5NH{-}HNC_6H_5} + 4H_2O]$$

Further, the conversion of hydrazobenzene to azoxybenzene and *vice-versa* can be done through azobenzene as follows:



$$\underset{\substack{\text{Hydrazobenzene}\\\text{[III]}}}{C_6H_5NH{-}HNC_6H_5} \underset{Zn/NaOH}{\overset{NaIO_3}{\rightleftharpoons}} \underset{\substack{\text{Azobenzene}\\\text{[II]}}}{C_6H_5{-}N{=}N{-}C_6H_5} \underset{Fe}{\overset{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OOH}{\rightleftharpoons}} \underset{\substack{\text{Azoxybenzene}\\\text{[I]}}}{C_6H_5{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}C_6H_5}$$

All these compounds [I, II and III] on reduction with Sn/HCl give aniline.

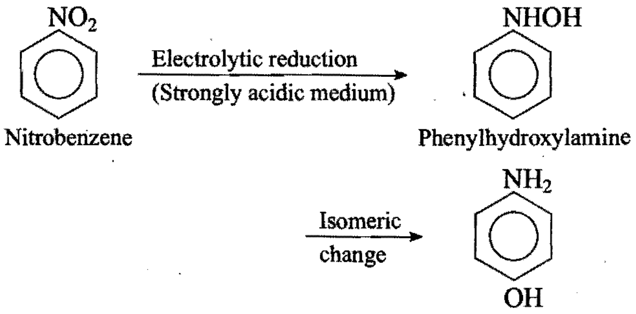
(d) Aromatic nitro compounds on reduction with $LiAlH_4$ give azo compounds and not primary amines.

$$\underset{\text{Nitrobenzene}}{2C_6H_5NO_2} + 8[H] \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Azobenzene}}{C_6H_5{-}N{=}N{-}C_6H_5} + 4H_2O$$

(e) Electrolytic reduction: In electrolytic reduction, it is believed that reaction proceeds through the same stages as discussed above but the nature of the final product depends upon the pH of the reaction medium.

(i) In weakly acidic solution, (dil. H_2SO_4), nitrobenzene is reduced to aniline (yield 90%).

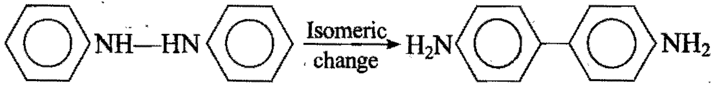
(ii) In strongly acidic solution, (conc. H_2SO_4), phenylhydroxylamine is first formed which undergoes isomeric change (intramolecular rearrangement) forming *p*-aminophenol.



Nitrobenzene Phenylhydroxylamine

p-Aminophenol

(iii) In alkaline medium, hydrazobenzene is first formed which undergoes isomeric change forming benzidine.



Hydrazobenzene Benzidine

Uses of nitrobenzene : Nitrobenzene is used,

(i) in manufacture of aniline and azo dyes.

(ii) as a solvent.

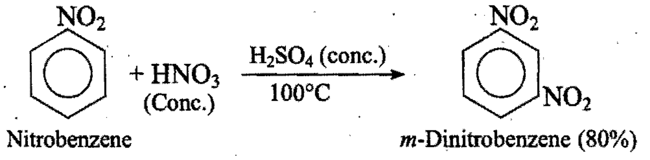
(iii) in the preparation of shoe polish and scenting cheap soaps.

(iv) as an oxidising agent.

Dinitro Compounds

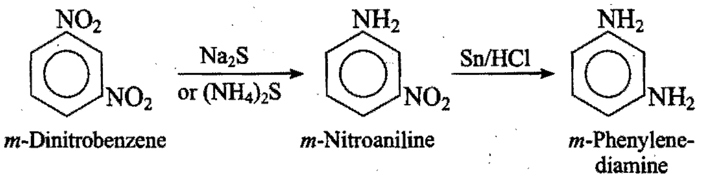
Of the three isomeric dinitro benzenes (*o*-, *m*-, *p*-), the *meta*-derivative is by far the most important.

***m*-Dinitrobenzene :** It is prepared by vigorous nitration of nitrobenzene (1 part) with a mixture of equal amounts of concentrated (or fuming) nitric acid and concentrated sulphuric acid.



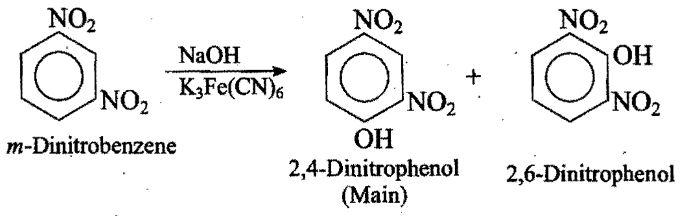
About 7% of the *ortho* isomer is also obtained which is removed during crystallization.

It is a pale yellow solid, m.pt. 90°C, insoluble in water but readily soluble in alcohol and ether. It is volatile in steam. When reduced with a mild reducing agent like sodium sulphide or ammonium hydrogen sulphide or ammonium sulphide, it reduces only one of the nitro group (stepwise reduction) without affecting the other nitro group to give *m*-nitroaniline. Such reductions are called **Selective reductions** (or **Zenin reduction**). *m*-nitroaniline can also be further reduced to *m*-phenylenediamine.



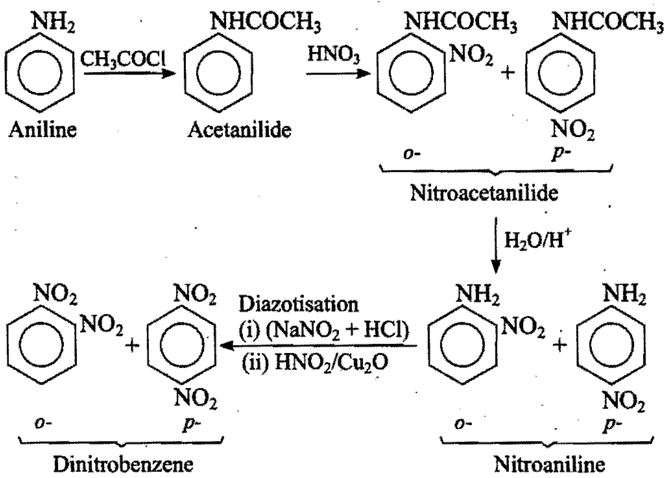
Both the nitro groups are tightly attached to the benzene nucleus and cannot be replaced by other atoms or groups (it differs from *o*- and *p*-dinitrobenzene in which one of the —NO_2 groups can be replaced by —OH or —NH_2 by boiling with aqueous sodium hydroxide or ethanolic ammonia at 130°C respectively).

With sodium hydroxide and potassium ferricyanide, it undergoes nucleophilic substitution yielding mainly 2,4-dinitrophenol and a small amount of 2,6-dinitrophenol.

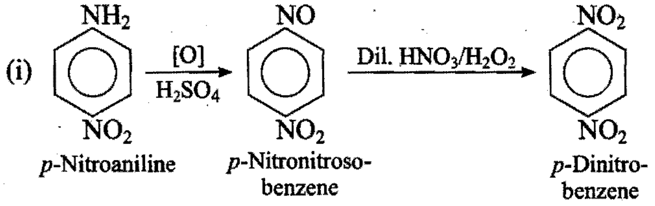


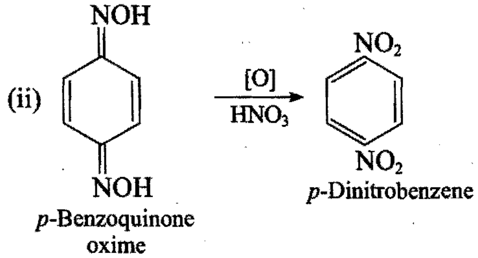
m-Dinitrobenzene is used in the manufacture of explosives (Roburite and Securite), *m*-phenylenediamine and dyestuffs.

***o*- and *p*-Dinitrobenzenes :** *o*- and *p*-dinitrobenzenes are obtained indirectly from aniline by first protecting the —NH_2 group with acetylation.

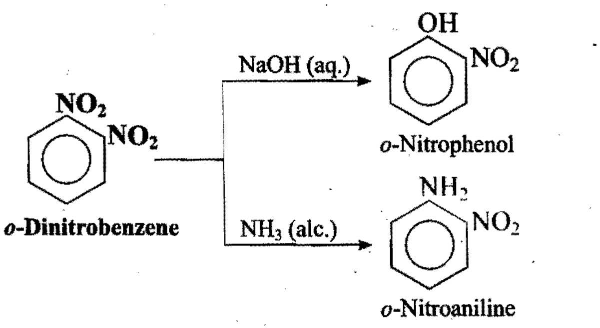


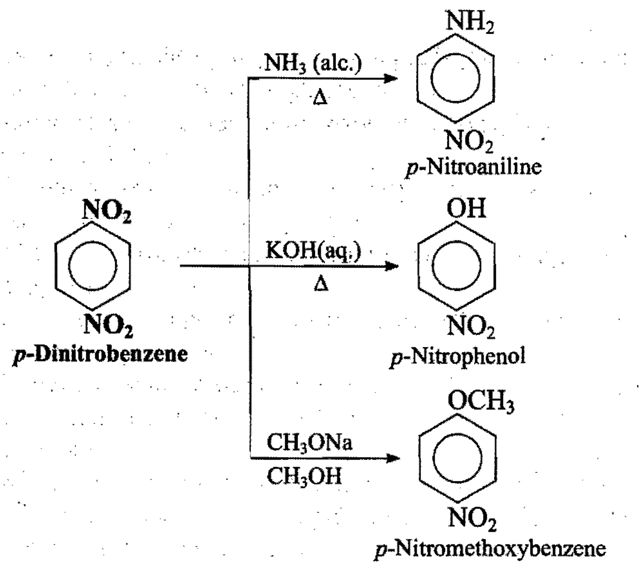
p-Dinitrobenzene may also be prepared as :



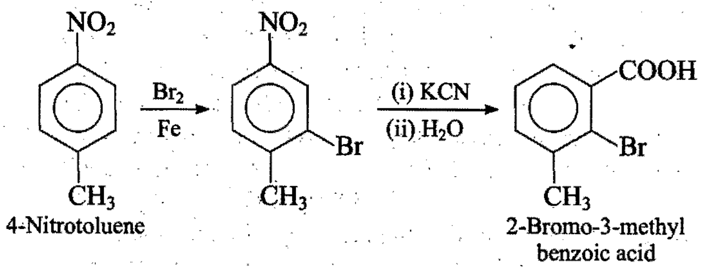


Both *o*- and *p*-dinitrobenzenes are colourless solids with m.pt. 118°C and 174°C respectively. They resemble the *m*-isomer in reduction with Na_2S or $(NH_4)_2S$, but differ in respect that one of the —NO_2 groups can be readily replaced by —NH_2, —OH or —OCH_3 group.





An interesting application of the **Von Richter reaction** (see **Section 16.8**) is the preparation of 2-bromo-3-methyl benzoic acid which, apparently, has not been prepared by any other means:



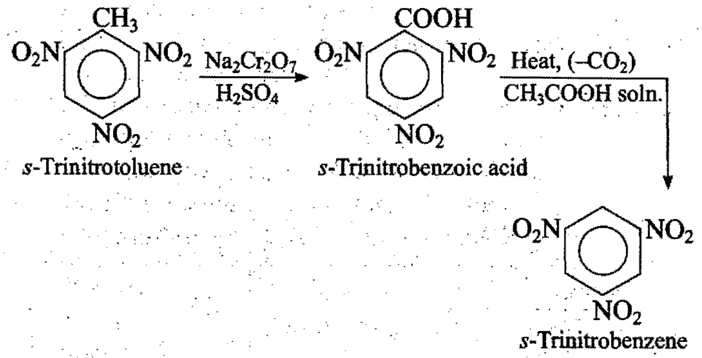
Trinitro Compounds

1,3,5-Trinitrobenzene (TNB) and 2,4,6-Trinitrotoluene (TNT) are the important trinitro compounds which are used as military explosives.

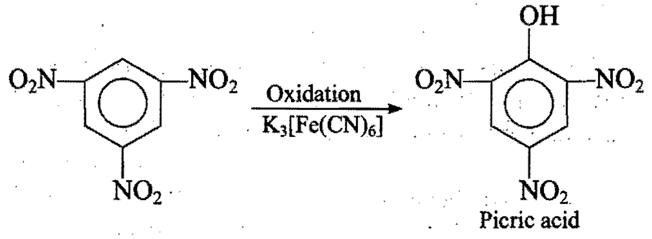
1,3,5-Trinitrobenzene (TNB) : It may be prepared by:

(i) Heating *m*-dinitrobenzene with a mixture of fuming nitric acid and fuming sulphuric acid for about 5 days.

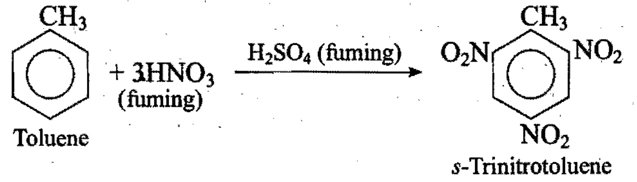
(ii) Oxidation of *s*-trinitrotoluene to *s*-trinitrobenzoic acid which on heating in acetic acid solution undergoes decarboxylation to give *s*-trinitrobenzene.



TNB on oxidation with alkaline potassium ferricyanide gives picric acid (2,4,6-trinitrophenol).



2,4,6-Trinitrotoluene (TNT) : It may be prepared by nitrating toluene with a mixture of fuming nitric acid and fuming sulphuric acid.



The —CH_3 group of TNT is reactive due to the presence of negative —NO_2 groups in *o*- and *p*-positions.

TNT forms yellow crystals, m.pt. 81°C. Due to low melting point it is filled in bombs and shells in molten state. It is a reasonably safe explosive as it requires strong detonation to set it off.

Its mixture with ammonium nitrate is extensively employed as blasting explosive and is known as **amatol.** Amanol is another outdoor blasting explosive. It contains 47% aluminium nitrate, 22% Al, 30% TNT and 1% charcoal.

When detonated, TNT explodes violently and decomposes into products which are all gases.

$$2CH_3C_6H_2(NO_3)_3 \longrightarrow 12CO + 2CH_4 + H_2 + 3N_2$$

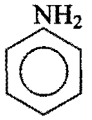
TNB is a colourless crystalline solid, m.pt. 122°C. It is a more powerful explosive than even TNT but is not commonly employed for this purpose on account of high cost of production.

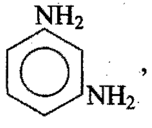
16.13 AROMATIC AMINO COMPOUNDS

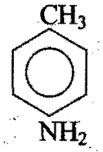
Aromatic amino compounds are of two types.

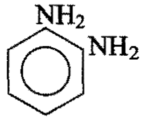
(1) Nucleus substituted amines: In this type of amines, the nitrogen atom of amino group is directly attached to aromatic ring. These are generally known as **arylamines** or aromatic amines. Arylamines are further classified as:

(i) Primary amines : When one or more amino (—NH_2) groups are attached to nucleus.

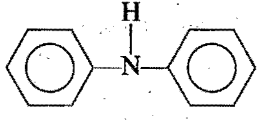

Aniline (Benzenamine)

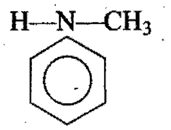

m-Diaminobenzene (*m*-phenylenediamine)


p-Amino toluene (*p*-toluidine)


o-Phenylene-diamine

(ii) Secondary amines : These amines contain the grouping, >NH, *i.e.*, two hydrogen atoms of NH_3 molecule have been replaced by two aryl groups or one aryl and one alkyl groups.

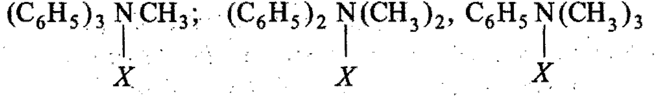

Diphenylamine or *N*-Phenylaniline


Methylphenylamine or *N*-Methylaniline

(iii) Tertiary amines : These amines contain the $\gt$N grouping, *i.e.*, all the three hydrogen atoms of NH_3 have been replaced by aryl groups or aryl and alkyl groups.

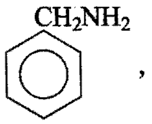
$(C_6H_5)_3N$, Triphenylamine
$C_6H_5N(CH_3)_2$ N,N-Dimethylaniline

Quaternary ammonium compounds : Like aliphatic amines, aromatic amines form quaternary ammonium compounds but purely aromatic quaternary compounds of the type $(C_6H_5)_4NX$ are unknown. The quaternary compounds containing both aryl and alkyl groups are known.

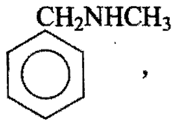


$$(C_6H_5)_3\underset{X}{\underset{|}{N}}CH_3;\quad (C_6H_5)_2\underset{X}{\underset{|}{N}}(CH_3)_2,\quad C_6H_5\underset{X}{\underset{|}{N}}(CH_3)_3$$

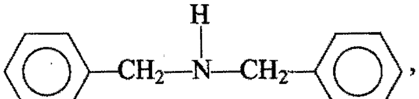
(2) Side-chain substituted amines or aralkylamines : In these amines, nitrogen of the amino group is not linked directly to the ring but is present in the side-chain. Examples are:



Benzylamine (1°)
(Phenylmethanamine)



N-methyl-
benzylamine (2°)



Dibenzylamine (2°)

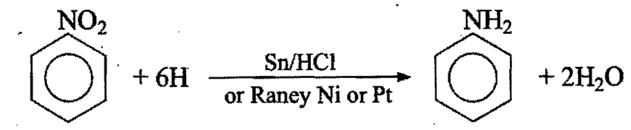
$(C_6H_5CH_2)_3N$
Tribenzylamine (3°)

These behave very much like the aliphatic amines.

The first member of each of the arylamine series and araliphatic amine series is described below:

[A] Aniline, $C_6H_5NH_2$, or Phenylamine or Aminobenzene or Benzenamine

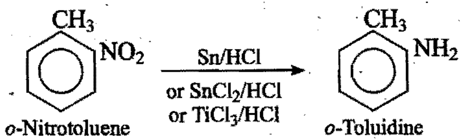
1. Laboratory preparation : Aniline is prepared in the laboratory by reduction of nitrobenzene with tin and hydrochloric acid.



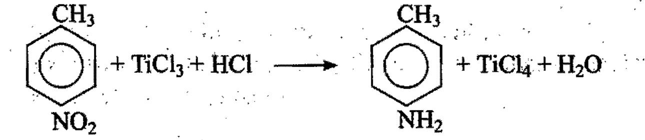
Nitrobenzene Aniline

$$3Sn + 12HCl \longrightarrow 3SnCl_4 + 12H$$
$$2C_6H_5NO_2 + 12H \longrightarrow 2C_6H_5NH_2 + 4H_2O$$
$$2C_6H_5NH_2 + SnCl_4 + 2HCl \longrightarrow (C_6H_5NH_2)_2H_2SnCl_6$$

Note : The above method is also used for the preparation of *o*-, *m*- or *p*-toluidines by taking respective nitrotoluenes.

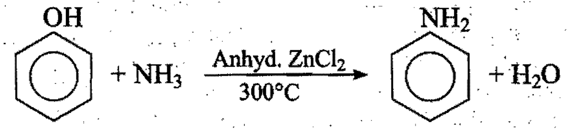


o-Nitrotoluene *o*-Toluidine

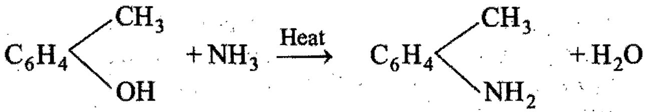


p-Nitrotoluene *p*-Toluidine

2. From phenols : Aniline is obtained when phenol is treated with ammonia in presence of anhydrous zinc chloride at 300°C.

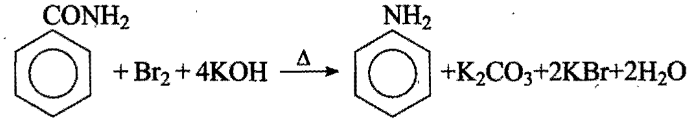


Phenol Aniline



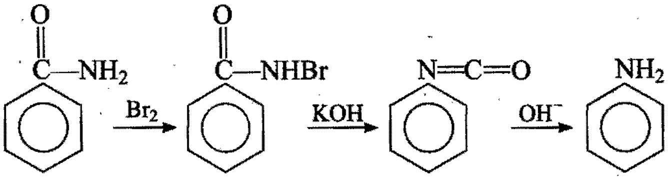
Cresols (*o*-, *m*-, *p*-) Toluidines (*o*-, *m*-, *p*-)

3. From benzamide (Hofmann's reaction) : Aniline is formed when benzamide is treated with bromine and caustic potash.



Benzamide Aniline

It involves intramolecular phenyl migration.

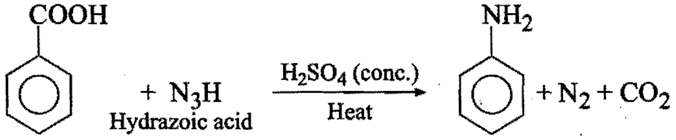


Benzamide *N*-Bromo-benzamide Phenyl-isocyanate Aniline

The reaction may also be expressed as follows :

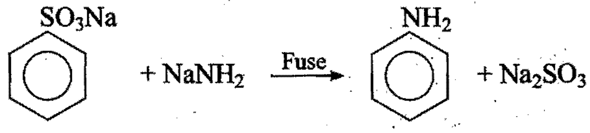
$$2KOH + Br_2 \longrightarrow KOBr + KBr + H_2O$$
$$C_6H_5CONH_2 + KOBr \longrightarrow C_6H_5NH_2 + CO_2 + KBr$$

4. From benzoic acid (Schmidt reaction) : Benzoic acid is dissolved in conc. H_2SO_4 and hydrazoic acid is dissolved in chloroform. Both solutions are mixed at 45°C.



Benzoic acid Aniline

5. From benzene sulphonic acid : The sodium salt of benzene sulphonic acid is fused with sodamide ($NaNH_2$) to obtain aniline.



Sodium benzene sulphonate Aniline

6. From phenyl isocyanide and phenyl isocyanate : By hydrolysis

$$\underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 2HOH \xrightarrow{\text{Heat}} \underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Formic acid}}{HCOOH}$$

$$\underset{\text{Phenyl isocyanate}}{C_6H_5NCO} + 2KOH \xrightarrow{\text{Hydrolysis}} \underset{\text{Aniline}}{C_6H_5NH_2} + K_2CO_3$$

7. From azobenzene, hydrazobenzene and nitroso compounds : By reduction with Sn/HCl or Zn/HCl or Fe/HCl.

$$\underset{\text{Azobenzene}}{C_6H_5N{=}NC_6H_5} + 4[H] \xrightarrow{\text{Zn/HCl}} 2C_6H_5NH_2$$

$$\underset{\text{Hydrazobenzene}}{C_6H_5NH{-}NHC_6H_5} + 2[H] \xrightarrow{\text{Zn/HCl}} 2C_6H_5NH_2$$

$$\underset{\text{Nitrosobenzene}}{C_6H_5NO} + 4[H] \xrightarrow[\text{or Fe/HCl}]{\text{Sn/HCl}} C_6H_5NH_2 + H_2O$$

8. From Grignard reagent : By the action of chloramine.

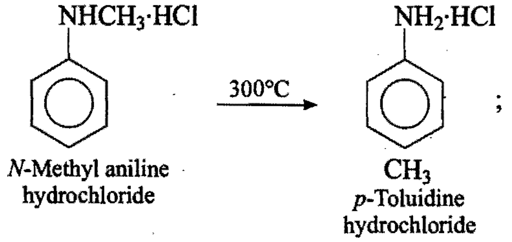
$$C_6H_5MgCl + Cl{-}NH_2 \xrightarrow{\Delta} C_6H_5NH_2 + MgCl_2$$

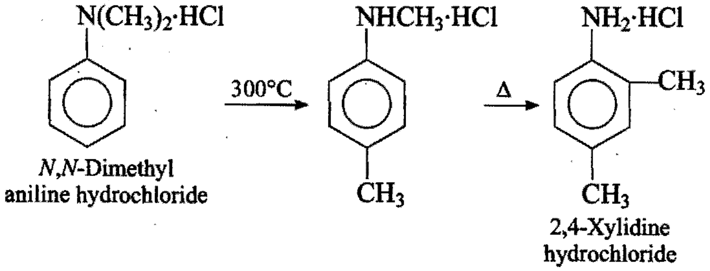
9. By Friedel-Crafts reaction :

$$\underset{\text{Benzene}}{C_6H_5H} + \underset{\text{Chloramine}}{Cl{-}NH_2} \xrightarrow[\Delta]{\text{Anhyd. AlCl}_3} C_6H_5NH_2 + HCl$$

$$\underset{\text{Benzene}}{C_6H_5H} + \underset{\text{Hydroxylamine}}{HOH_2N} \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O$$

10. By Hofmann-Martius reaction : The isomerisation of alkyl aniline hydrochlorides to primary amino compounds on strong heating at 300°C, is known as Hofmann-Martius rearrangement.





In this reaction, an alkyl group migrates from N-atom to carbon atom of benzene nucleus preferentially at *p*-position, if occupied then at *o*-position.

Manufacture : Aniline is obtained on commercial scale by the following methods:

1. From nitrobenzene : Large quantities are obtained by reduction of nitrobenzene in presence of iron fillings, water and small amount of HCl. The reaction may be supposed to take place as follows:

$$3Fe + 6HCl \longrightarrow 3FeCl_2 + 6H$$

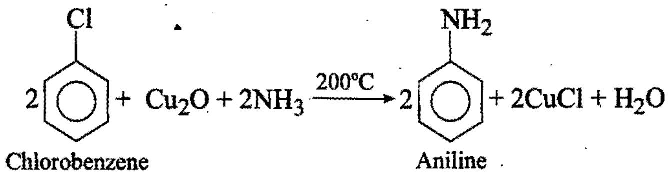
$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$$

$$C_6H_5NO_2 + 6Fe(OH)_2 + 4H_2O \longrightarrow C_6H_5NH_2 + 6Fe(OH)_3$$

The reduction of nitrobenzene can also be done with hydrogen in presence of nickel catalyst or cupric oxide (CuO) or vanadium-platinum (V-Pt) catalyst at 400°C. This is known as vapour phase reduction. Aniline is prepared **in the laboratory** (same method) by the reduction of nitrobenzene with tin and HCl.

2. From chlorobenzene : Aniline can also be manufactured by the action of ammonia on chlorobenzene at 200°C under 300 atmospheric pressure in presence of cuprous oxide as catalyst. Excess of ammonia is always employed as to check the formation of phenol by side reaction.

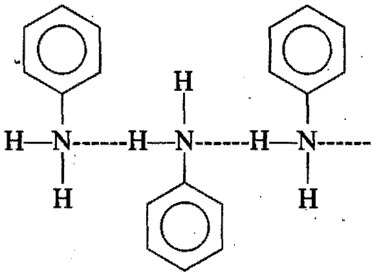


or $$C_6H_5Cl + KNH_2 \xrightarrow[\text{Low temp.}]{\text{Liquid NH}_3} C_6H_5NH_2 + KCl$$

Physical properties

(i) Fresh aniline is a colourless oily liquid. On standing the colour becomes dark brown due to action of air and light.
(ii) Its boiling point is 183°C.
(iii) It is slightly heavier than water.
(iv) It has a characteristic odour which is not pleasant.
(v) It is slightly soluble in water but readily soluble in organic solvents.
(vi) It is steam volatile.
(vii) It is toxic in nature.

High boiling point of aniline is due to intermolecular H-bonding.



p-substituted anilines, being the most symmetric, have the highest melting points. Thus, *p*-toluidine is solid at room temperature (m.pt. 45°C) while *o*- and *m*-toluidines are liquids (b.pt. 201°C and 200°C respectively).

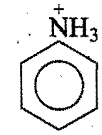
- **Chemical properties :** Aniline is a primary amine. It shows properties both of benzene nucleus and amino group ($—NH_2$).

Reaction Involving $—NH_2$ Group

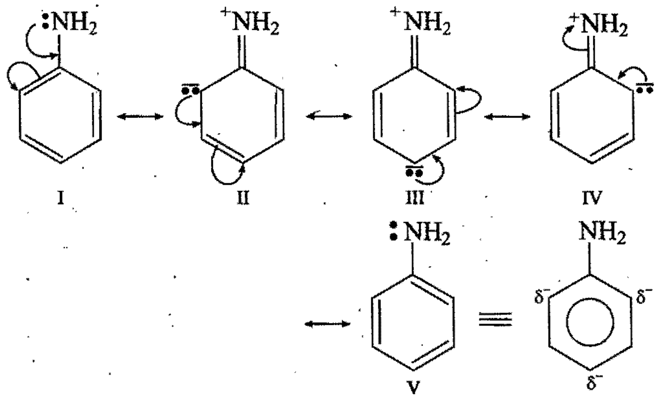
1. Basic nature : The basicity is a measure of a compound's ability to accept a proton (H^+). Aniline is a weak base (almost neutral towards litmus) as it forms salts with strong mineral acids (*i.e.*, protonated hence, basic in nature). It accepts a proton as follows:

$$C_6H_5\ddot{N}H_2 + H^+ \longrightarrow C_6H_5\overset{+}{N}H_3 \text{ or}$$

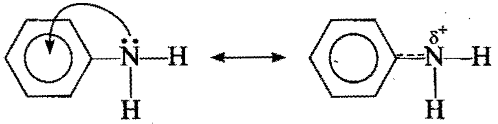
Anilinium ion



Weaker basic nature of aniline as compared to aliphatic amines can be explained on the basis of **resonance.** In aliphatic amines, the non-bonding electron pair of N is localized and is fully available for coordination with a proton. On the other hand, in aniline or other aromatic amines, the non-bonding electron pair is delocalized into benzene ring by resonance and the electron donating capacity of nitrogen for protonation is considerably decreased as compared to that of NH_3 and aliphatic amines.



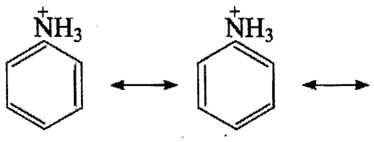
Hence, $—NH_2$ group activates benzene nucleus for *o*- and *p*-electrophilic attack.



Resonance hybrid

Lower stability of anilinium ion than aniline.

Anilinium ion **(cation)** formed by aniline on accepting a proton is less resonance stabilized (having only two resonating forms) than aniline (having I to V resonating forms).



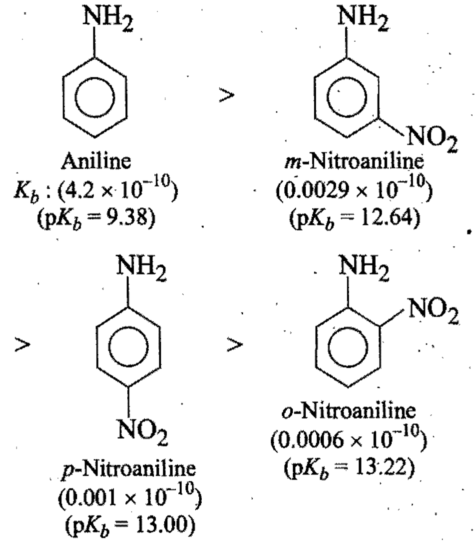
No other resonating structure possible.

Thus, electron density is less on N-atom due to which aniline or other aromatic amines are less basic than aliphatic amines.

Effect of Substituents on the Basicity of Aromatic Amines

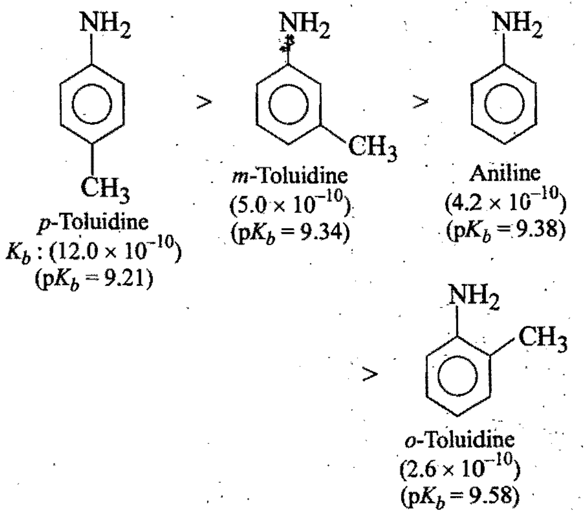
In general, any group which when present on benzene ring has electron **withdrawing effect** ($—NO_2$, $—CN$, $—SO_3H$, $—COOH$, $—Cl$, C_6H_5, etc.) **decreases basicity of aniline** (Nitroaniline is less basic than aniline as nitro group is electron withdrawing group (*–I* group) and aniline is more basic than diphenylamine), **while a group which has electron repelling effect ($—NH_2$, $—OR$, $R—$, etc.)** at the para-position increases basicity of aniline. Toluidine is more basic than aniline as $—CH_3$ group is electron repelling group (+*I* group).

(a) Nitroanilines



Ortho substituted anilines are weaker bases than anilines regardless of the nature of the substituent whether electron withdrawing or electron repelling. This is called ***ortho*** **effect** and is probably due to a combination of steric acid electronic factors.

(b) Toluidines



(c) Phenylenediamines


p-Phenylenediamine
K_b : (14.0×10^{-10})
($pK_b = 7.86$)

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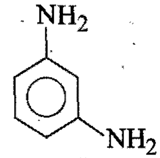
m-Phenylenediamine
(10.0×10^{-10})
($pK_b = 9.00$)

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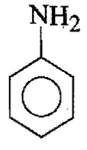
Aniline
(4.2×10^{-10})
($pK_b = 9.38$)

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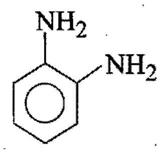

o-Phenylenediamine
(3.0×10^{-10})
($pK_b = 9.52$)

Similarly, the basic character of some other amines have the following order:

Chloroanilines: *p*-isomer > *m*- > *o*-

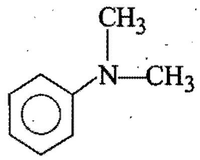
Other amines

$R_2NH > RNH_2 > C_6H_5CH_2NH_2 > NH_3 > C_6H_5NH_2$

Weaker basic nature of aniline as compared to aliphatic amines can be explained on the basis of **resonance.**

Effect of Substituents on N-atom

When the hydrogen atoms of the amino group in primary arylamines are replaced by **electron releasing (donating) alkyl groups,** it increases the basicity of aromatic amines; so *N*-alkylated anilines are stronger bases than aniline because of steric effect.


N,N-Dimethylaniline
K_b : (11.7×10^{-10})

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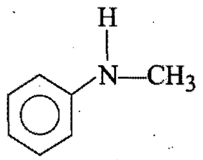
N-Methylaniline
(7.1×10^{-10})

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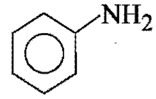
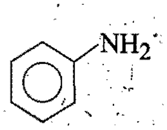

Aniline
(4.2×10^{-10})

Ethyl group being bigger than methyl has more steric effect, so *N*-ethylaniline is stronger base than *N*-methyl aniline. Thus, basic character is:

$$\underset{N,N\text{-Diethyl aniline}}{C_6H_5N(C_2H_5)_2} > \underset{N\text{-Ethyl aniline}}{C_6H_5NHC_2H_5} > \underset{N,N\text{-Dimethyl aniline}}{C_6H_5N(CH_3)_2} > \underset{N\text{-Methyl aniline}}{C_6H_5NHCH_3} > \underset{\text{Aniline}}{C_6H_5NH_2}$$

Similarly, the presence of **electron withdrawing groups** (such as phenyl, C_6H_5 group) decreases the basicity. For example, triphenylamine is less basic than diphenylamine which in turn is less basic than aniline.


Aniline

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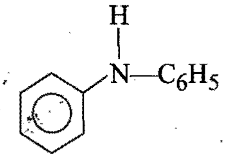
Diphenylamine

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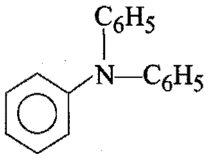

Triphenylamine

Thus,

$$NH_3 > C_6H_5NHC_2H_5 > C_6H_5NHCH_3 > C_6H_5NH_2 > C_6H_5NHC_6H_5$$

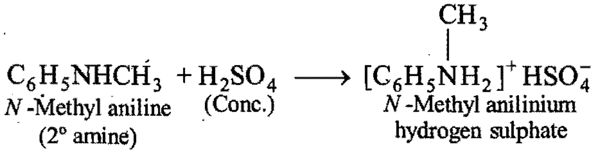
Aniline forms salts with strong acids.

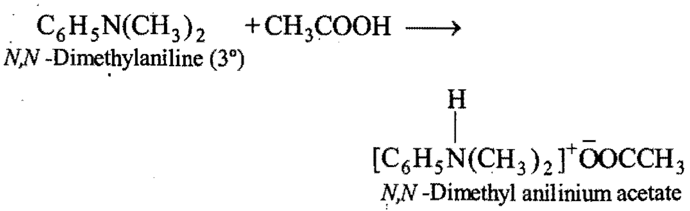
$$C_6H_5NH_2 + \underset{\text{(Conc.)}}{HCl} \longrightarrow \underset{\substack{\text{Aniline hydrochloride or}\\ \text{Anilinium chloride}}}{C_6H_5NH_3Cl(C_6H_5NH_2 \cdot HCl)}$$

$$\underset{\text{Aniline}}{2C_6H_5NH_2} + \underset{\text{(Conc.)}}{H_2SO_4} \longrightarrow \underset{\text{Aniline sulphate}}{(C_6H_5NH_2)_2H_2SO_4}$$

$$2C_6H_5NH_2 + \underset{\substack{\text{Chloroplatinic}\\ \text{acid}}}{H_2PtCl_6} \longrightarrow \underset{\text{Aniline platinic chloride}}{(C_6H_5NH_2)_2H_2PtCl_6}$$

$$\underset{\text{Aniline}}{2C_6H_5NH_2} + \underset{\substack{\text{Chloro-}\\ \text{stannic acid}}}{H_2SnCl_6} \longrightarrow \underset{\text{Aniline stannic chloride}}{(C_6H_5NH_2)_2H_2SnCl_6}$$


$$\underset{\substack{N\text{-Methyl aniline}\\ (2^\circ\text{ amine})}}{C_6H_5NHCH_3} + \underset{\text{(Conc.)}}{H_2SO_4} \longrightarrow \underset{\substack{N\text{-Methyl anilinium}\\ \text{hydrogen sulphate}}}{[C_6H_5\overset{CH_3}{\overset{|}{N}}H_2]^+HSO_4^-}$$


$$\underset{N,N\text{-Dimethylaniline }(3^\circ)}{C_6H_5N(CH_3)_2} + CH_3COOH \longrightarrow \underset{N,N\text{-Dimethyl anilinium acetate}}{[C_6H_5\overset{H}{\overset{|}{N}}(CH_3)_2]^+\bar{O}OCCH_3}$$

These salts are decomposed by alkalies to regenerate aniline.

2. Alkylation : Aniline reacts with alkyl halides forming secondary amines, tertiary amines or quaternary ammonium salt depending on the concentration of alkyl halide.

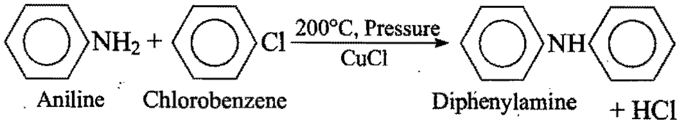
$$\underset{1^\circ\text{ Amine}}{C_6H_5NH_2} + CH_3I \xrightarrow{\Delta} \underset{\substack{N\text{-Methyl aniline}\\ (2^\circ\text{ Amine})}}{C_6H_5NHCH_3} + HI$$

$$\underset{2^\circ\text{ Amine}}{C_6H_5NHCH_3} + CH_3I \xrightarrow{\Delta} \underset{\substack{N,N\text{-Dimethyl aniline}\\ (3^\circ\text{ Amine})}}{C_6H_5N(CH_3)_2} + HI$$

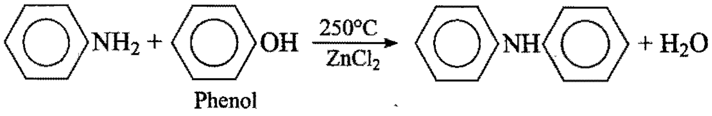
$$\underset{3^\circ\text{ Amine}}{C_6H_5N(CH_3)_2} + CH_3I \longrightarrow \underset{\substack{\text{Trimethyl anilinium iodide}\\ \text{(Quaternary salt)}}}{C_6H_5N(CH_3)_3I}$$

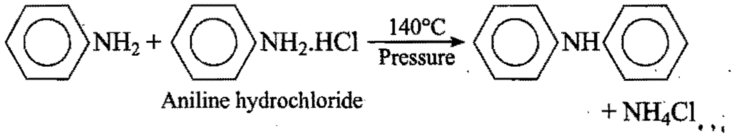
With methyl iodide, the process is commonly known as **exhaustive methylation.**

But **Arylation** of aniline is difficult (formation of diphenylamine).



+ HCl





Aniline hydrochloride

3. Acylation : Aniline reacts with acid chlorides or acid anhydrides in presence of dilute NaOH or pyridine to form anilides.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Acetyl chloride}}{ClCOCH_3} \xrightarrow[\text{Heat, (–HCl)}]{\text{Pyridine}} \underset{\substack{\text{Acetanilide}\\(N\text{-Acetyl aniline})}}{C_6H_5NHCOCH_3}$$

$$C_6H_5NH_2 + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \xrightarrow[(-CH_3COOH)]{\text{Pyridine}} \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3}$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Benzoyl chloride}}{ClCOC_6H_5} \xrightarrow[(-HCl)]{\text{Aq. NaOH}} \underset{\substack{\text{Benzanilide}\\(N\text{-phenylbenzamide})}}{C_6H_5NHCOC_6H_5}$$

These reactions are used for the protection of $—NH_2$ group.

Note : These alkylation and acylation undergo Friedel-Crafts reaction if carried out in presence of anhydrous $AlCl_3$. But **aniline itself does not undergo Friedel-Crafts reaction** because amino group of aniline acts as a base and forms salt with Lewis acid, $AlCl_3$, *i.e.*, $C_6H_5\overset{+}{N}H_2\cdot AlCl_3^-$.

Benzoylation of aniline is known as Schotten-Baumann reaction.

4. Carbylamine reaction : When heated with chloroform and alcoholic potassium hydroxide, aniline forms phenyl isocyanide. It has very offensive smell.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + \underset{\text{(Alc.)}}{3KOH} \xrightarrow{\text{Heat}} \underset{\text{Phenyl isocyanide}}{C_6H_5\overset{\rightarrow}{=}NC} + 3KCl + 3H_2O$$

This is a test of aniline and other primary amines only (aromatic and aliphatic both) and is known as isocyanide test (a distinction test for primary amines only).

5. Reaction with aldehydes : Aniline condenses with aromatic aldehydes to form **benzaniline** or **anils** or **Schiff bases** in presence of trace of an acid as catalyst, anhydrous zinc chloride.

$$C_6H_5NH_2 + \underset{\text{Benzaldehyde}}{OHCC_6H_5} \xrightarrow[\Delta]{H^+ \text{or } ZnCl_2} \underset{\substack{\text{Benzylidene aniline}\\\text{(Schiff base)}}}{C_6H_5N{=}CHC_6H_5} + H_2O$$

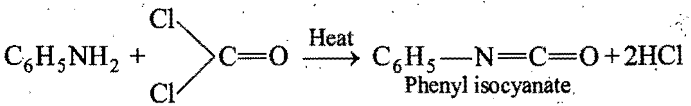
Schiff base on hydrolysis yields aniline again. The reaction is employed to protect the amino group during nitration. But when reduced, it forms secondary amine.

$$\underset{\text{Schiff base}}{C_6H_5N{=}CHC_6H_5} \xrightarrow[\text{Ni}]{2H} \underset{\text{Benzyl aniline (2° Amine)}}{C_6H_5NHCH_2C_6H_5}$$

6. Action of alkali metals : Aniline on heating with alkali metals, produces compounds in which one or both hydrogen atoms of the amino group get replaced by alkali metals to form potassium anilide.

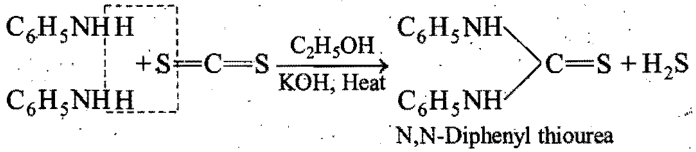
$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[\text{Heat}]{K} C_6H_5NHK \xrightarrow[\text{Heat}]{K} C_6H_5NK_2$$

7. Reaction with carbonyl chloride : Aniline combines readily with carbonyl chloride to form phenyl isocyanate.



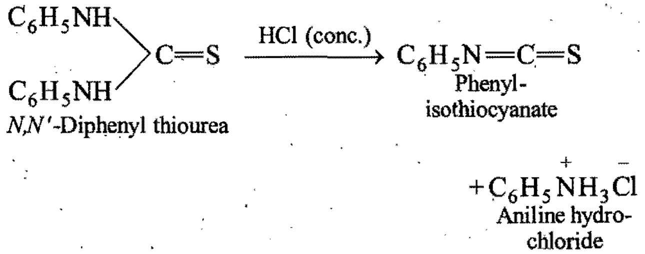
$$C_6H_5NH_2 + Cl_2C{=}O \xrightarrow{\text{Heat}} \underset{\text{Phenyl isocyanate}}{C_6H_5—N{=}C{=}O} + 2HCl$$

8. Reaction with carbon disulphide : Aniline, when heated with ethanolic carbon disulphide and solid KOH, forms diphenyl thiourea which upon treatment with conc. HCl gives phenyl isothiocyanate.



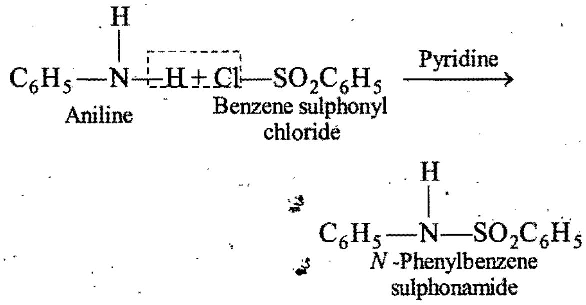
$$2\,C_6H_5NHH + S{=}C{=}S \xrightarrow[\text{KOH, Heat}]{C_2H_5OH} \underset{\text{N,N-Diphenyl thiourea}}{(C_6H_5NH)_2C{=}S} + H_2S$$

N, N'-Diphenyl thiourea is used as an accelerator during vulcanization of rubber.



$$\underset{N,N'\text{-Diphenyl thiourea}}{(C_6H_5NH)_2C{=}S} \xrightarrow{\text{HCl (conc.)}} \underset{\text{Phenyl-isothiocyanate}}{C_6H_5N{=}C{=}S} + \underset{\text{Aniline hydrochloride}}{C_6H_5\overset{+}{N}H_3\overset{-}{Cl}}$$

9. Sulphonylation (Reaction with benzene sulphonyl chloride) : Aniline reacts with benzene sulphonyl chloride (Hinsberg's reagent) to form *N*-phenylbenzene sulphonamide which is soluble in alkali.



$$\underset{\text{Aniline}}{C_6H_5—NH—H} + \underset{\text{Benzene sulphonyl chloride}}{Cl—SO_2C_6H_5} \xrightarrow{\text{Pyridine}} \underset{N\text{-Phenylbenzene sulphonamide}}{C_6H_5—NH—SO_2C_6H_5}$$

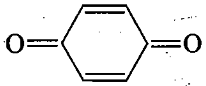
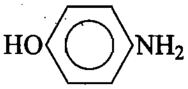
Sec. amine also reacts, but the product so formed is insoluble in alkali (it is Hinsberg's method for separation of *pri. sec.* and *tert.* amines).

10. Reaction with Grignard reagents : Aniline combines with Grignard reagents to form corresponding alkanes.

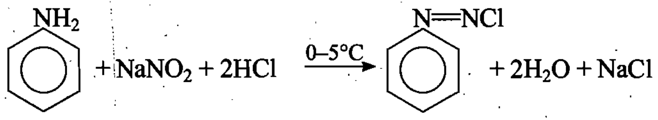
$$\underset{\text{Methyl magnesium iodide}}{CH_3MgI} + C_6H_5NH_2 \longrightarrow \underset{\text{Methane}}{CH_4} + C_6H_5NHMgI$$

$$\underset{\text{Ethyl magnesium bromide}}{C_2H_5MgBr} + C_6H_5NH_2 \longrightarrow \underset{\text{Ethane}}{C_2H_6} + C_6H_5NHMgBr$$

11. Oxidation : Aniline is readily oxidised because it is highly susceptible to atmospheric oxidation and turns dark red on exposure to air due to oxidation. It forms a number of products depending upon the nature of oxidising agent.

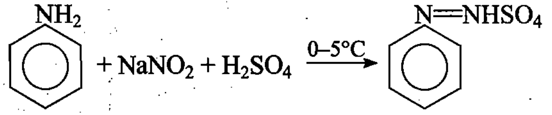
Oxidising agent	Products
Acidified $KMnO_4$ or ($Na_2Cr_2O_7 + CuSO_4$ + dil. acid)	Aniline black (a dye)
Alkaline $KMnO_4$	Azobenzene; $C_6H_5N{=}NC_6H_5$
Neutral $KMnO_4$	Azobenzene and nitrobenzene
Chromic acid ($Na_2Cr_2O_7$ + Conc. H_2SO_4)	p-Benzoquinone; 
Sodium hypochlorite or HOCl	p-Aminophenol, 
Caro's acid (H_2SO_5)	Nitrobenzene and nitrosobenzene
Conc. nitric acid	Decomposes
Bleaching powder	Deep violet colour

12. Diazotisation [Action of nitrous acid ($NaNO_2 + HCl$)] : Diazotisation is a reaction in which ice cooled solution of an aromatic primary amine (having —NH_2 group directly attached to nucleus) in an inorganic acid reacts with sodium nitrite solution leading to the formation of diazonium salts **(Diazo reaction).**



Aniline

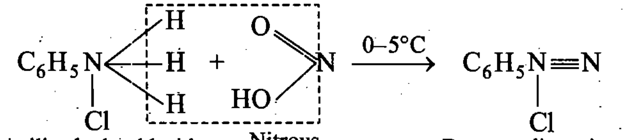
Benzene diazonium chloride



Benzene diazonium hydrogen sulphate

$$C_6H_5NH_2 + HCl \xrightarrow{0\text{–}5°C} C_6H_5NH_2\cdot HCl \text{ (or } C_6H_5NH_3^+Cl^-)$$

Aniline hydrochloride



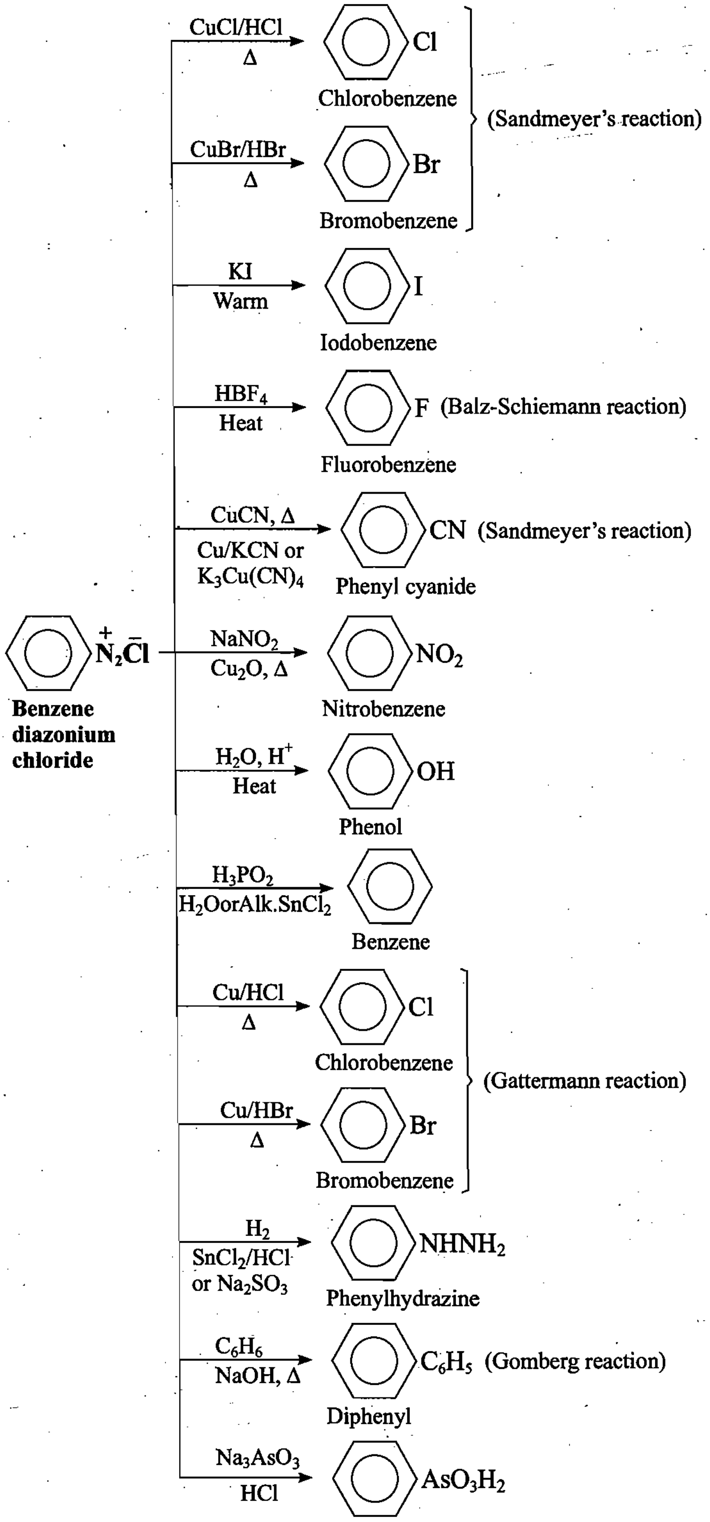
Aniline hydrochloride Nitrous acid Benzene diazonium chloride

or $C_6H_5\overset{+}{N}_2\overset{-}{Cl}$ or $[Ar—\overset{+}{N}{\equiv}N:]X^-$
(Blomstrand formula)

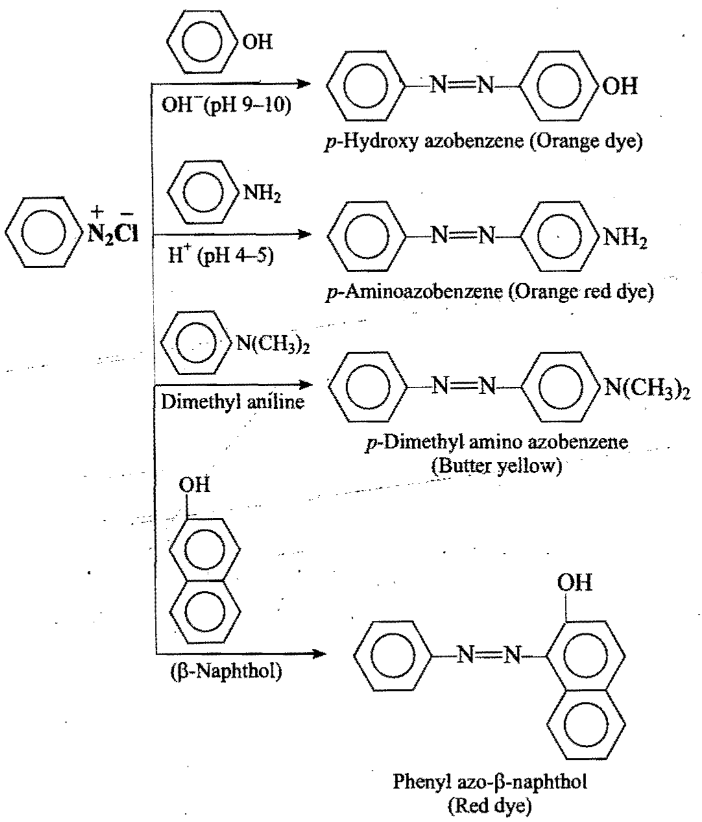
$$[\underset{\text{Sod. nitrite}}{NaNO_2} + HCl \longrightarrow NaCl + \underset{\text{Nitrous acid}}{HNO_2}]$$

Mineral acid should be added in excess in diazotisation of arylamines so as to prevent the coupling of benzene diazonium chloride with excess of arylamine.

Benzene diazonium chloride is extremely useful synthetic reagent. It is used in the preparation of many organic compounds.



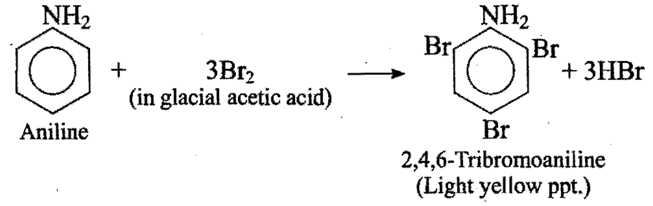
Coupling reactions:



Reactions of benzene nucleus

The benzene ring of aniline undergoes halogenation, sulphonation and nitration **(Electrophilic substitution).** The —NH_2 group is *o*-, *p*-directing and highly activating.

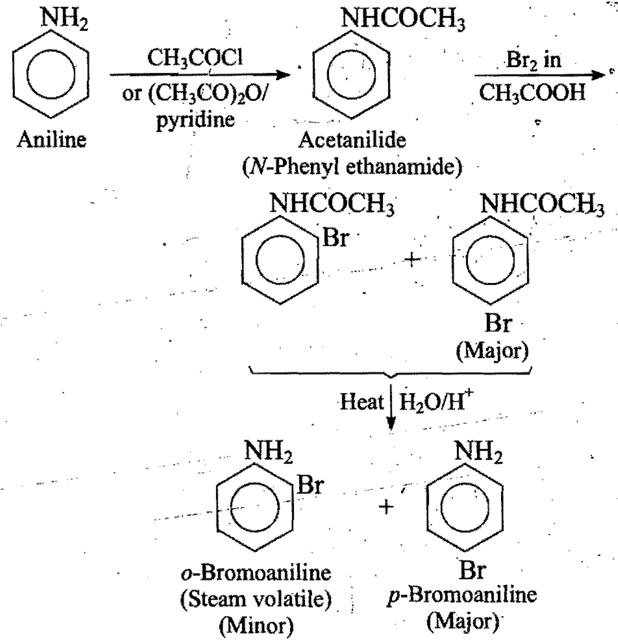
1. Halogenation : Presence of amino group in the nucleus facilitates halogenation. Chlorine and bromine water react very readily and form trichloro and symmetrical tribromo aniline, respectively,



In chlorination, a water free solvent such as chloroform should be used otherwise oxidation takes place.

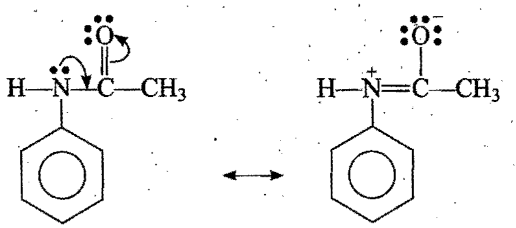
The reaction is used for estimation of aniline.

However, monochloro or monobromo derivative of aniline can be prepared if —NH_2 group is first protected by acetylation on account of oxidation of —NH_2 group.



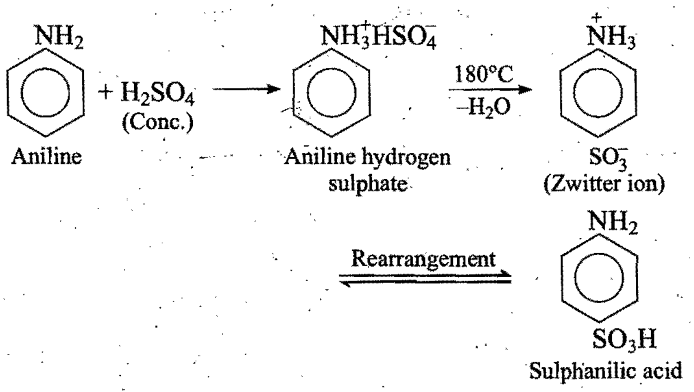
Halogenation of aniline is faster in polar solvents but slower in non-polar solvents.

Purpose of acylation : The acetyl group being electron withdrawing attracts the lone pair of electrons of the N-atom towards carbonyl group.



As a result, the activating effect of —NH_2 group is reduced. This method is called protection of —NH_2 group by acetylation. It is often used to control the rate of substitution and to prevent the formation of di and tri substitution products.

2. Sulphonation : Aniline reacts with conc. H_2SO_4 at 180°C to give sulphanilic acid (*p*-aminobenzene sulphonic acid), the *p*-isomer is known to be the most stable isomer.

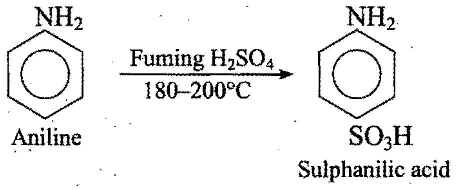


The given process is known as **Baking.**

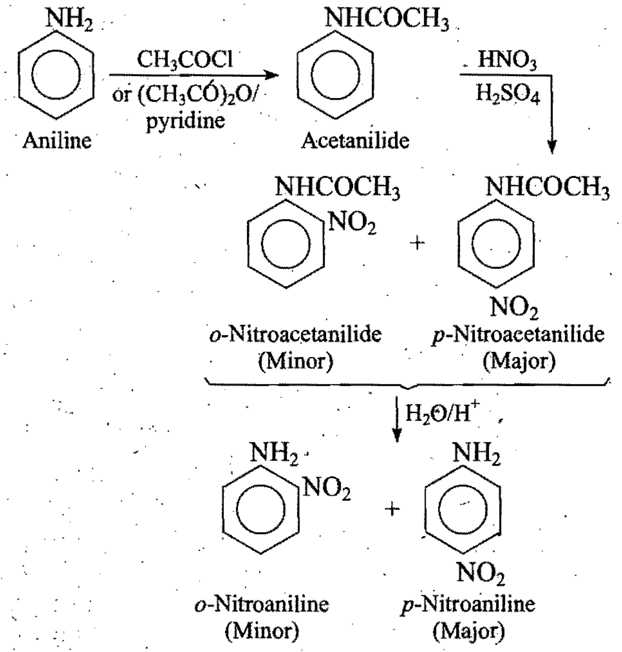
Sulphanilic acid has an acidic group (—SO_3H) as well as basic (—NH_2) group in the same molecule and thus exist as **Zwitter ion** or dipolar ion. Therefore, sulphanilic acid has high melting point and is practically insoluble in water. It is soluble in dilute NaOH (to form p-$NH_2C_6H_4SO_3^-Na$) but not in dil. HCl (because —SO_3^- group is a weak base and so does not accept a proton (H^+) from dil. HCl.)

$$H_2N—C_6H_4—SO_3H \rightleftharpoons \underset{\text{Zwitter ion}}{H_3\overset{+}{N}—C_6H_4SO_3^-}$$

However, aniline on heating with fuming sulphuric acid at 180–200°C, gives p-aminobenzene sulphonic acid (sulphanilic acid).

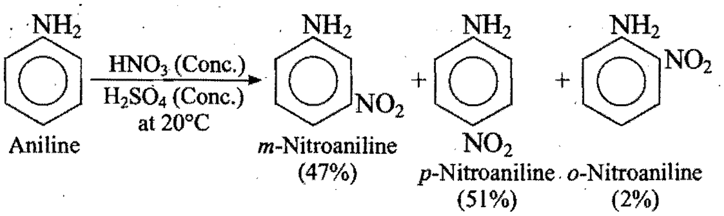


3. Nitration : Direct nitration of aniline is not possible on account of oxidation of —NH_2 group. However, nitration can be carried after protecting the —NH_2 group by acetylation to give acetanilide which is nitrated and finally hydrolysed to give o- and p-nitroanilines.

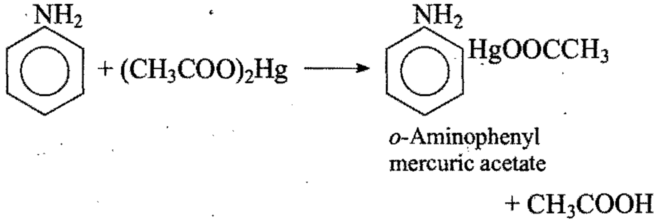


Since, nitration involves in strongly acidic medium, so protonation of aniline also takes place forming anilinium ion ($\overset{+}{N}H_3$) which, being m-directing and deactivating forms mainly m-nitroaniline.

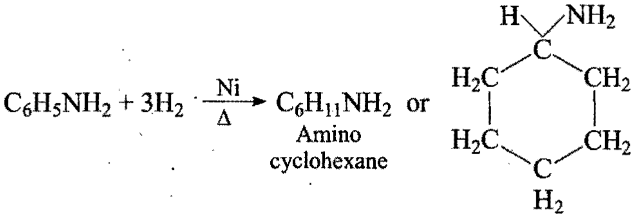
That is why, during direct nitration of aniline (—NH_2 group is o-,p-directing and activating), besides the o-,p-derivatives a significant amount of *meta* derivative is also formed.



4. Mercuration : When treated with alcoholic solution of mercuric acetate, aniline undergoes mercuration.



5. Catalytic hydrogenation : Aniline undergoes hydrogenation in presence of finely divided nickel at high temperature to form aminocyclohexane.



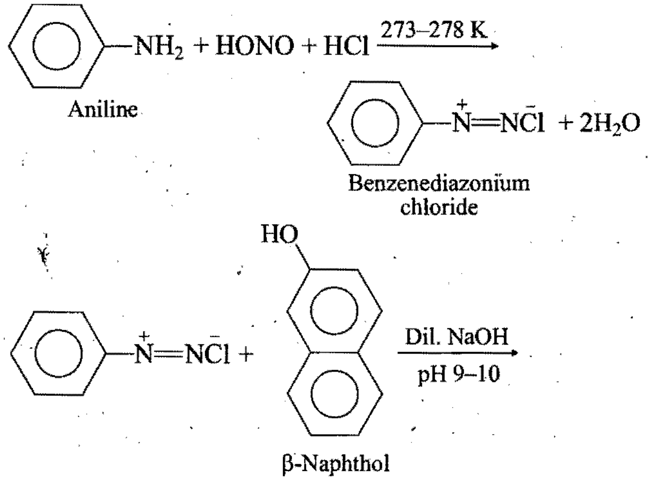
Uses : (i) Aniline is used in the manufacture of benzene diazonium chloride which is the starting material for many organic compounds especially azo dyes.

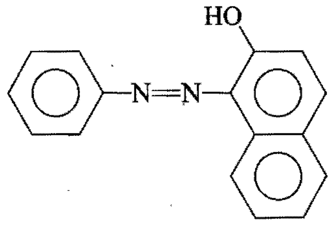
(ii) It is used for making Schiff bases which act as antioxidants in rubber industry.

(iii) Many useful derivatives such as acetanilide, sulphanilic acid and sulpha drugs are obtained from aniline.

Tests : (i) It gives carbylamine test.

(ii) **Dye test :** Aniline is first diazotised with $NaNO_2 + HCl$ at 273–278 K. On adding alkaline solution of β-naphthol to the diazotised product, a scarlet red dye is formed.





1-Phenylazo-2-naphthol
(Orange dye)

(iii) On adding bromine water to aniline, a pale pinkish precipitate is formed.

(iv) When bleaching powder is added to aqueous solution of aniline, a purple colour is produced which fades on standing.

(v) To a solution of aniline in sulphuric acid add a small amount of potassium dichromate solution. A red colour which slowly changes to deep blue is obtained.

[B] Benzylamine, $C_6H_5CH_2NH_2$ (Phenylmethanamine)

Methods of Preparation

Benzylamine is best regarded as phenyl substituted methylamine and may be prepared :

1. By reduction of benzonitrile or benzaldoxime or benzamide.

$$\underset{\text{Benzonitrile}}{C_6H_5CN} + 4[H] \xrightarrow[\text{or } LiAlH_4/\text{ether}]{Na/C_2H_5OH} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2}$$

$$\underset{\text{Benzaldoxime}}{C_6H_5CH{=}NOH} + 4[H] \xrightarrow[\text{or } LiAlH_4/\text{ether}]{Na/C_2H_5OH} C_6H_5CH_2NH_2$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + 4[H] \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4/\text{ether}} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} + H_2O$$

2. By the action of bromine and caustic potash on phenylacetamide (Hofmann degradation).

$$\underset{\text{Phenyl acetamide}}{C_6H_5CH_2CONH_2} + Br_2 + 4KOH \xrightarrow{\Delta} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

3. By heating benzylchloride with alcoholic ammonia under pressure.

$$C_6H_5CH_2Cl + 2NH_3 \xrightarrow{\Delta} C_6H_5CH_2NH_2 + NH_4Cl$$

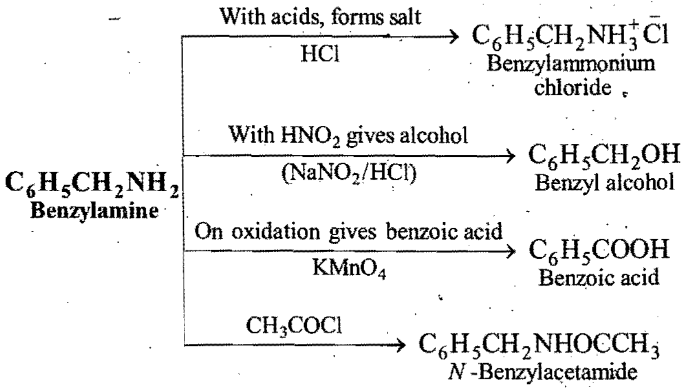
4. By action of hydrazoic acid on phenylacetic acid in presence of conc. H_2SO_4 at 50–55° C.

$$C_6H_5CH_2COOH + N_3H \xrightarrow[50\text{–}55°C]{\text{Conc. } H_2SO_4} C_6H_5CH_2NH_2 + N_2 + CO_2$$

5. By reductive amination of benzaldehyde.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow[-H_2O]{NH_3} \underset{\text{Unstable}}{[C_6H_5CH{=}NH]} \xrightarrow{H_2/Ni} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2}$$

Properties : It is a colourless liquid, boiling point 185°C. It has an ammoniacal odour and is a stronger base than isomeric toluidines but weaker than methylamine. It is soluble in water. It gives the following reactions, and closely resembles aliphatic amines in chemical behaviour:



$$\underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \xrightarrow[HCl]{\text{With acids, forms salt}} \underset{\text{Benzylammonium chloride}}{C_6H_5CH_2\overset{+}{N}H_3\overset{-}{Cl}}$$

$$\xrightarrow[(NaNO_2/HCl)]{\text{With } HNO_2 \text{ gives alcohol}} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

$$\xrightarrow[KMnO_4]{\text{On oxidation gives benzoic acid}} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

$$\xrightarrow{CH_3COCl} \underset{N\text{-Benzylacetamide}}{C_6H_5CH_2NHOCCH_3}$$

Problem 21. *How will you differentiate between:*

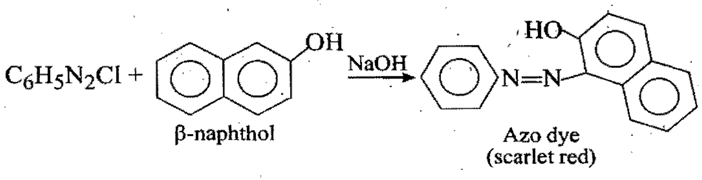
(*a*) *aniline and ethylamine (aromatic and aliphatic amines)?*

(*b*) *aniline and benzylamine?*

(*c*) *aniline* (1°), *methylaniline* (2°), *and dimethylaniline* (3°)?

Solution : (a) Aniline reacts with nitrous acid from $NaNO_2/HCl$ at 0–5°C to form a diazonium salt which gives a scarlet azo dye with β-naphthol in NaOH.

$$C_6H_5NH_2 \xrightarrow[0\text{–}5°C]{HONO/HCl} \underset{\text{Benzene diazonium chloride}}{C_6H_5\overset{+}{N}_2\overset{-}{Cl}}$$



Ethylamine reacts with nitrous acid to produce ethyl alcohol and nitrogen gas (seen as bubbles).

$$C_2H_5NH_2 + ONOH \longrightarrow C_2H_5OH + N_2 + H_2O$$

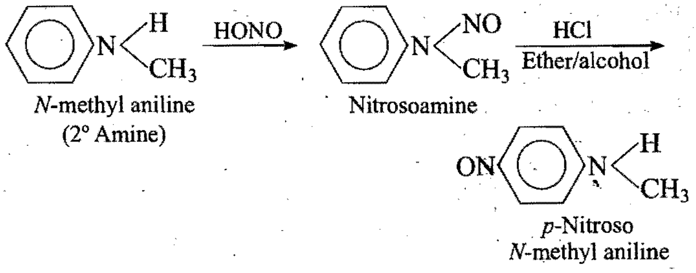
(b) Aniline gives dye test [see (a) part]

Benzylamine reacts with nitrous acid to form benzyl alcohol and nitrogen gas (seen as bubbles).

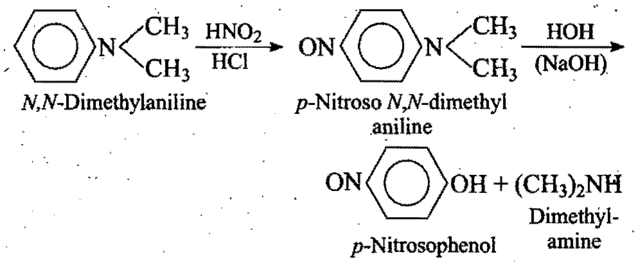
$$C_6H_5CH_2NH_2 + ONOH \longrightarrow C_6H_5CH_2OH + N_2 + H_2O$$

(c) Aniline (1° Amine) reacts with nitrous acid to form diazonium salt which gives dye test [see (a) part].

Methyl aniline (2° Amine) forms nitrosoamine (yellow oily liquid) on treatment with nitrous acid, which is stable at room temperature. However, on reaction with HCl in ether and alcohol, the nitroso (—NO) group migrates to *para*–position.



Dimethyl aniline (3° Amine) forms *p*-nitroso derivative with nitrous acid which on hydrolysis gives *p*-nitrosophenol and dimethylamine (2°).



16.14 SOME IMPORTANT DERIVATIVES OF ANILINE

1. Acetanilide (Antifeberin), *N*-Phenylacetamide $C_6H_5NHCOCH_3$

Acetanilide is formed by acetylation of aniline either by boiling with glacial acetic acid (in presence of $ZnCl_2$) or by action of acetyl chloride or acetic anhydride.

$$C_6H_5NH_2 + CH_3COOH \xrightarrow{ZnCl_2} C_6H_5NHCOCH_3 + H_2O$$

$$C_6H_5NH_2 + CH_3COCl \longrightarrow C_6H_5NHCOCH_3 + HCl$$

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$$

Properties : It is a colourless, crystalline substance having melting point 114°C. It is sparingly soluble in cold water but more soluble in hot water. It is hydrolysed again into aniline with strong acids or alkalies.

$$C_6H_5NHCOCH_3 + H_2O \longrightarrow C_6H_5NH_2 + CH_3COOH$$

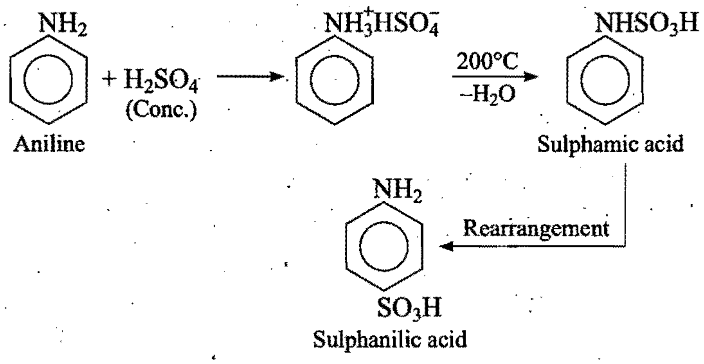
Anilide is an *ortho* and *para* directing group. Acetanilide is a useful intermediate product in various reactions of aniline, *e.g.*, nitration, *i.e.*, whenever, it is necessary to protect the amino group.

[See properties of aniline (Reaction of benzene nucleus) on page 980.]

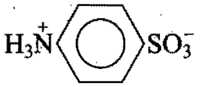
Acetanilide has been used in medicine as antifeberin (or febrifuge) for lowering body temperature (antipyretic) and to relieve headache. On account of its toxic nature, its use as a drug is not finding favour and is replaced by more effective and less toxic drugs.

2. Sulphanilic Acid (*p*-Aminobenzene sulphonic acid), *p*-$NH_2C_6H_4SO_3H$

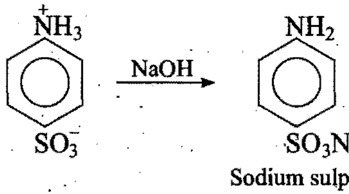
It is formed when aniline is heated with conc. H_2SO_4 at about 200°C. Anilinium hydrogen sulphate is first formed which changes to sulphamic acid by losing a molecule of water on continuous heating. Finally, there is rearrangement to form stable sulphanilic acid (*p*-isomer).



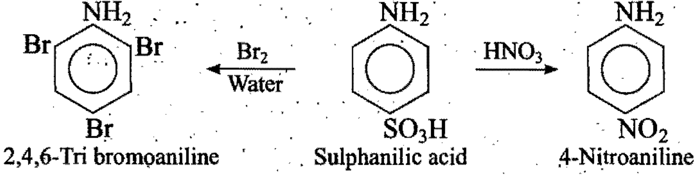
Properties : It is a white solid which decomposes at 288°C. It is sparingly soluble in cold water but soluble in hot water. It is also insoluble in organic solvents. It possesses **Zwitter ion** structure due to internal salt formation or dipolar ion.


(Zwitter ion)

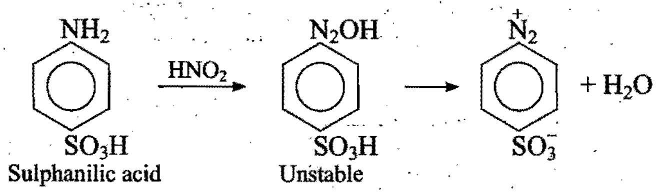
It is a strong acid and dissolves in alkalies to form salts.



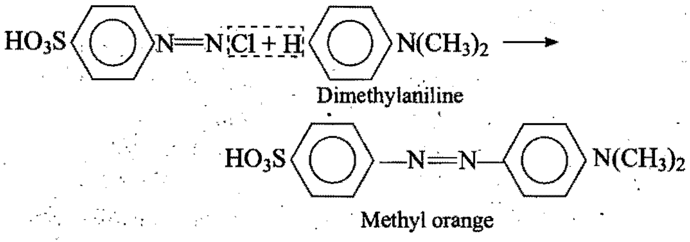
When treated with HNO_3 (conc.), sulphonic group is replaced by a nitro group. Similarly on bromination, the sulphonic group is eliminated and 2,4,6-tribromoaniline is formed.



It can be diazotised.



The diazotised sulphanilic acid gives coupling reaction with dimethylaniline and forms methyl orange.



Uses : It is used for making azo dyes, sulphanilamide drugs, sulphapyridine and sulphathiazole, etc., which are widely used against bacterial infections.

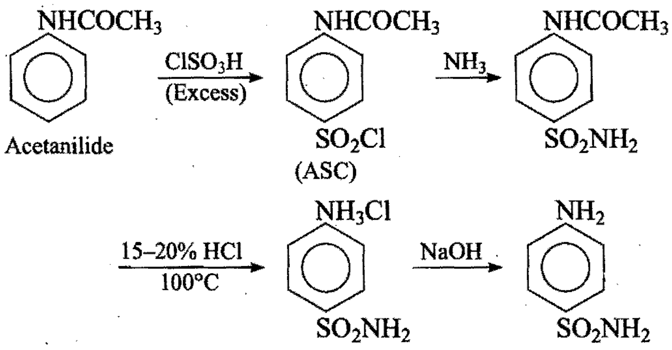
3. Sulphanilamide (*p*-Aminobenzene sulphonamide),

The preparation is done in three steps:

(i) First step : Acetanilide is treated with chloro sulphonic acid (excess).

(ii) Second step : The acetanilide sulphonyl chloride (ASC) so formed is reacted with ammonia.

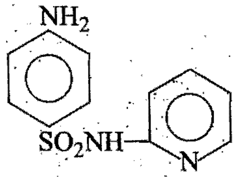
(iii) Third step : The product of the second step is hydrolysed with 15–20% HCl at 100°C.



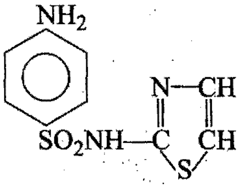
Sulphanilamide

Properties : It is a colourless crystalline compound, melting point 166°C. It is used in the manufacture of various sulpha drugs used in curing diseases like pneumonia, gonorrhoea, dysentry and bacterial infection. The important sulpha drugs are:

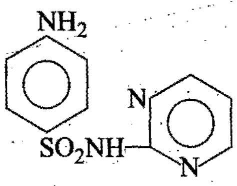
Sulphapyridine



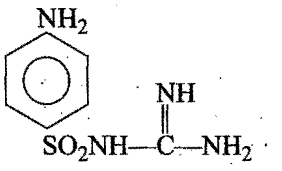
Sulphathiazole



Sulphadiazine

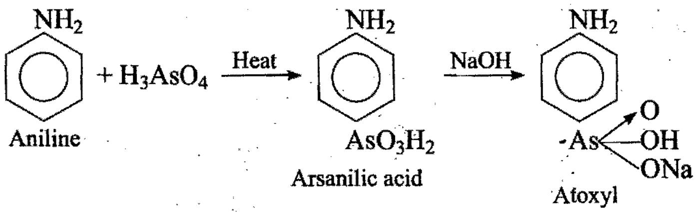


Sulphaguanidine



4. Atoxyl (Sodium salt of Arsanilic acid)

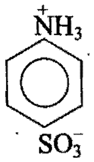
It is formed by heating aniline with arsenic acid.



Arsanilic acid forms mono sodium salt known as atoxyl with NaOH. Atoxyl is used as medicine for treating African sleeping sickness.

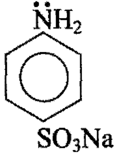
Problem 22. *Sulphanilic acid cannot be readily acetylated with* $(CH_3CO)_2O$ *but its sodium salt can be readily acetylated. Explain.*

Solution : Sulphanilic acid exists as a Zwitter ion.



For acetylation, nitrogen atom should have a lone pair of electrons to donate to the carbon atom of a CO group in acetic anhydride. The Zwitter ion's nitrogen does not have lone pair of electrons and thus, it is not possible to acetylate free sulphanilic acid.

However, the sodium salt has a lone pair available on nitrogen atom and so it is readily acetylated.



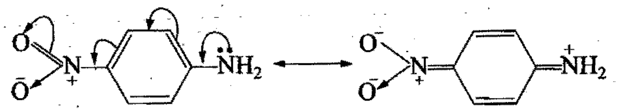
Problem 23. (*a*) *Why p-nitroaniline is less basic than aniline?*

(*b*) *Aniline dissolves in* HCl.

(*c*) *Aniline undergoes bromination in ortho and para position but in presence of strong acid it gives m-bromo aniline.*

(*d*) *Why aniline does not undergo Friedel-Crafts reaction?*

Solution : (a) Aniline is less basic because the lone pair of electrons on nitrogen is less available for donation to proton as it is delocalised into the benzene ring by resonance. The nitro group is electron-withdrawing group. It decreases basicity by further drawing electrons into the benzene ring.

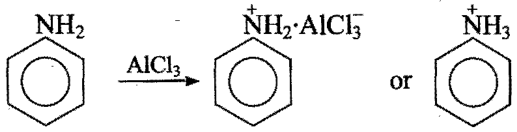


(b) Aniline, being basic in nature, forms salt with HCl which dissolves.

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5\overset{+}{N}H_3Cl^-$$

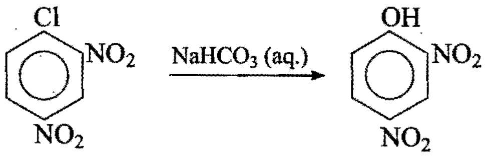
(c) $—NH_2$ group is *o*- and *p*-directing. However, in presence of strong acid aniline combines with proton to form $C_6H_5\overset{+}{N}H_3$ and $—\overset{+}{N}H_3$ group is *m*-directing. Thus, *m*-bromo product is formed in presence of strong acid.

(d) In presence of Lewis acid ($AlCl_3$), the group becomes electron withdrawing (deactivating group).



Problem 24. *In the preparation of* 2,4-*dinitrochlorobenzene from chlorobenzene by nitration, the reaction product should not be washed with aqueous solution of* $NaHCO_3$ *to remove the unused acid. Explain.*

Solution : 2,4-Dinitrochlorobenzene shows nucleophilic substitution reaction, *i.e.*, —Cl can be replaced by —OH group in presence of $NaHCO_3$ which makes the solution alkaline.

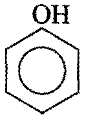


16.15 AROMATIC HYDROXY COMPOUNDS

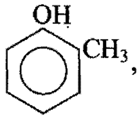
Aromatic hydroxy compounds are of two types :

1. Phenols : Phenols are compounds in which the hydroxy group, —OH, is directly linked with the aromatic ring. They can be mono, di or tri hydric phenols depending upon whether they contain one, two or three hydroxyl groups on the benzene ring. Methyl phenols are called **cresols** or they are hydroxy derivatives of toluene.

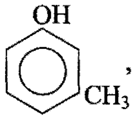
Monohydric phenols : Examples are phenol and cresols.



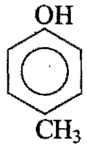
Phenol or Hydroxybenzene (Benzenol)



2-Methylphenol (*o*-cresol)

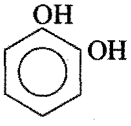


3-Methylphenol (*m*-cresol)

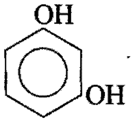


4-Methylphenol (*p*-cresol)

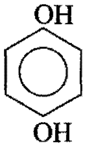
Dihydric phenols : Examples are **dihydroxy benzenes** (1,2 and 1,3 and 1,4).



Benzene-1,2-diol or Catechol

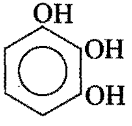


Benzene-1,3-diol or Resorcinol

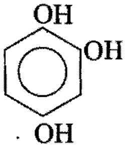


Benzene-1,4-diol or Quinol (Hydroquinone)

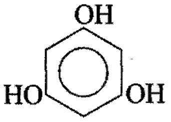
Trihydric phenols : Examples are **trihydroxy benzenes** (1, 2, 3 and 1, 2, 4 and 1, 3, 5).



Benzene-1,2,3-triol or Pyrogallol



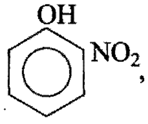
Benzene-1,2,4-triol or Hydroxyquinol



Benzene-1,3,5-triol or Phloroglucinol

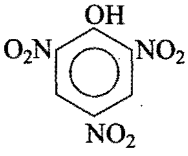
Further they can be substituted **phenols.** Examples are:

p-Chlorophenol



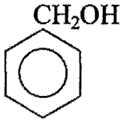
o-Nitrophenol

p-Nitroso phenol

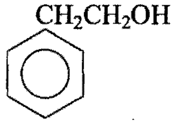


Picric acid

2. Aromatic alcohols : Compounds, in which the hydroxy group is present in the side-chain are termed aromatic alcohols. Examples are:



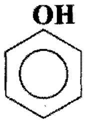
Benzyl alcohol (C_7H_8O)



2-Phenylethanol

Phenols are distinctly acidic while alcohols are neutral. Phenols have a characteristic odour and toxic in nature. They possess strong intermolecular hydrogen bonding and hence, the boiling points of phenols are higher than aliphatic alcohols. The first member of the series is most important compound and is named phenol.

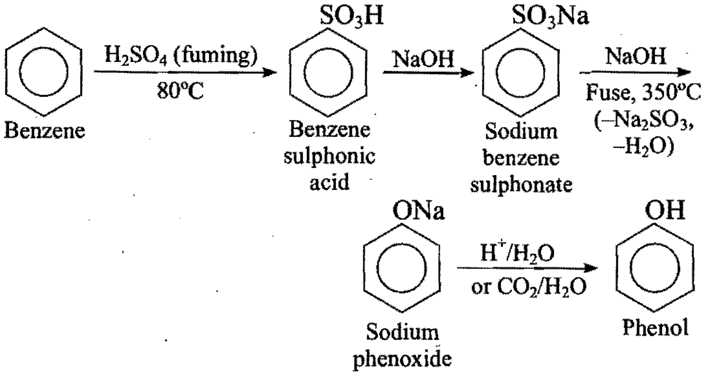
Phenol (Carbolic acid), C_6H_5OH or or Hydroxybenzene



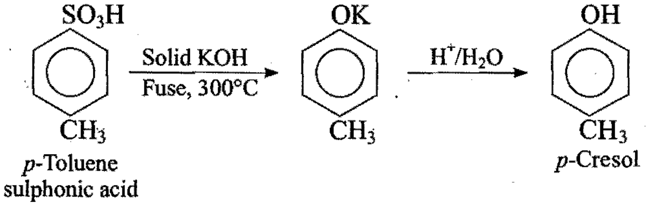
It was discovered by Runge in the middle oil fraction of coal tar distillation and named it 'carbolic acid' (carbo = coal, oleum = oil). Phenol containing 5% water is liquid at room temperature and is termed as carbolic acid. It is also present in traces in human urine.

Methods of Preparation of Phenols

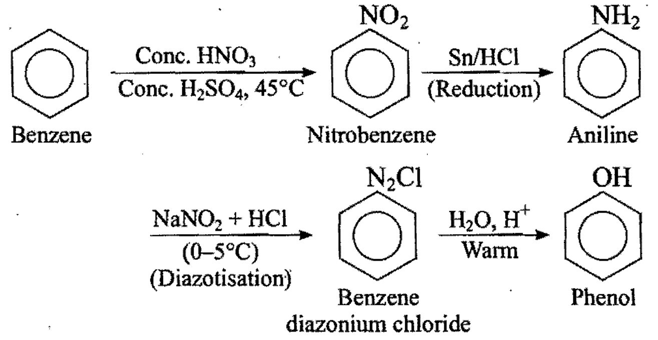
1. From benzene sulphonic acid (Alkali fusion of sulphonates) : Sodium salt of benzene sulphonic acid is fused with sodium hydroxide at 300 – 350°C, when sodium phenoxide is formed. Sodium phenoxide on treatment with dilute acid or carbon dioxide yields phenol. The start can be made with benzene.

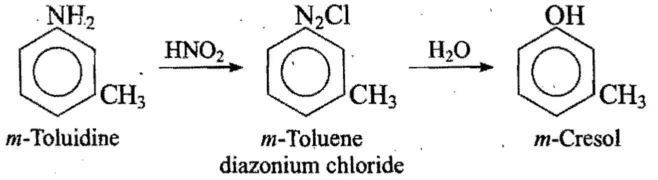


This is one of the **laboratory methods** for the preparation of phenol. Similarly methyl phenols (cresols) can be prepared.

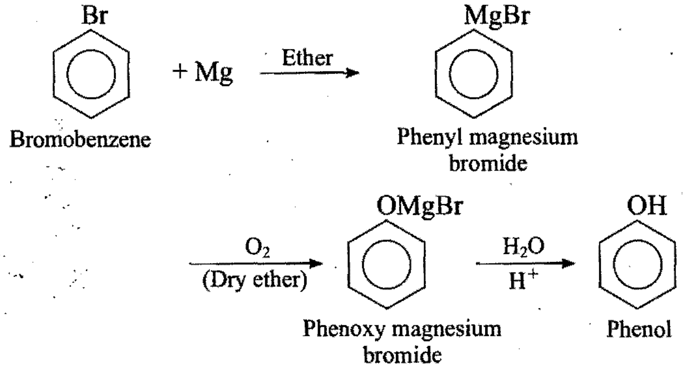


2. From benzene diazonium chloride (By hydrolysis) : When benzene diazonium chloride solution is warmed with water or dilute acids phenol is formed with evolution of nitrogen. The phenol from solution is recovered by steam distillation. In this case also, benzene can be taken as the starting material. This is also a laboratory method.

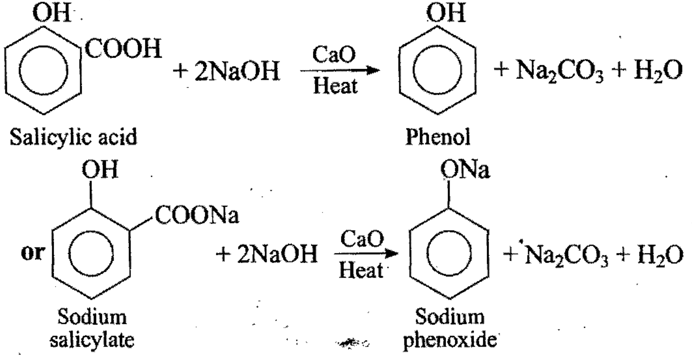


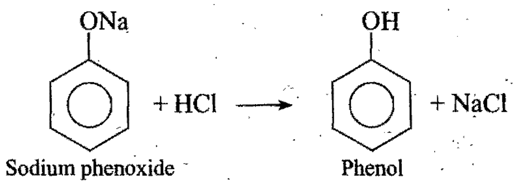


3. From Grignard reagents : Chlorobenzene or bromobenzene is first converted into phenyl magnesium halide in presence of dry ether. The Grignard reagents on reaction with oxygen and subsequent hydrolysis by a mineral acid, yield phenol.



4. From salicylic acid by decarboxylation : When salicylic acid or its sodium salt is distilled with soda lime, decarboxylation occurs and phenol is formed.





Manufacture or Industrial Preparation

1. From coal-tar : Phenol is commercially obtained from middle oil fraction (170–230°C). It consists of phenol, cresols and naphthalene. The fraction is cooled when naphthalene separates out. The remaining oil is treated with H_2SO_4 to remove basic impurities. Phenol is then extracted with dilute caustic soda. The aqueous layer is separated and phenol is obtained with sulphuric acid or carbon dioxide. The oily layer is separated and then fractionally distilled. The fraction collected between 181–182°C is the phenol.

2. Raschig's process : Chlorobenzene is formed by the interaction of benzene, hydrogen chloride and air at 250°C in presence of catalyst cupric chloride and ferric chloride. It is hydrolysed by superheated steam at 425°C to form phenol and HCl. This is one of the latest methods for the synthesis of phenol. HCl may be again used to convert more of benzene into chlorobenzene.

$$\underset{\text{Benzene}}{C_6H_6} + HCl + \tfrac{1}{2}O_2 \xrightarrow[250°C]{CuCl_2/FeCl_3} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + H_2O$$

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + \underset{\text{Steam}}{H_2O} \xrightarrow{425°C} \underset{\text{Phenol}}{C_6H_5OH} + HCl$$

3. Dow process : This process involves alkaline hydrolysis of chlorobenzene. Large quantities of phenol are formed by heating chlorobenzene with a 10% solution of caustic soda or sodium carbonate at 300°C under a very high pressure (200 atm).

$$\underset{\substack{\text{Chloro-}\\\text{benzene}}}{C_6H_5Cl} + 2NaOH \xrightarrow[\text{High pressure}]{300°C} \underset{\substack{\text{Sodium}\\\text{phenoxide}}}{C_6H_5ONa} + NaCl + H_2O$$

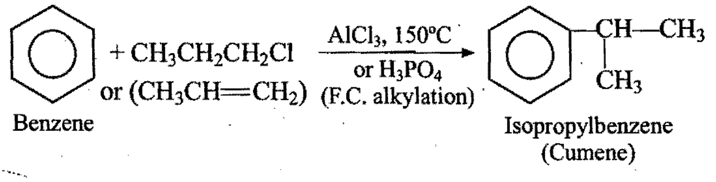
Sodium phenoxide on treatment with mineral acid yields phenol.

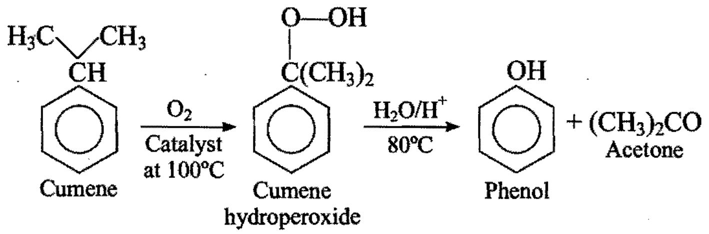
$$2C_6H_5ONa + H_2SO_4 \longrightarrow 2\underset{\text{Phenol}}{C_6H_5OH} + Na_2SO_4$$

4. Oxidation of benzene : This is the latest method for the manufacture of phenol. The mixture of benzene and air is passed over vanadium pentoxide at 315°C. Benzene is directly oxidised to phenol.

$$2\underset{\text{Benzene}}{C_6H_6} + O_2 \xrightarrow[315°C]{V_2O_5} 2C_6H_5OH$$

5. Oxidation of isopropyl benzene (Cumene) : Cumene is oxidised with oxygen or air into cumene hydroperoxide in presence of a catalyst. This is decomposed by dilute sulphuric acid into phenol and acetone.





Physical Properties

(i) Phenol is a colourless crystalline, deliquescent solid. It attains pink colour on exposure to air and light.

(ii) Its melting point is 42°C and boiling point 182°C. The boiling point of phenol is much higher than the corresponding aromatic hydrocarbons and the haloarenes.

(iii) It has a peculiar characteristic smell and a strong corrosive action on skin.

(iv) It is soluble in water due to the formation of **inter-molecular H-bonding** among themselves and with water.

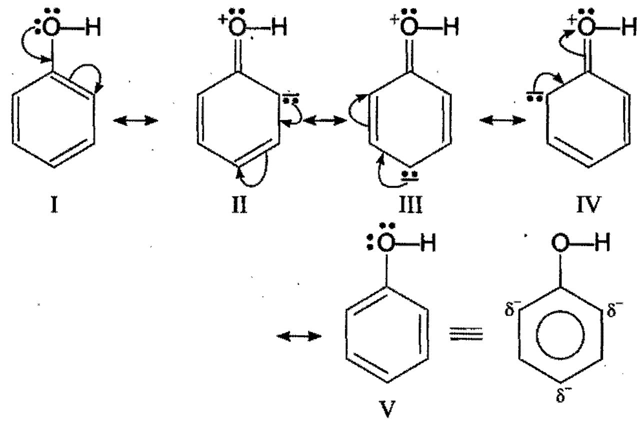
(v) It is poisonous in nature but acts as antiseptic and disinfectant.

Chemical Properties

1. Acidic nature : Phenol is a weak acid* . The acidic nature of phenol is due to the formation of stable phenoxide ion in solution (cleavage of C—O—H bond).

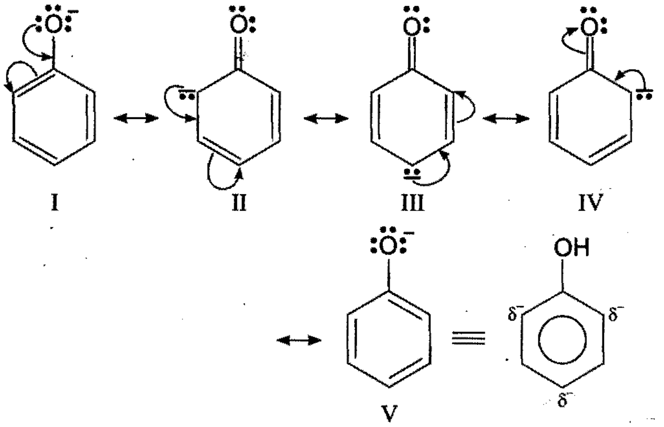
$$C_6H_5OH + H_2O \rightleftharpoons \underset{\text{Phenoxide ion}}{C_6H_5O^-} + H_3O^+$$

The various resonating (contributing) structures of **phenol** and **phenoxide ion** are as follows:



Resonating structures of phenol

As a result of resonance, it weakens the polar O—H bond and thus facilitates the release of proton (H^+) to give phenoxide ion which is more stabilized than phenol.



Resonating structures of phenoxide ion

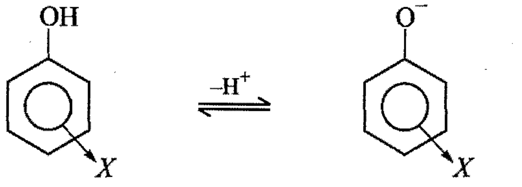
The negative charge is spread throughout the benzene ring in resonating structures of phenoxide ion (I to V) whereas the resonating structures of phenol (II, III and IV) involve separation of positive and negative charges. This charge delocalization is a stabilizing factor in the phenoxide ion and increase acidity of phenol. [No resonance is possible in alkoxide ions (RO^-) derived from alcohols. The negative charge is localized on oxygen atom. Thus, alcohols are not acidic.]

$$\underset{\substack{\text{Alcohol}\\ \text{(More stable)}}}{R{-}\ddot{\underset{..}{O}}{-}H} \rightleftharpoons \underset{\substack{\text{Alkoxide ion}\\ \text{(Less stable)}}}{R{-}\ddot{\underset{..}{O}}\!:^-} + H^+$$

Effects of Substituents on the Acidity of Phenols

The presence of electron attracting or withdrawing groups **(EWG)** (*e.g.*, X = —NO_2, —X (halogens), —CHO, —COOH, —CN, etc.), on the benzene ring and electron releasing or donating groups **(EDG)**, (*e.g.*, Y = R—, —NH_2, —NR_2, —OR, etc.) also affects the acidic strength. In general:

(i) Electron withdrawing groups, EWG (*X*) stabilize the phenoxide ion more by dispersing the negative charge relative to phenol (*i.e.*, proton release becomes easy) and thus increase the acidic strength of phenols.



Acid strength is more X stabilizes the anion

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* Phenols are much more acidic than alcohols but less than carboxylic acids or even carbonic acid. This is indicated by the values of ionisation constants (K_a). The relative acidity follows the following order:

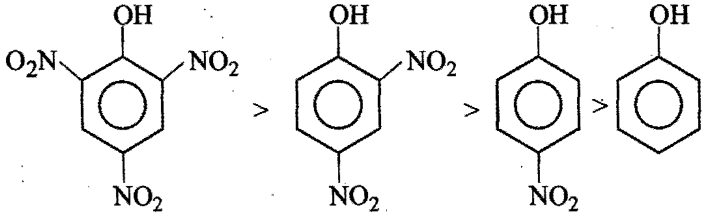
K_a (approx.)	(10^{-5})	>	(10^{-7})	>	(10^{-10})	>	(10^{-14})	>	(10^{-18})
	$RCOOH$ Carboxylic acid		H_2CO_3 Carbonic acid		C_6H_5OH Phenol		HOH Water		ROH Alcohols
pK_a value	5	<	7	<	8–10	<	14	<	16–18

Further, the particular effect is more when the substituent is present on *o*- and *p*- positions than in *m*-position to the phenolic group. Thus, acidic strength of nitrophenols decreases in the order:

p-Nitro phenol > *o*-Nitro phenol > *m*-Nitro phenol > Phenol

p*K*$_a$: 7.15 < 7.23 < 8.40 < 9.98

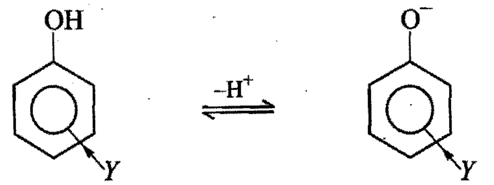
Further, greater the number of electron withdrawing groups at *o*- and *p*-positions, more acidic is the phenol, *e.g.*,



2,4,6-Trinitrophenol 2,4-Dinitrophenol 4-Nitrophenol Phenol

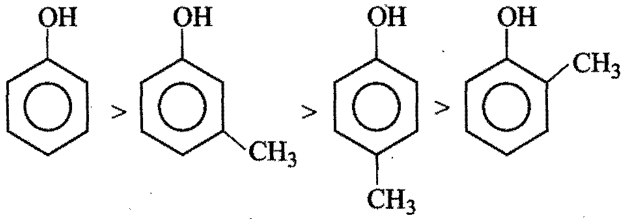
p*K*$_a$: 0.71 < 4.0 < 7.15 < 9.98

(ii) Electron releasing groups, EDG (*Y*) destabilize the phenoxide ion by donating electrons and intensify the negative charge relative to phenol (*i.e.*, proton release becomes difficult) and thus decreases the acidic strength of phenol.



Acid strength is less *Y* destabilizes the anion

The effect is more when the substituent is present on *o*- and *p*-positions than in *m*-position with respect to the —OH group. Thus, cresols (methyl phenols) are less acidic than phenol.



Phenol *m*-Cresol *p*-Cresol *o*-Cresol

p*K*$_a$: 9.98 10.08 10.14 10.28

However, *m*-methoxy and *m*-amino phenols are stronger acidic than phenol because of $-I$ effect (of $—OCH_3$ and $—NH_2$ groups) and absence of $+R$ effect, *i.e.*,

m-Methoxy phenol > *m*-Amino phenol > Phenol

p*K*$_a$: 9.65 9.87 9.98

> *o*-Methoxy phenol > *p*-Methoxy phenol

10.00 10.21

Greater the value of K_a or lower the value of pK_a, stronger will be the acid. Some other examples of acidic nature of phenols are:

Chloro phenols — *o*- > *m*- > *p*-
Cresols — *m*- > *p*- > *o*-
Dihydric phenols — *m*- > *p*- > *o*-

The acidic nature of phenol is observed in the following:

(i) Phenol changes blue litmus to red.

(ii) Highly electropositive metals react with phenol.

$$2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$$

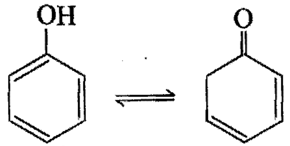
(iii) Phenol reacts with strong alkalies to form phenoxides.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

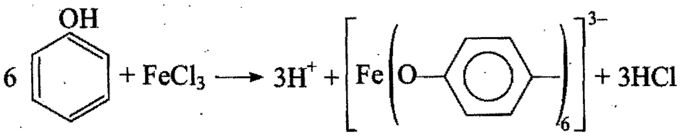
However, phenol does not decompose sodium carbonate or sodium bicarbonate, *i.e.*, CO_2 is not evolved because phenol is weaker than carbonic acid.

2. Reactions of —OH group :

(i) Reaction with FeCl$_3$: Phenol gives violet colouration with ferric chloride solution (neutral) due to the formation of a coloured iron complex, which is a characteristic to the existence of keto-enol tautomerism in phenols (predominantly enolic form).



Enol Keto



(Violet complex)

This is the **test of phenol.** In general, all compounds containing enolic group ($\mathrm{C{=}\overset{|}{C}{—}OH}$) give different colours with neutral $FeCl_3$. However, the colour of complexes may vary from violet to blue, green or red, etc., depending upon the nature of phenol.

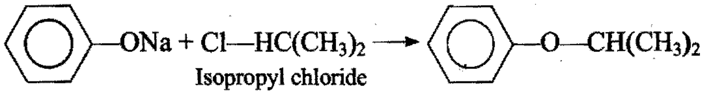
(ii) Ether formation : Phenol reacts with alkyl halides or dialkyl sulphate in alkali solution to form phenyl ethers (Williamson's synthesis). The phenoxide ion is a nucleophile and will replace halogenation of alkyl halide.

$$\underset{\text{Phenol}}{C_6H_5OH} + NaOH \longrightarrow \underset{\text{Sod. phenoxide}}{C_6H_5ONa} + H_2O$$

$$\underset{\text{Sod. phenoxide}}{C_6H_5ONa} + \underset{\substack{\text{Methyl}\\\text{chloride}}}{ClCH_3} \xrightarrow{\text{Heat}} \underset{\substack{\text{Methylphenyl}\\\text{ether (Anisole)}}}{C_6H_5OCH_3} + NaCl$$

$$\underset{\text{Pot. phenoxide}}{C_6H_5OK} + \underset{\substack{\text{Ethyl}\\\text{iodide}}}{IC_2H_5} \xrightarrow{\text{Heat}} \underset{\substack{\text{Ethoxybenzene}\\\text{(Phenetole)}}}{C_6H_5—O—C_2H_5} + KI$$

$$\underset{\text{Phenol}}{2C_6H_5OH} + \underset{\substack{\text{Diethyl}\\\text{sulphate}}}{(C_2H_5)_2SO_4} \xrightarrow[\Delta]{\text{2NaOH(aq.)}} \underset{\text{Phenetole}}{2C_6H_5OC_2H_5} + Na_2SO_4 + 2H_2O$$



Isopropyl chloride Isopropyl phenyl ether

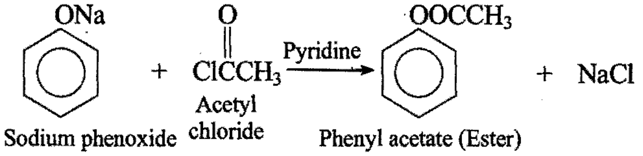
Ethers are also formed when vapours of phenol and an alcohol are heated over thoria (ThO_2) or Al_2O_3.

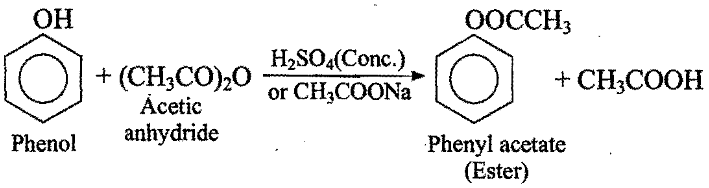
$$\underset{\text{Methanol}}{C_6H_5OH + HOCH_3} \xrightarrow{\Delta,\, ThO_2} \underset{\text{Methoxy benzene}}{C_6H_5—O—CH_3}$$

(iii) Ester formation (Reaction with acid chlorides and anhydrides) : Phenol reacts with acid chlorides (in presence of a base catalyst, pyridine) or with acid anhydrides (in presence of either acids, conc. H_2SO_4 or base pyridine or sodium acetate, etc.) to form phenyl esters in excellent yield.

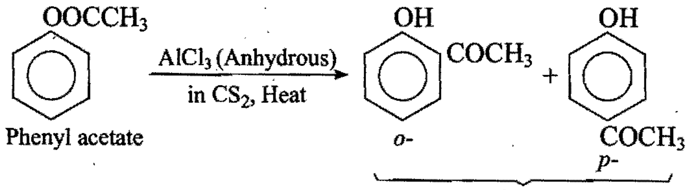
$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

(a) Acylation :

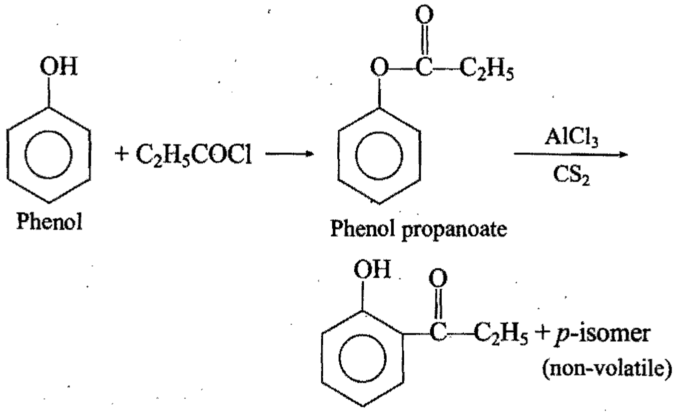




The phenyl esters on treatment with anhydrous $AlCl_3$ in presence of CS_2 as solvent undergo **Fries rearrangement** in which acyl (acetyl or benzoyl, etc.) group migrates from the phenolic oxygen atom to the *o*- and *p*-positions of the benzene ring to give *o*- and *p*- hydroxy ketones.

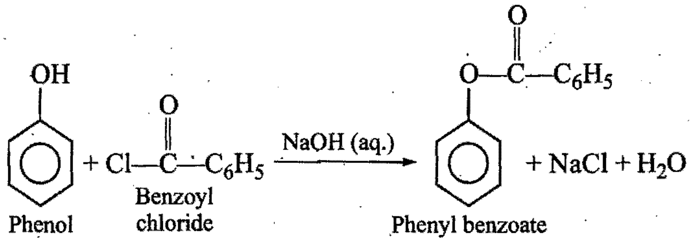


Hydroxy acetophenone

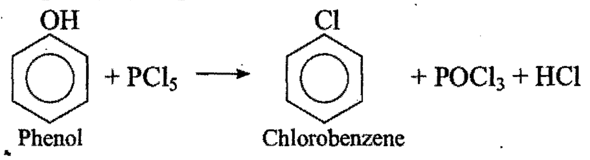


Ethyl *ortho* hydroxy phenyl ketone (Steam volatile)

(b) Benzoylation : Phenol reacts with benzoyl chloride in presence of aqueous NaOH to form phenyl benzoate (an ester). This reaction is called **Schotten-Baumann reaction.**

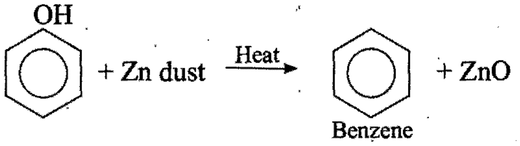


(iv) Reaction with PCl_5 : Phenol reacts with PCl_5 to form chlorobenzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.

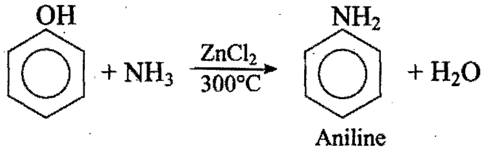


$$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$$

(v) Reaction with zinc dust : When phenol is distilled with zinc dust, benzene is obtained.



(vi) Reaction with ammonia : Phenol reacts with ammonia in presence of anhydrous zinc chloride at 300°C or $(NH_4)_2SO_3—NH_3$ at 150°C to form aniline. This conversion of phenol into aniline is called **Bucherer reaction.**

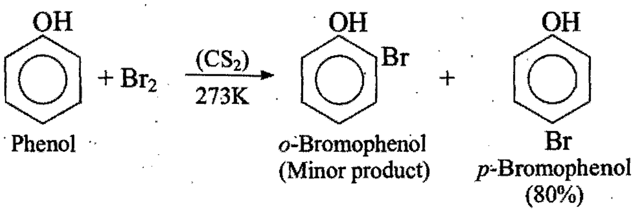


(vii) Action of P_2S_5 : By heating phenol with phosphorus penta sulphide, thiophenols are formed.

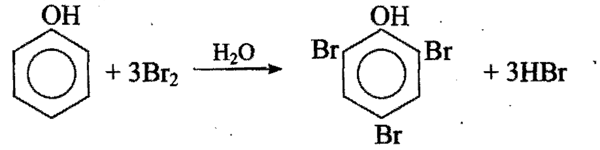
$$5C_6H_5OH + P_2S_5 \longrightarrow \underset{\text{Thiophenol}}{5C_6H_5SH} + P_2O_5$$

3. Reactions of benzene nucleus (Electrophilic aromatic substitution) : The —OH group is *ortho* and *para*-directing. It activates the benzene nucleus towards electrophilic substitution reactions at *o*- and *p*-positions.

(i) Halogenation : Phenol reacts with bromine in carbon disulphide (or $CHCl_3$) at low temperature to form mixture of *ortho* and *para* bromophenols.

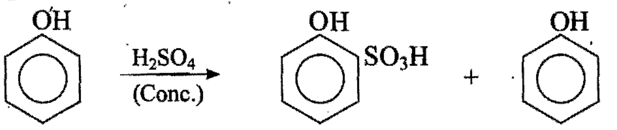


Phenol forms a white precipitate with excess of bromine water yielding 2,4,6-tribromophenol (white precipitates).



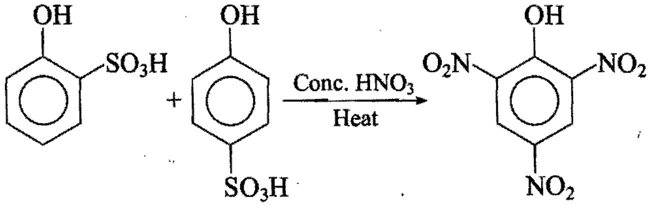
Phenol 2,4,6-Tribromophenol

(ii) Sulphonation : Phenol reacts with conc. H_2SO_4 readily to form mixture of *ortho* and *para* hydroxy benzene sulphonic acids.



Phenol *o*-Hydroxy benzene sulphonic acid *p*-Hydroxy benzene sulphonic acid

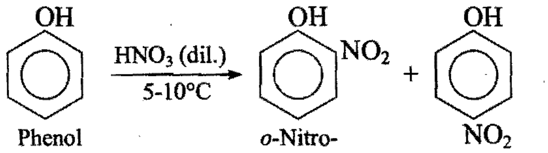
At low temperature (25°C), the *ortho*-isomer is the major product, whereas at 100°C, it gives mainly the *para*-isomer. This mixture on further heating with conc. HNO_3 forms picric acid.



Picric acid

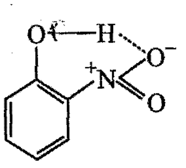
During this reaction nitration with simultaneous replacement of the sulphonic acid (—SO_3H) group by the nitro group also occurs.

(iii) Nitration : Phenol reacts with dilute nitric acid at 5–10°C to form *ortho*- and *para*-nitrophenols, but the yield is poor due to oxidation of phenolic group. The —OH group is activating group, hence, nitration is possible with dilute nitric acid.

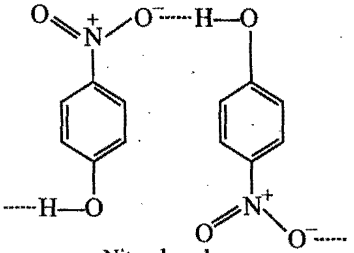


Phenol *o*-Nitrophenol (40%) *p*-Nitrophenol (15%)

The *o*- and *p*-isomers can be separated by steam distillation since *o*-isomer is much more volatile in steam due to *chelation* **(intramolecular H-bonding)** in it while *p*-isomer is not steam volatile due to association of molecules by **intermolecular H-bonding.**



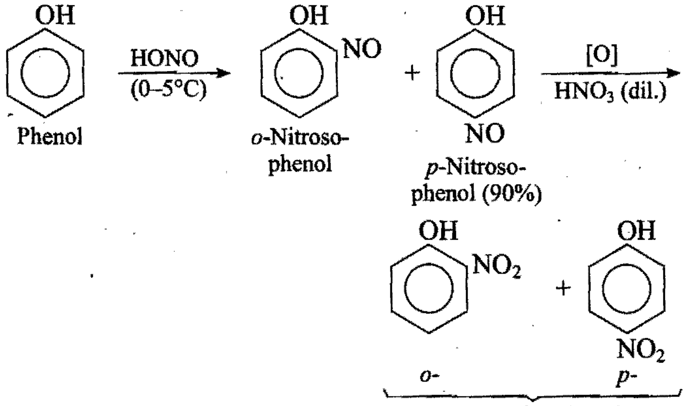
o-Nitrophenol (Intramolecular H-bonding)



p-Nitrophenol (Intermolecular H-bonding)

The *p*-isomers have very high boiling point because of intermolecular H-bonding while their solubility in water is due to H-bonding with water molecules.

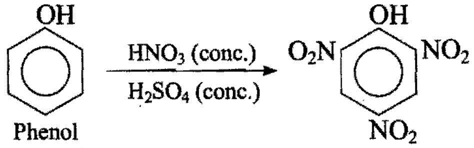
It is believed that the mechanism of the above reaction involves the formation of *o*- and *p*-nitrosophenols with nitrous acid, HNO_2 ($NaNO_2$ + HCl) at 0–5°C, which gets oxidised to *o*- and *p*-nitrophenols with dilute nitric acid.



Phenol *o*-Nitrosophenol *p*-Nitrosophenol (90%) Nitrophenol

Ortho and *para*-nitrophenols are more acidic than phenol.

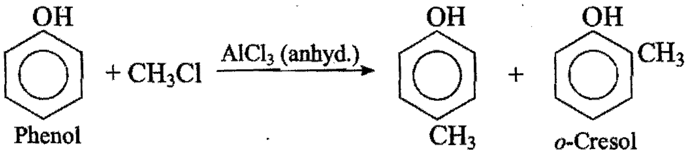
However, when phenol is treated with concentrated HNO_3 in presence of concentrated H_2SO_4, 2,4,6-trinitrophenol (picric acid) is formed.



Phenol 2,4,6-Trinitrophenol (Picric acid)

To get better yield (90%) of picric acid, first sulphonation of phenol is made and then nitrated. Presence of —SO_3H group prevents oxidation of phenol.

(iv) Friedel-Crafts reaction : Phenol when treated with methyl chloride in presence of anhydrous aluminium chloride, *p*-cresol (4-methyl phenol) is the main product. A very small amount of *o*-cresol is also formed.



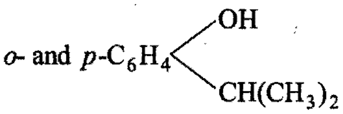
Phenol *p*-Cresol (Major product) *o*-Cresol (Minor)

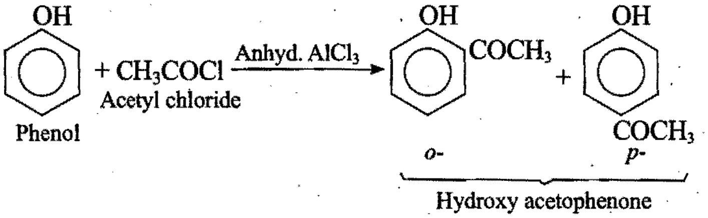
RX and $AlCl_3$ give poor yields because $AlCl_3$ coordinates with O. So, **Ring alkylation** also takes place as follows:

$$C_6H_5OH + AlCl_3 \longrightarrow C_6H_5OAlCl_2 + HCl$$

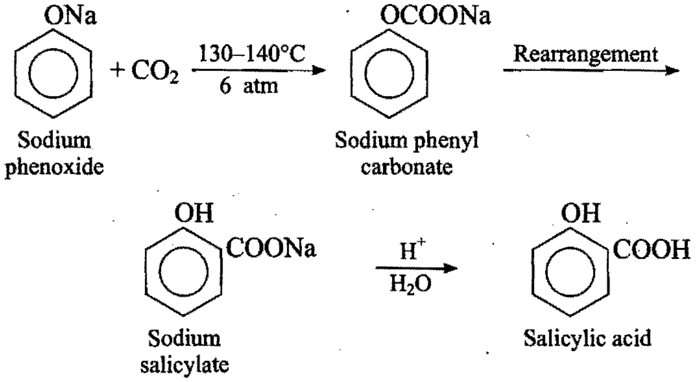
Thus, to carry out successful Friedel-Crafts reaction with phenol it is necessary to use a large amount of $AlCl_3$. The ring alkylation takes place as follows:

$$C_6H_5OH + \begin{cases} CH_3CH{=}CH_2 \\ (CH_3)_2CHOH \end{cases} \xrightarrow[\text{or HF}]{H_2SO_4}$$


o- and p-$C_6H_4\begin{cases}OH\\CH(CH_3)_2\end{cases}$

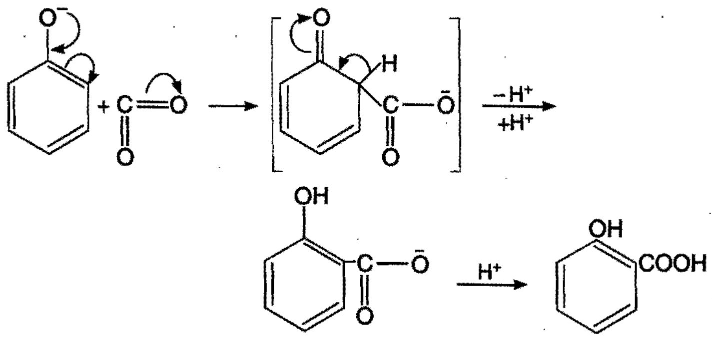


(v) Kolbe-Schmidt reaction or Kolbe's reaction This involves the interaction of sodium phenoxide with carbon dioxide at 130–140°C under pressure of (4–7) atmospheres followed by acid hydrolysis, salicylic acid (o-Hydroxy benzoic acid) is formed.



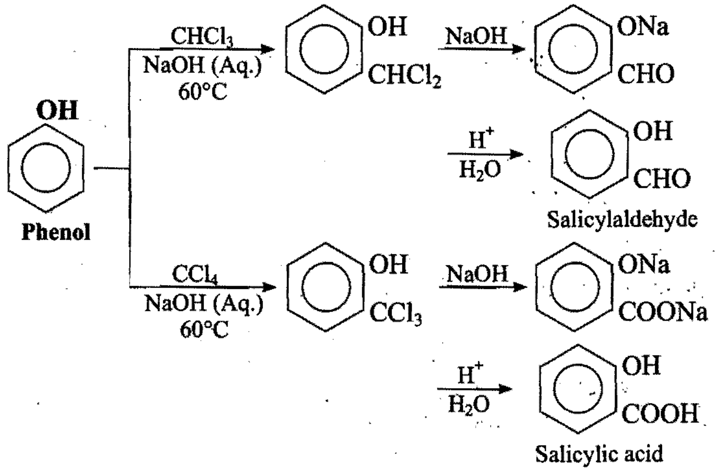
The probable **Mechanism** is :

$$C_6H_5OH \longrightarrow C_6H_5O^- + H^+$$



At higher temperature (250–300°C), p-isomer is obtained.

(vi) Reimer-Tiemann reaction : Phenol, on refluxing with chloroform and sodium hydroxide (aq.) at 60°C followed by acid hydrolysis yields salicylaldehyde (o-hydroxy benzaldehyde) and a very small amount of p-hydroxy benzaldehyde. However, when carbon tetrachloride is used, salicylic acid (predominating product) is formed. This reaction is called **Reimer-Tiemann reaction.**



Mechanism

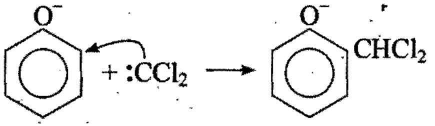
The electrophile is dichloromethylene $:CCl_2$ generated from chloroform by the action of a base.

$$\underset{\text{Chloroform}}{OH^- + CHCl_3} \rightleftharpoons HOH + :CCl_3 \longrightarrow Cl^- + \underset{\substack{\text{Dichlorocarbene}\\\text{(Electrophile)}}}{:CCl_2}$$

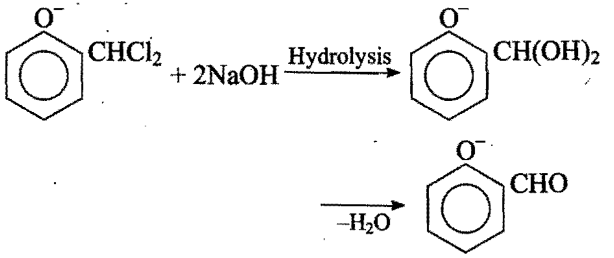
Reimer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxide ring.

(i) $\underset{\text{Phenol}}{C_6H_5OH} \longrightarrow \underset{\text{Phenoxide}}{C_6H_5O^-} + H^+$

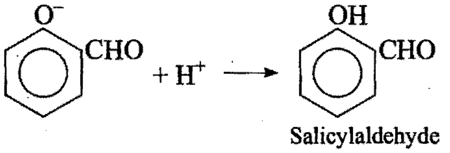
(ii) Attack of electrophile ($:CCl_2$) on phenoxide ion.



(iii)

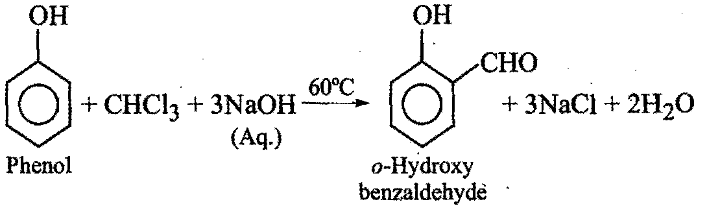


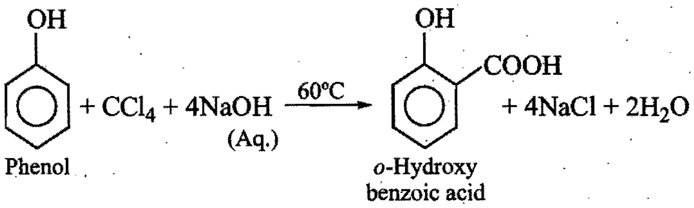
(iv)



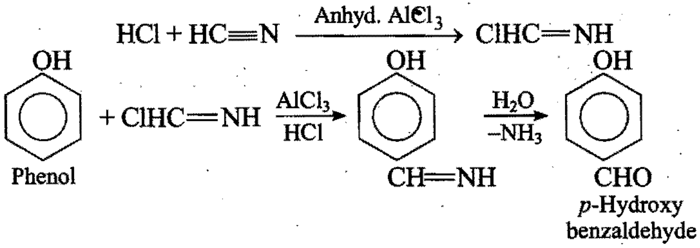
Salicylaldehyde

So,

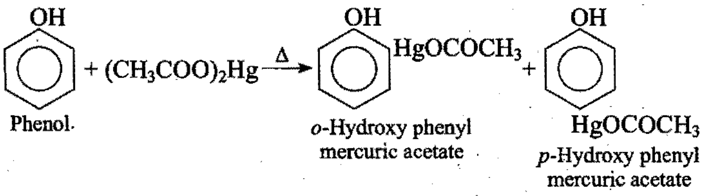




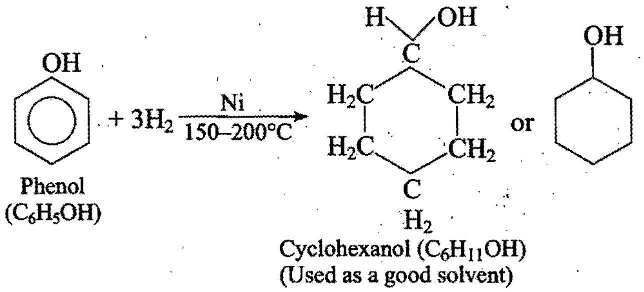
(vii) Gattermann's reaction : Phenol, when treated with liquid hydrogen cyanide and hydrochloric acid gas in presence of anhydrous aluminium chloride yields mainly *p*-hydroxy benzaldehyde **(Formylation).**



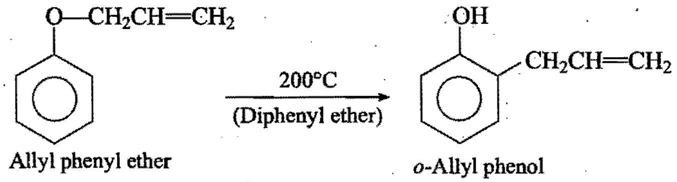
(viii) Mercuration : Phenol when heated with mercuric acetate undergoes mercuration to form *o*- and *p*-isomers.

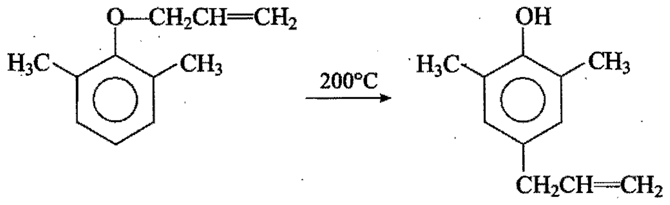


(ix) Hydrogenation : Phenol, when hydrogenated in presence of a nickel catalyst at about 150–200°C, forms cyclohexanol.

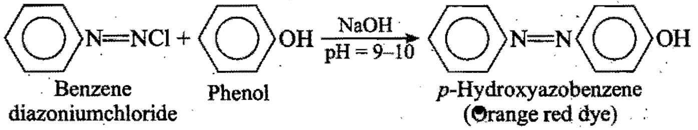


(x) Claisen rearrangement : This is the rearrangement of allyl aryl ethers to allyl phenols. No catalyst is required and it occurs when the substrate is heated alone to about 200°C or in some inert solvent like diphenyl ether. Allyl group migrates to *ortho*-position and if *ortho*-position is already occupied, *para*-isomer is obtained.

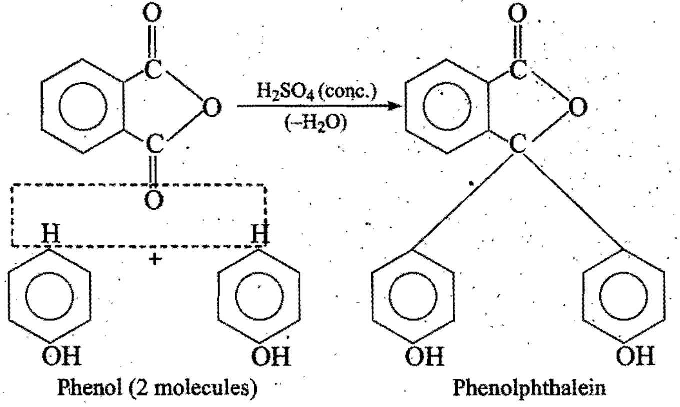




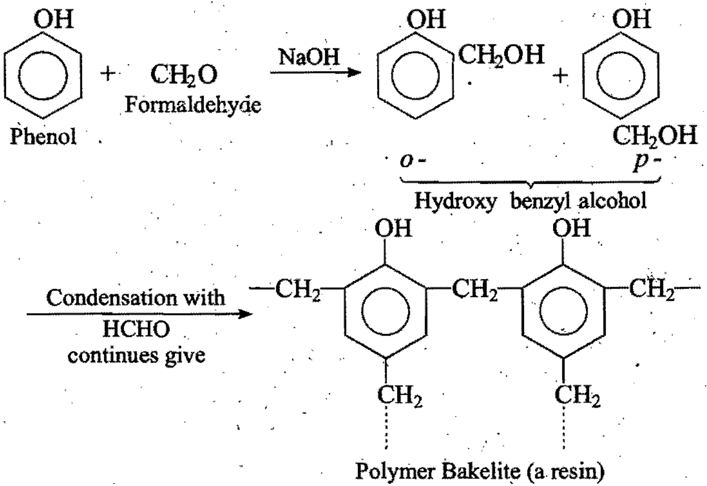
4. Miscellaneous reactions : (i) Coupling reactions : (a) Phenol couples with benzene diazonium chloride in presence of slightly alkaline medium at low temperature to form a red dye (*p*-hydroxy azobenzene).



(b) Phenol couples with phthalic anhydride in presence of concentrated H_2SO_4 to form a dye, (phenolphthalein) used as an indicator.



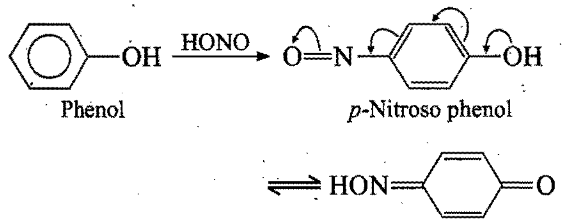
(ii) Condensation with formaldehyde : Phenol condenses with formaldehyde (excess) in presence of sodium hydroxide or acid (H^+) for about a week to form a cross-linked polymer known as **bakelite** which is used in the manufacture of electrical goods.



(iii) Liebermann's nitroso reaction : When phenol is reacted with $NaNO_2$ and concentrated H_2SO_4, it gives a deep green or blue colour which changes to red on dilution with water. When made alkaline with NaOH original green or blue colour is restored. This reaction is known as Liebermann's nitroso reaction and is used as a **test of phenol.**

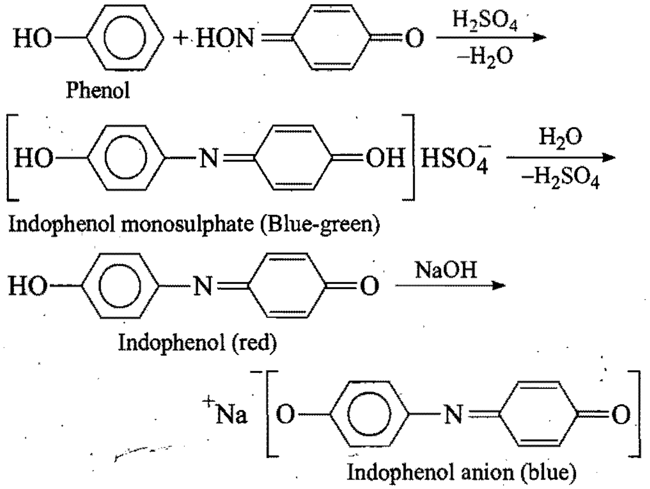
(a) Phenol reacts with nitrous acid to give *p*-nitrosophenol which is tautomeric with the monoxime of quinone.

$$(\underset{\text{Sod. nitrite}}{2NaNO_2} + H_2SO_4 \longrightarrow 2HNO_2 + Na_2SO_4)$$



Phenol p-Nitroso phenol

(b) In the presence of conc. H_2SO_4, the monoxime condenses with phenol to give a blue-green solution which on dilution gives indophenol (red colour). With excess of NaOH, sodium salt of indophenol (deep blue colour) is produced.



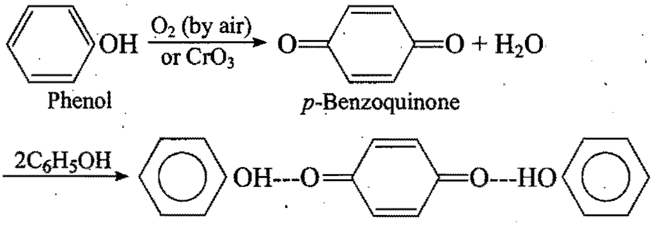
Phenol

Indophenol monosulphate (Blue-green)

Indophenol (red)

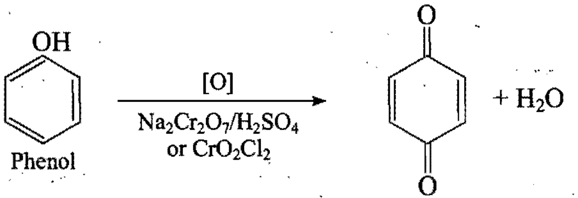
Indophenol anion (blue)

(iv) Oxidation : Phenol turns pink or red or brown on exposure to air and light due to slow oxidation. The colour is probably due to the formation of quinone and phenoquinone.



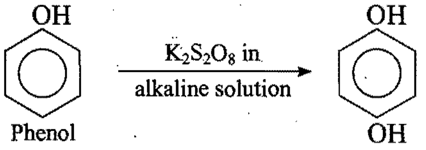
Phenol p-Benzoquinone

Phenoquinone (red)



Phenol p-Benzoquinone

But on oxidation with potassium persulphate in alkaline solution, phenol forms 1,4-dihydroxy benzene (Quinol). This is known as **Elbs persulphate oxidation.**



Phenol Quinol

Uses : Phenol is extensively used in industry. The important applications of phenol are:

(i) as an antiseptic in soaps, lotions and ointments. A powerful antiseptic is **"Dettol"** which is a phenol derivative (2,4-dichloro-3,5-dimethyl phenol).

(ii) in the manufacture of azo dyes, phenolphthalein, etc.

(iii) in the preparation of picric acid used as an explosive and for dyeing silk and wool.

(iv) in the manufacture of cyclohexanol required for the production of nylon and used as a solvent for rubber and lacquers.

(v) as a preservative for ink.

(vi) in the manufacture of phenol-formaldehyde plastics such as bakelite.

(vii) in the manufacture of drugs like aspirin, salol, phenacetin, etc.

(viii) for causterising wounds caused by the bite of mad dogs.

(ix) as a starting material for the manufacture of nylon and artificial tannins.

(x) in the preparation of disinfectants, fungicides and bactericides.

Tests of phenol : (i) Aqueous solution of phenol gives a violet colouration with a drop of ferric chloride.

(ii) Aqueous solution of phenol gives a white precipitate of 2,4,6-tribromophenol with bromine water.

(iii) Phenol gives **Liebermann's nitroso reaction.**

$$\text{Phenol in conc. sulphuric acid} \xrightarrow[\text{Excess of water}]{NaNO_2} \text{Red colour} \xrightarrow[\text{(Excess)}]{NaOH} \text{Blue colour}$$

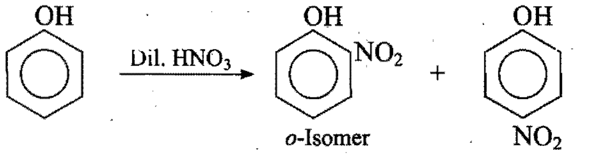
(iv) Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali, and is used as an indicator **(Phthalein test).**

(v) With ammonia and sodium hypochlorite, phenol gives blue colour.

DERIVATIVES OF PHENOL

1. Nitrophenols

Phenol easily undergoes nitration. *Ortho* and *para* nitrophenols are obtained by nitration of phenol with dilute HNO_3 in cold. *Ortho* isomer is separated by steam distillation as it is steam volatile.

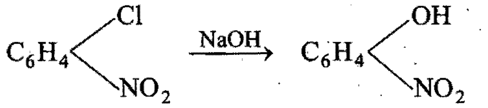


o-Isomer (Steam volatile) p-Isomer (Non-volatile)

o- and p-forms are also obtained by treating chloro or bromonitrobenzene with caustic alkali at 120°C.

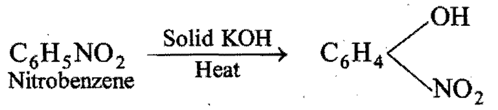
Difference between Phenol and Alcohol

	Property	Phenol (C_6H_5OH)	Alcohol (C_2H_5OH)
1.	Odour	Typical phenolic odour.	Pleasant alcoholic odour.
2.	Nature, reaction with alkali	Acidic, dissolves in sodium hydroxide forming sodium phenoxide.	Neutral, no reaction with alkalies.
3.	Reaction with neutral $FeCl_3$	Gives violet colouration due to formation of complex compound.	No reaction.
4.	Reaction with halogen acids	No reaction with halogen acids.	Forms ethyl halides.
5.	Oxidation	Pink or brown colour due to formation of quinone and phenoquinone.	Undergoes oxidation to give acetaldehyde and acetic acid.
6.	Reaction with HCHO	Forms polymer (bakelite)	No reaction.
7.	Liebermann's nitroso reaction	Positive.	Does not show.
8.	Coupling with benzene diazonium chloride	Forms azo dye.	Does not form any dye.
9.	Reaction with PCl_5	Mainly forms triphenyl phosphate.	Forms ethyl chloride.
10.	Iodoform test	Does not show.	Positive.



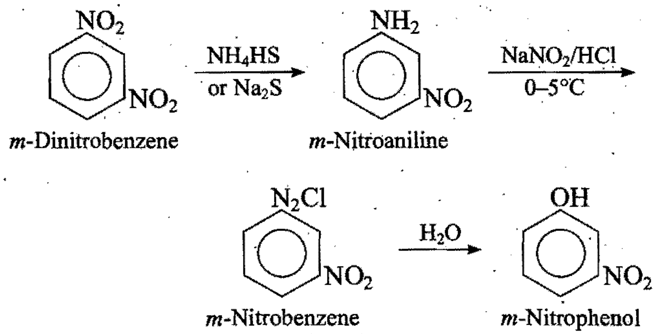
o- and *p*-chloro-nitrobenzenes *o*- and *p*-nitrophenol

When heated with solid potassium hydroxide, nitrobenzene produces a mixture of *o*- and *p*-nitrophenols.



o- and *p*-nitrophenols

m-Nitrophenol is obtained from *m*-dinitrobenzene. One of the nitrogroup is converted into —NH_2 group which is diazotised. The diazonium compound on boiling yields *m*-nitrophenol.



Properties : *o*-Nitrophenol is a yellow coloured crystalline compound, while *m*- and *p*-isomers are colourless crystalline compounds.

Isomer	*ortho*	*meta*	*para*
m.pt. (°C)	45	97	114

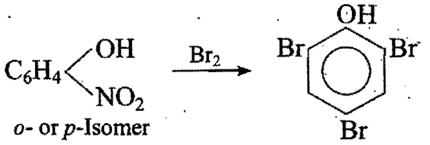
The lowest melting point of *o*-isomer is due to **intramolecular hydrogen bonding** whereas *meta* and *para* isomers possess **intermolecular hydrogen bonding** and thus, they have higher melting points.

They are stronger acids than phenol. The order is:

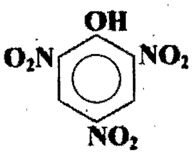
p-isomer > *o*-isomer > *m*-isomer > phenol

When reduced, they form corresponding aminophenols.

o- and *p*-nitrophenols react with bromine water to form 2,4,6-tribromophenol by replacement of nitro group.

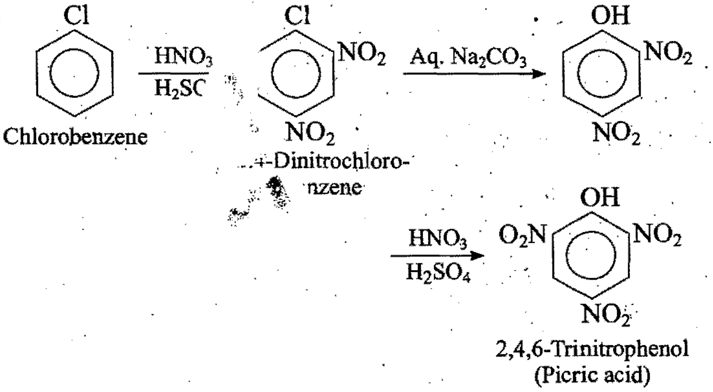


2. Picric Acid (2,4,6-Trinitrophenol) or

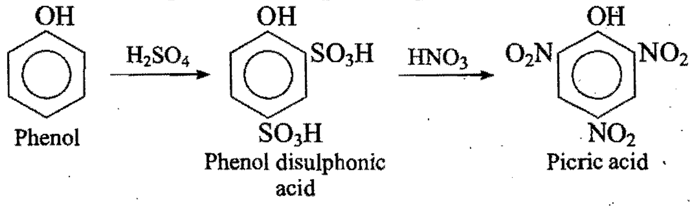


It is obtained when phenol is treated with conc. HNO_3. However, the yield is very poor. It is prepared on an industrial scale as below :

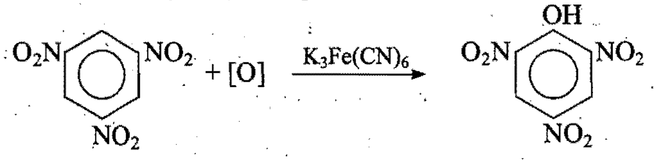
(i) From Chlorobenzene :



(ii) From phenol through disulphonic acid :

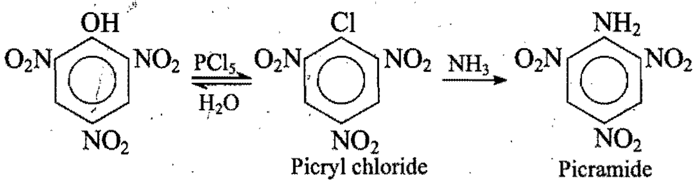


It may be prepared in the laboratory by oxidation of *s*-trinitrobenzene (TNB) with potassium ferricyanide.



Properties : It is a yellow crystalline solid, m.pt. 122°C. It is insoluble in cold water but soluble in hot water and in ether. It is bitter in taste. Due to the presence of three electronegative nitro groups, it is a stronger acid than phenol and its properties are comparable to the carboxylic acid. It neutralises alkalies and decomposes carbonates with evolution of carbon dioxide.

Dry picric acid as well as its potassium or ammonium salts explode violently when detonated. It reacts with PCl_5 to form picryl chloride which on shaking with NH_3 yields picramide.



When distilled with a paste of bleaching powder, it gets decomposed and yields chloropicrin, CCl_3NO_2, as one of the products and is thus employed for the manufacture of tear gas.

It forms yellow, orange or red coloured molecular compounds called picrates with aromatic hydrocarbons, amines and phenols which are used for characterization of these compounds.

Note : Picrates are explosive in nature and explode violently when heated. These are prepared carefully.

Uses : It is used as a yellow dye for silk and wool, as an explosive and as an antiseptic in treatment of burns.

3. Anisole (Methyl phenyl ether) $C_6H_5OCH_3$ or (Methoxy benzene)

It is prepared by following reactions :

(i) By the action of methyl iodide on sodium phenoxide.

$$C_6H_5ONa + ICH_3 \longrightarrow C_6H_5OCH_3 + NaI$$

See **sec. 10.4.**

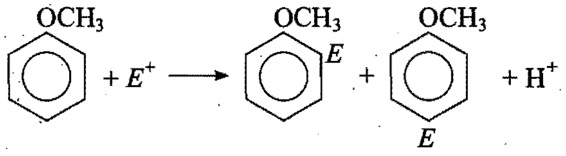
(ii) By passing vapours of phenol and methyl alcohol over heated thoria.

$$C_6H_5OH + CH_3OH \xrightarrow{ThO_2} C_6H_5OCH_3 + H_2O$$

(iii) By methylation of phenol with diazomethane.

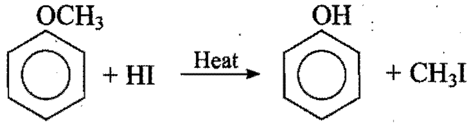
$$C_6H_5OH + CH_2N_2 \longrightarrow C_6H_5OCH_3 + N_2$$

Properties : It is a pleasant smelling liquid. It is used as a solvent in some organic reactions. Anisole undergoes electrophilic substitution reactions. —OCH_3 group is *o*- and *p*- directing.



See **section 10.5.**

Anisole is decomposed by conc. hydroiodic acid again into phenol.

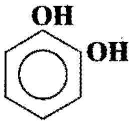


This reaction is used for estimation of methoxy group **(Zeisel's method).**

Dihydric Phenols

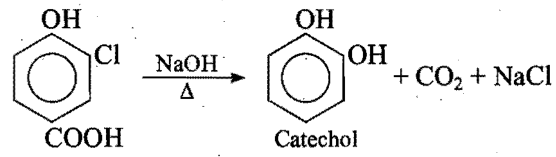
Three isomeric dihydric phenols are catechol, resorcinol and quinol.

Catechol (1, 2-Dihydroxy benzene),

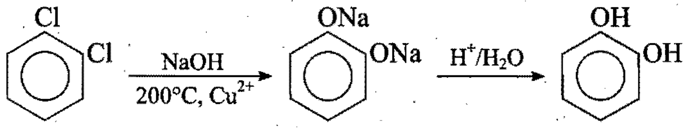


It may be prepared by following methods :

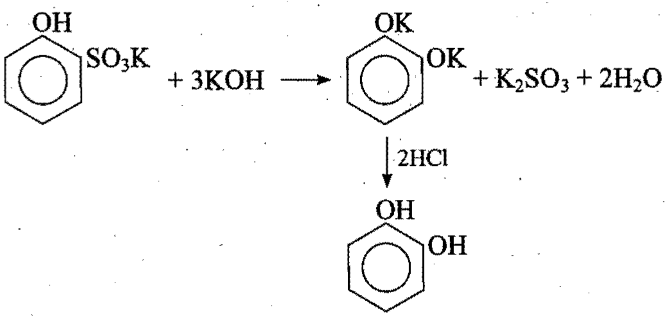
(i) By fusion of chloro substituted phenolic acid with caustic soda.



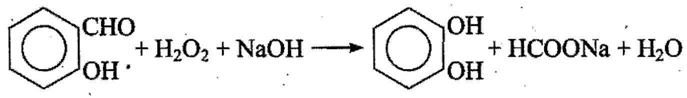
or by hydrolysis of *o*-dichlorobenzene or *o*-chlorophenol with dilute NaOH solution at 200°C and in the presence of copper sulphate catalyst.



(ii) By fusing alkali salt of *o*-phenol sulphonic acid with caustic alkali and then hydrolysing the product with mineral acid.

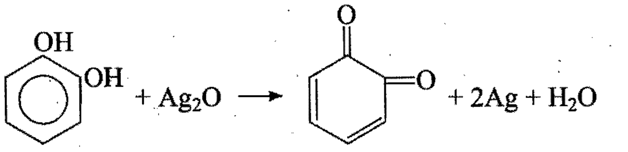


It may be conveniently prepared in the laboratory by treating salicylaldehyde with alkaline H_2O_2.



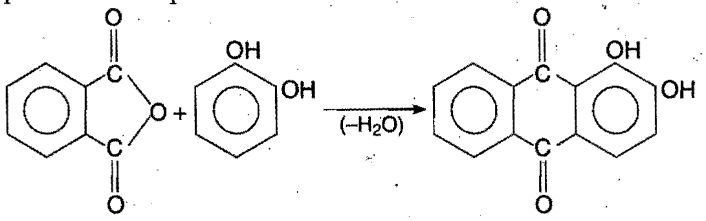
Salicylaldehyde Catechol

Properties : It is a colourless crystalline solid, m.pt. 105°C. It is soluble in water. It is affected on exposure to air and light. It acts as a reducing agent as it reduces Tollens' reagent in cold and Fehling's solution on heating. With silver oxide it is oxidised to *o*-benzoquinone.



o-Benzoquinone

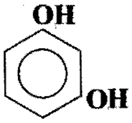
It forms insoluble lead salt (white ppt.) when treated with lead acetate solution and gives green colour with $FeCl_3$ which changes to red on adding Na_2CO_3 solution. It forms alizarin dye stuff when condensed with phthalic anhydride in the presence of sulphuric acid.



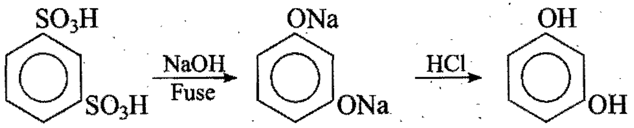
Phthalic anhydride Alizarin

It finds use as photographic developer, in the manufacture of alizarin (Dye) and adrenaline hormone and as an antioxidant (inhibitor in auto oxidation) for preserving gasoline.

Resorcinol (1,3-Dihydroxy benzene),

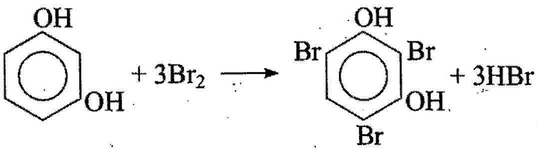


It is prepared by alkali fusion of 1,3-benzene disulphonic acid (Industrial method).

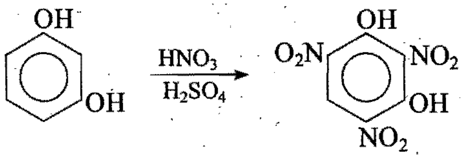


Properties : It is a colourless crystalline solid, m.pt. 110°C. It is affected on exposure by air and light. It is soluble in water, alcohol and ether. It shows tautomerism. Its aqueous solution gives violet colour with $FeCl_3$. It reduces Fehling's solution and Tollens' reagent on warming.

With bromine water, it gives a crystalline precipitate, 2,4,6-tribromoresorcinol.

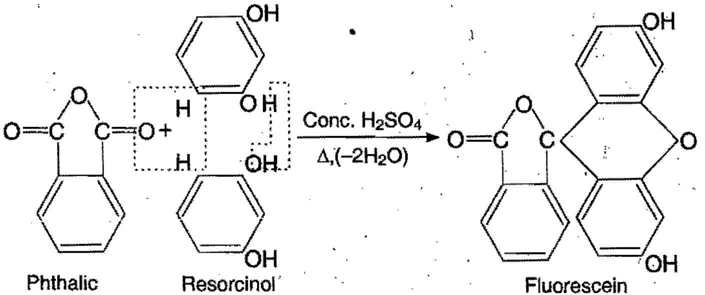


On nitration, it forms 2,4,6-trinitro-1,3-dihydroxy benzene.



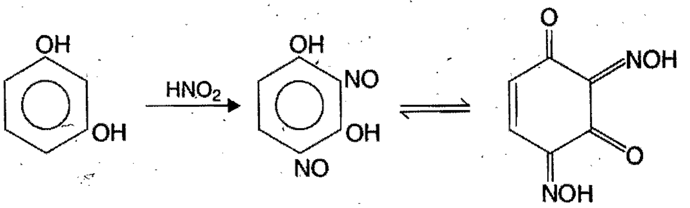
Styphnic acid

It condenses with phthalic anhydride and forms fluorescein.

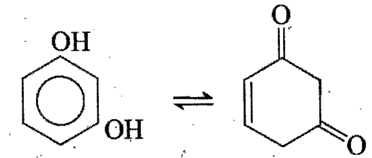


Phthalic anhydride Resorcinol (2 moles) Fluorescein

With nitrous acid, it forms 2,4-dinitrosoresorcinol



Resorcinol behaves as a tautomeric compound. This is shown by the fact that it forms a dioxime and a bisulphite derivative.

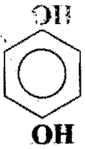


Dienol form Diketo form

Uses : (i) It is used as antiseptic and for making dyes.

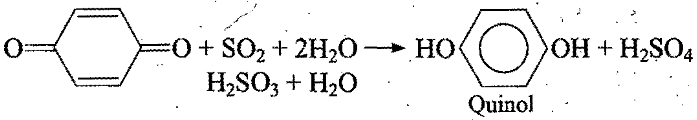
(ii) It is also used in the treatment of eczema. 2,4,6-Trinitroresorcinol is used as an explosive.

Hydroquinone or Quinol (1,4-Dihydroxy benzene),



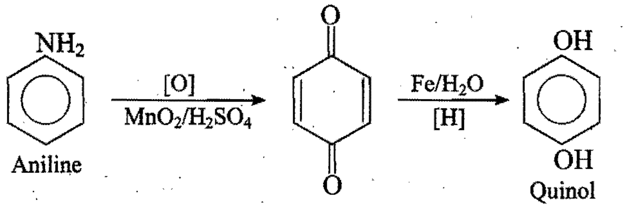
It is formed by reduction of *p*-benzoquinone with sulphurous acid ($H_2SO_3 = H_2O + SO_2$), *i.e.*,

$$[H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2H]$$



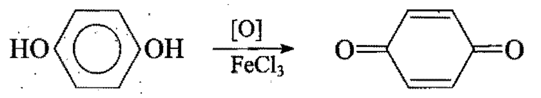
Quinol

(*p*-Benzoquinone is obtained by oxidation of aniline).



Properties : It is a colourless crystalline solid, m.pt. 170°C. It is soluble in water. It also shows tautomerism. It gives blue colour with $FeCl_3$ solution.

It acts as a powerful reducing agent as it is easily oxidised to *p*-benzoquinone. It reduces Tollens' reagent and Fehling's solution.



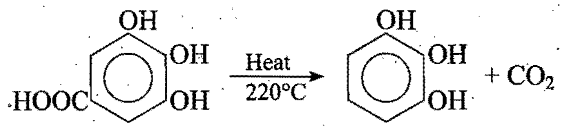
Due to this property, it is used as photographic developer.

It is used as an antiseptic, developer in photography, in the preparation of quinhydrone electrode and as an antioxidant.

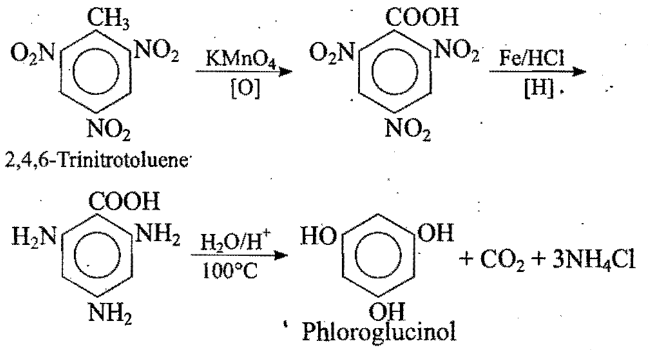
Trihydric Phenols

Three trihydroxy isomeric derivatives of benzene are Pyrogallol (1,2,3), Hydroxy quinol (1,2,4) and Phloroglucinol (1,3,5).

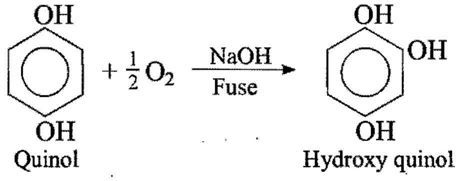
Pyrogallol is obtained by heating aqueous solution of gallic acid at 220°C.



Phloroglucinol is obtained from trinitrotoluene (TNT) by following sequence of reactions:



Hydroxy quinol is prepared by the alkaline fusion of hydroquinone in air.



The three isomers are colourless crystalline compounds. All are soluble in water and their aqueous solutions give characteristic colour with $FeCl_3$. For example, Pyrogallol-red; Hydroxy quinol-greenish brown; Phloroglucinol-bluish violet. Alkaline solutions absorb oxygen rapidly from air.

Uses of pyrogallol : (i) As a developer in photography.

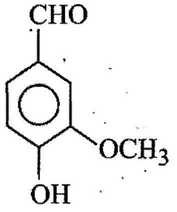
(ii) As a hair dye.

(iii) In treatment of skin diseases like eczema.

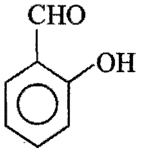
(iv) For absorbing unreacted oxygen in gas analysis.

16.16 AROMATIC ALDEHYDES AND KETONES

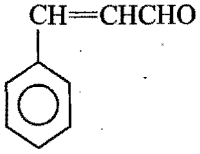
Aldehydes and ketones are widely spread in plants and animal kingdom. They play an important role in biochemical processes of life. They add fragrance and flavour to nature. For example, vanillin (from vanilla beans), salicylaldehyde (from meadow sweets) and cinnamaldehyde (from cinnamon), etc have pleasant fragrances.



4-Hydroxy-3-methoxy benzaldehyde (Vanillin)



2-Hydroxy benzaldehyde (Salicylaldehyde)



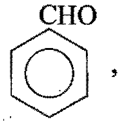
3-Phenylprop-2-en-1-al (Cinnamaldehyde)

Aromatic aldehydes are of two types:

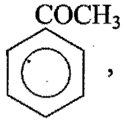
(i) The compounds in which —CHO group is attached directly to an aromatic ring, *e.g.*, benzaldehyde, C_6H_5CHO.

(ii) Those in which aldehyde (—CHO) group is attached to side-chain, *e.g.*, phenyl acetaldehyde, $C_6H_5CH_2CHO$. They closely resemble with aliphatic aldehydes.

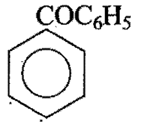
Aromatic ketones are compounds in which a carbonyl group ($>C{=}O$) is attached to either two aryl groups or one aryl group and one alkyl group. Examples are:



Benzaldehyde (Benzene carbaldehyde)

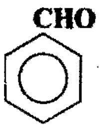


Acetophenone (Methyl phenyl ketone)

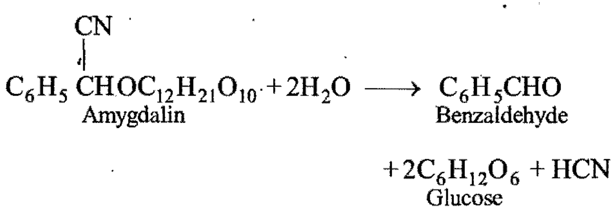


Benzophenone (Diphenyl ketone)

Benzaldehyde, C_6H_5CHO (or Benzenecarbaldehyde)



Benzaldehyde is the simplest aromatic aldehyde. It occurs in bitter almonds in the form of its glucoside, **amygdalin** ($C_{20}H_{27}O_{11}N$). When amygdalin is boiled with dilute acids, it hydrolyses into benzaldehyde, glucose and HCN.



$$\underset{\text{Amygdalin}}{C_6H_5\overset{\overset{CN}{|}}{C}HOC_{12}H_{21}O_{10}} + 2H_2O \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Glucose}}{2C_6H_{12}O_6} + HCN$$

Benzaldehyde is also known as *oil of bitter almonds*.

Methods of Preparation

1. Laboratory method : It is conveniently prepared by boiling benzyl chloride with copper nitrate or lead nitrate solution in a current of carbon dioxide.

$$\underset{\text{Benzyl chloride}}{2C_6H_5CH_2Cl} + \underset{\substack{\text{or}\\ Pb(NO_3)_2}}{Cu(NO_3)_2} \xrightarrow[CO_2]{\text{Heat}} \underset{\text{Benzaldehyde}}{2C_6H_5CHO} + CuCl_2 + 2HNO_2$$

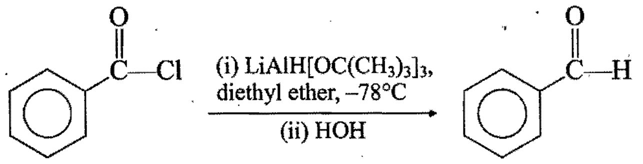
$$[2HNO_2 \longrightarrow NO + NO_2 + H_2O]$$

2. By Rosenmund reaction : It is done when hydrogen is bubbled through a solution of benzoyl chloride in xylene in presence of palladium catalyst poisoned by $BaSO_4$ till evolution of HCl ceases (catalytic reduction of benzoyl chloride).

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + H_2 \xrightarrow[\text{(Boiling xylene)}]{Pd/BaSO_4,\ S} C_6H_5CHO + HCl$$

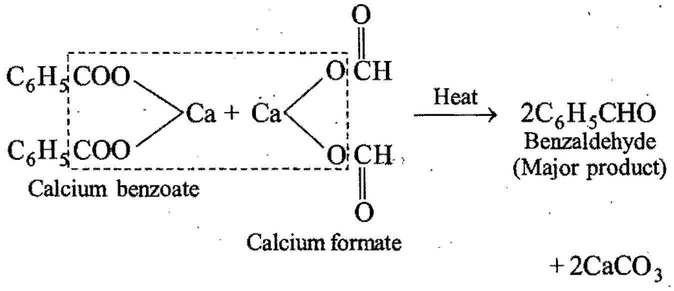
The catalyst is poisoned to small extent by the addition of sulphur or quinoline to prevent further reduction of aldehydes to alcohols.

Acyl chlorides can be reduced to aldehyde by treating them with Lithium tri-*tert*. butoxy aluminium hydride, $LiAlH[OC(CH_3)_3]_3$, at −78°C.

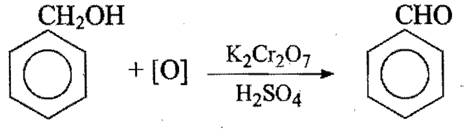


Benzoyl chloride Benzaldehyde

3. By dry distillation of a mixture of calcium benzoate and calcium formate, the main product benzaldehyde is formed. Other possible compounds like diphenyl ketone and formaldehyde are also formed.



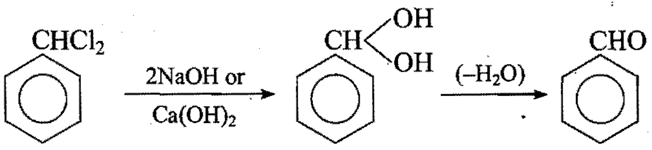
4. By oxidation of benzyl alcohol : This involves the treatment of benzyl alcohol with dil. HNO_3 or acidic potassium dichromate or chromic anhydride in acetic anhydride or with copper catalyst at 350°C.



Benzyl alcohol Benzaldehyde

This method is used for commercial production of benzaldehyde.

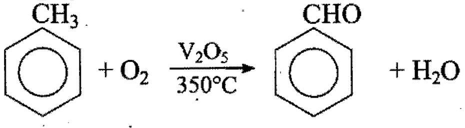
5. By hydrolysis of benzal chloride : Benzal chloride on hydrolysis yields benzaldehyde. The hydrolysis can be done by aqueous caustic soda or milk of lime.



Benzal chloride Intermediate (unstable) Benzaldehyde

This is also an industrial method.

6. By oxidation of toluene : (a) The oxidation of toluene is done with air or oxygen in the presence of vanadium pentoxide (V_2O_5) at 350°C to give benzaldehyde.



Toluene Benzaldehyde

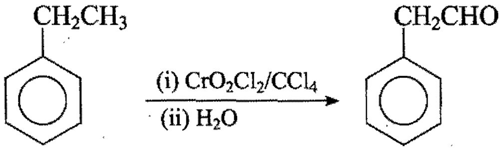
Commercially, the oxidation of toluene is done with air diluted with nitrogen (to prevent complete oxidation) at 500°C in the presence of oxides of Mn, Mo, or Zr as catalyst.

Partial oxidation of toluene with manganese dioxide and dil. sulphuric acid at 35°C, also forms benzaldehyde.

(b) Etard's reaction : Chromyl chloride dissolved in CS_2 or CCl_4 is made to react with toluene in CS_2 when a brown coloured product is formed. This product is decomposed with water when benzaldehyde is formed. This is Etard's reaction and is used in **laboratory** for preparation of benzaldehyde.

$$\underset{\text{Toluene}}{C_6H_5CH_3} + 2CrO_2Cl_2 \xrightarrow[\text{or } CS_2]{CCl_4} \underset{\text{Brown addition product}}{C_6H_5CH_3\cdot 2CrO_2Cl_2} \xrightarrow[\text{(Hydrolysis)}]{H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

In case, the side-chain contains a group higher than —CH_3 group, the end carbon atom of the chain is oxidised by CrO_2Cl_2 to —CHO group.

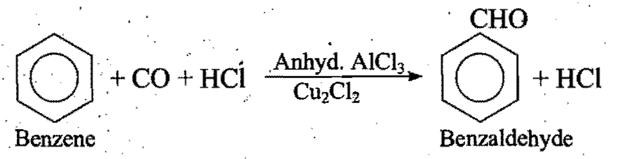


Ethylbenzene Phenylethanal

(c) Benzaldehyde is also formed by oxidation of toluene with chromic oxide in acetic anhydride. Benzaldehyde formed reacts with acetic anhydride to form benzylidene diacetate which on hydrolysis with alkali or an acid yields benzaldehyde.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[(CH_3CO)_2O]{CrO_3,[O]} \underset{\text{Benzylidene diacetate}}{C_6H_5CH(OCOCH_3)_2} \xrightarrow[\text{(Hydrolysis)}]{OH^-/H_2O} C_6H_5CHO + 2CH_3COOH$$

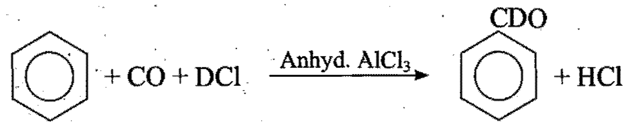
7. Gattermann-Koch aldehyde synthesis : Benzene is converted into benzaldehyde by passing a mixture of carbon monoxide and HCl gas under high pressure of 90 atmospheres into the ether solution of benzene in presence of anhydrous aluminium chloride and cuprous chloride **(Formylation of benzene).**



$$C_6H_6 + HCOCl \xrightarrow[CuCl]{Anhyd.\ AlCl_3} C_6H_5CHO + HCl$$

This is an industrial method.

Thus, HCl (reactant) and HCl (product) are different. H of HCl (reactant) and CO appear in the form of —CHO in the benzene nucleus. It is confirmed by the fact that using isotopic DCl instead of HCl would form —CDO and not —CHO.



This is an electrophilic substitution in which $H—\overset{+}{C}=O$ (formyl cation) is an electrophile needed for formylation. The formation of electrophile occurs probably in the following manner.

$$\underset{}{HCl + CO} \longrightarrow \underset{\text{Formyl chloride}}{HCOCl}$$

$$HCOCl + AlCl_3 \longrightarrow H—\overset{+}{C}=O + AlCl_4^-$$

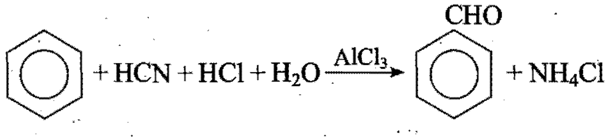
8. Gattermann reaction : In this reaction, a mixture of benzene and anhydrous $AlCl_3$ is treated with HCN and HCl gas. This aldehyde synthesis with HCN is called **Gattermann formylation** or **Gattermann aldehyde synthesis.**

$$HC{\equiv}N + HCl + AlCl_3 \longrightarrow H\overset{+}{C}=NH + AlCl_4^-$$

$$\underset{\text{Benzene}}{C_6H_5H} + H\overset{+}{C}=NH \longrightarrow C_6H_5CH=\overset{+}{N}H_2$$

$$C_6H_5CH=\overset{+}{N}H_2 + H_2O + AlCl_4^- \xrightarrow{Boil} C_6H_5CHO + NH_3 + AlCl_3 + HCl$$

Thus,

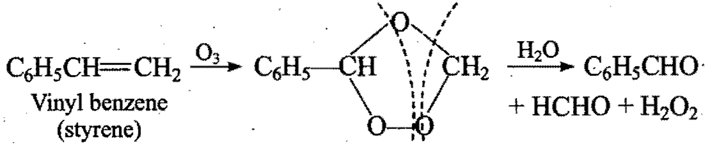


9. Stephen's reduction : Benzaldehyde is obtained by partial reduction of phenyl cyanide (benzonitrile) with stannous chloride and passing dry HCl gas in ethereal solution followed by hydrolysis of the aldimine stannic chloride with water.

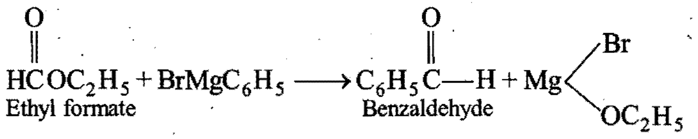
$$\underset{\text{Phenyl cyanide}}{C_6H_5C{\equiv}N} + 2H + HCl \xrightarrow[Ether]{HCl/SnCl_2}$$

$$\underset{\text{Aldimine complex}}{[C_6H_5CH=NH]_2H_2SnCl_6} \xrightarrow[Boil]{H_2O} \underset{\text{Benzaldehyde}}{2C_6H_5CHO}$$

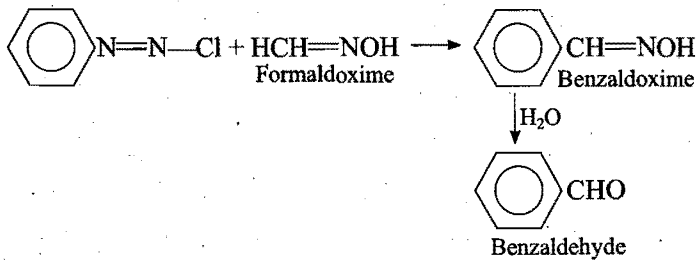
10. By ozonolysis of styrene : The ozonide of styrene (vinyl benzene) on hydrolysis yields benzaldehyde.



11. Grignard reaction : By treating phenyl magnesium bromide with a reagent ethyl formate, benzaldehyde is obtained in good yield. Other reagents like carbon monoxide or ethyl *ortho*-formate or HCN can also be used.



12. From Diazonium salt : By treating with formaldoxime followed by hydrolysis yields benzaldehyde.



13. Sommelet reaction : Oxidation of $—CH_2Cl$ to —CHO group by using urotropine $(CH_2)_6N_4$, is called Sommelet reaction. Benzyl chloride on refluxing with hexamethylene tetramine in aqueous alcoholic solution yields benzaldehyde.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } (CH_2)_6N_4/C_2H_5OH} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

Physical properties : (i) Benzaldehyde is a colourless oily liquid. Its boiling point is 179°C.

(ii) It has smell of bitter almonds.

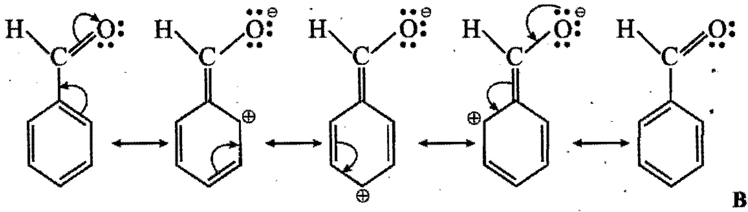
(iii) It is sparingly soluble in water but highly soluble in organic solvents.

(iv) It is a steam volatile.

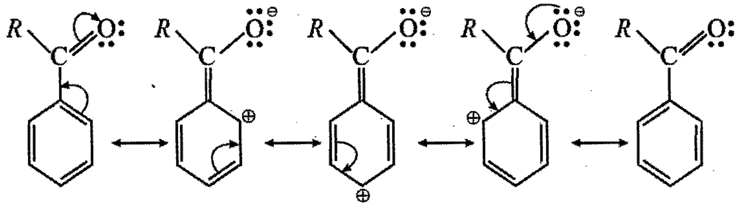
(v) It is heavier than water (sp. gr. 1.0504 at 15°C).

(vi) It is poisonous in nature.

Chemical properties : In general, **aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones.** For example, benzaldehyde is less reactive than aliphatic aldehyde. It can be explained on the basis of electron releasing resonance effect of benzene ring. The resonating structures of benzaldehyde are:



It is clear from the resonating structures that due to electron releasing resonance effect (+*R* effect) of benzene ring, the magnitude of the positive charge on the carbonyl group decreases and consequently it becomes less susceptible to the nucleophilic attack. Thus, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones.



Resonating structures of aromatic ketones

The order of reactivity of aromatic aldehydes and ketones is:

$$\underset{\text{Phenyl acetaldehyde}}{C_6H_5CH_2CHO} > \underset{\text{Benzaldehyde}}{C_6H_5CHO} > \underset{\text{Acetophenone}}{C_6H_5COCH_3} > \underset{\text{Benzophenone}}{C_6H_5COC_6H_5}$$

In general, the presence of a H-atom on the carbonyl group ($H-\overset{O}{\overset{\|}{C}}-$) of aldehyde makes them much more reactive than ketones. Also, this H-atom is responsible for many reactions in which aldehydes differ from ketones.

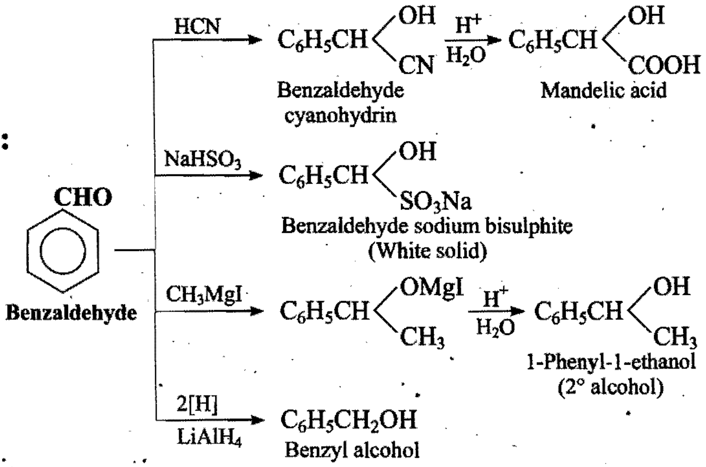
The molecule of benzaldehyde consists of an aldehydic group and benzene nucleus. It resembles formaldehyde in most of the reactions of aldehydic group as both have no α-hydrogen atoms. However, benzaldehyde is less reactive than formaldehyde and other aliphatic aldehydes.

Reactions in which benzaldehyde resembles aliphatic aldehydes:

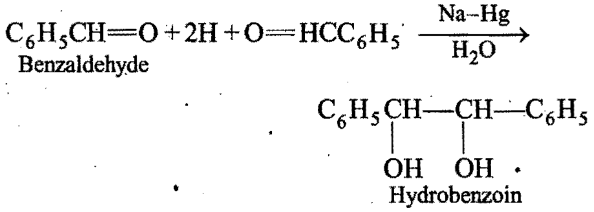
1. Addition reactions : The carbonyl group is polar as oxygen is more electronegative than carbon.

$$\gt\overset{\delta^+}{C}=\overset{\delta^-}{O}$$

Thus, the positive part of the polar reagent always goes to the carbonyl oxygen and negative part goes to carbonyl carbon.

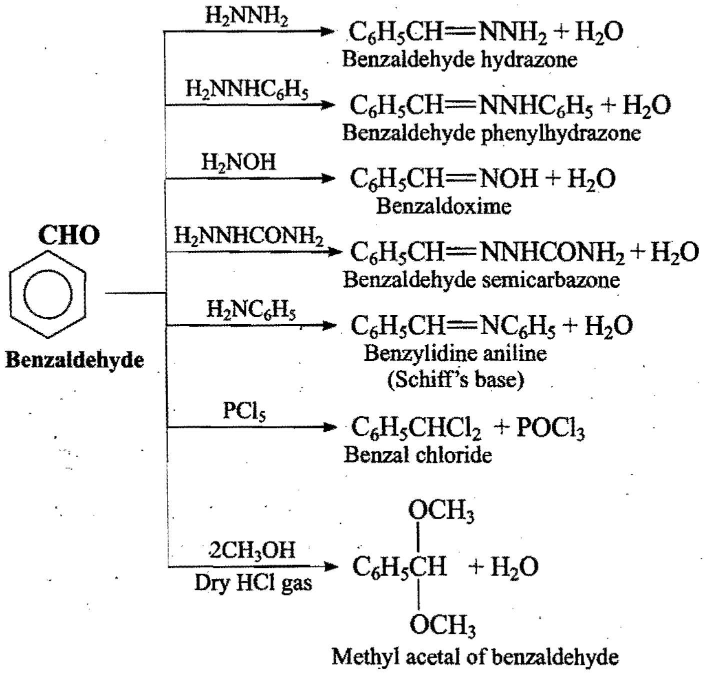


However on reduction with sodium amalgam and water, benzaldehyde gives hydrobenzoin,



$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + 2H + O{=}HCC_6H_5 \xrightarrow[H_2O]{Na-Hg} \underset{\text{Hydrobenzoin}}{C_6H_5\underset{OH}{\underset{|}{C}H}-\underset{OH}{\underset{|}{C}H}-C_6H_5}$$

2. Reactions involving replacement of carbonyl oxygen :



3. Oxidation : Benzaldehyde is readily oxidised to benzoic acid even on exposure to air.

$$C_6H_5CHO \xrightarrow{[O]} C_6H_5COOH$$

Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$ and dilute HNO_3 can be used as oxidising agents for oxidation.

4. Reducing properties : Benzaldehyde is a weak reducing agent. It reduces ammoniacal silver nitrate solution (Tollens' reagent) to give silver mirror but does not reduce Fehling's solution.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + Ag_2O \longrightarrow 2Ag + \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

5. Clemmensen's reduction : With amalgamated zinc and conc. HCl, benzaldehyde is reduced to toluene.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + 4H \xrightarrow[\text{HCl (conc.)}]{\text{Zn–Hg}} C_6H_5CH_3 + H_2O$$

6. Wolff-Kishner reduction : Benzaldehyde is reduced to hydrocarbon toluene in the presence of excess of hydrazine and strong base, KOH or potassium *tert.* butoxide on heating at 200°C. The best solvent for the reaction is ethylene glycol.

$$C_6H_5CH{=}O + 4H \xrightarrow[200°C]{H_2NNH_2/\text{KOH, glycol}} \underset{\text{Toluene}}{C_6H_5CH_3} + H_2O + N_2$$

7. Schiff reaction : It restores pink colour to Schiff reagent (aqueous solution of *p*-rosaniline hydrochloride decolourized by passing sulphur dioxide).

8. Tischenko reaction : On heating benzaldehyde with aluminium alkoxide (ethoxide) and a little of anhydrous $AlCl_3$ or $ZnCl_2$, it undergoes an intermolecular oxidation and reduction (like aliphatic aldehydes) to form acid and alcohol respectively as such and react to produce benzyl benzoate (an ester).

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \xrightarrow[\Delta]{Al(OC_2H_5)_3} \underset{\text{Benzyl benzoate (ester)}}{C_6H_5CH_2OOCC_6H_5}$$

Reactions in which benzaldehyde differs from aliphatic aldehydes :

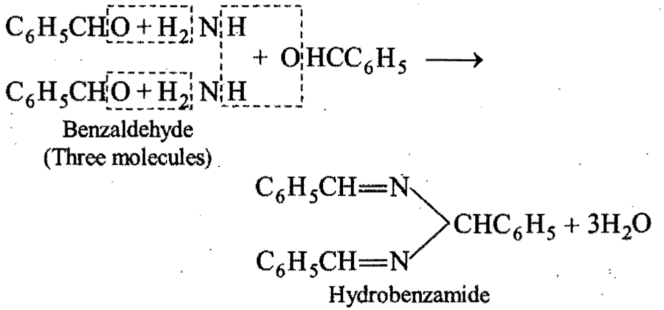
1. With Fehling's solution : Unlike aliphatic aldehydes, benzaldehyde does not reduce Fehling's solution.

The weaker oxidising agents like Fehling's solution (or Benedict's solution) fails to oxidise benzaldehyde to benzoic acid because the C—H bond in aldehyde is strong (due to increase of electron density in C—H bond of the aldehyde group) and hence, only stronger oxidising agents like Tollens' reagent can oxidise C—H bond to form carboxylic acids but Fehling's solution does not.

2. Action of chlorine : Benzoyl chloride is formed when chlorine is passed through benzaldehyde at its boiling point in absence of halogen carrier. This is because in benzaldehyde there is no α-hydrogen atom present which could be replaced by chlorine.

$$C_6H_5CHO + Cl_2 \xrightarrow[\Delta]{170°C} C_6H_5COCl + HCl$$

3. Reaction with ammonia : Benzaldehyde on treatment with ammonia forms a different complex compound known as hydrobenzamide instead of usual addition product.

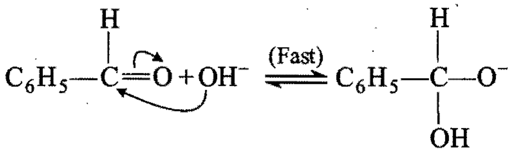


4. Cannizzaro's reaction : Benzaldehyde on treatment with 50% aqueous or ethanolic alkali solution does not form resin like acetaldehyde but undergoes Cannizzaro's reaction like formaldehyde, *i.e.*, one molecule is oxidised and one is reduced with the formation of benzoic acid and benzyl alcohol respectively (Disproportionation reaction). Benzaldehyde like formaldehyde does not contain α-hydrogen atom.

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \xrightarrow[(50\%)]{KOH} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Potassium benzoate}}{C_6H_5COOK}$$

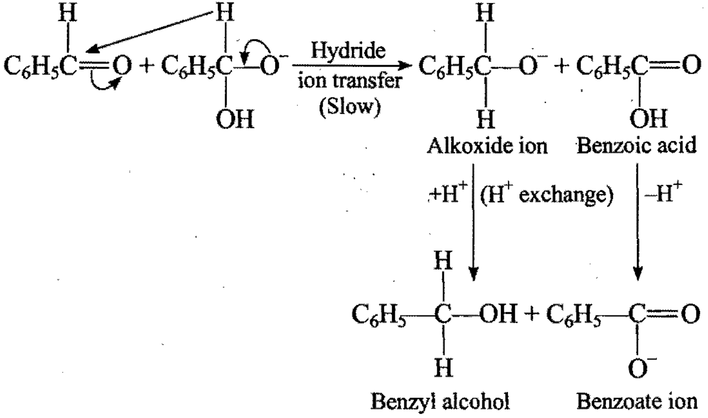
The possible **Mechanism** is :

(i) First step is the reversible addition of hydroxide ion to carbonyl group.



$$C_6H_5\text{—}\overset{H}{\underset{}{C}}{=}O + OH^- \underset{}{\overset{\text{(Fast)}}{\rightleftharpoons}} C_6H_5\text{—}\overset{H}{\underset{OH}{C}}\text{—}O^-$$

(ii) Second step is the transfer of hydride ion directly to the another aldehyde molecule, the latter is thus reduced to alkoxide ion and the former (ion I) is oxidised to an acid.



$$C_6H_5\overset{H}{C}{=}O + C_6H_5\overset{H}{\underset{OH}{C}}\text{—}O^- \xrightarrow[\text{(Slow)}]{\text{Hydride ion transfer}} \underset{\text{Alkoxide ion}}{C_6H_5\overset{H}{\underset{H}{C}}\text{—}O^-} + \underset{\text{Benzoic acid}}{C_6H_5\overset{}{\underset{OH}{C}}{=}O}$$

$$\underset{\text{Benzyl alcohol}}{C_6H_5\text{—}\overset{H}{\underset{H}{C}}\text{—}OH} + \underset{\text{Benzoate ion}}{C_6H_5\text{—}\underset{O^-}{C}{=}O}$$

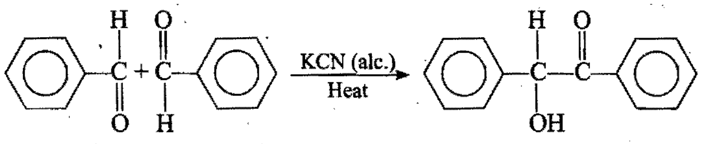
(iii) Third step is exchange of protons to give most stable pair : alcohol and acid anion.

So, one molecule of aldehyde acts as hydride donor and the other acts as hydride acceptor. In other words, Cannizzaro's reaction is an example of self reduction and oxidation.

Note : Two different aldehydes each having no α-hydrogen atom, exhibit **crossed Cannizzaro's reaction** when heated in alkaline solution.

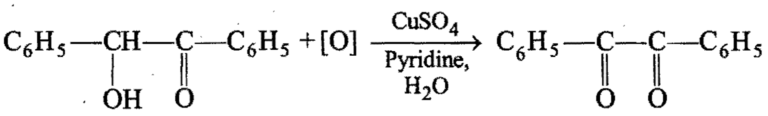
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Formaldehyde}}{HCHO} \xrightarrow[\text{Heat}]{NaOH} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. formate}}{HCOONa}$$

5. Benzoin condensation : When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide, two molecules of benzaldehyde condense together to form **benzoin.** This is called benzoin condensation.



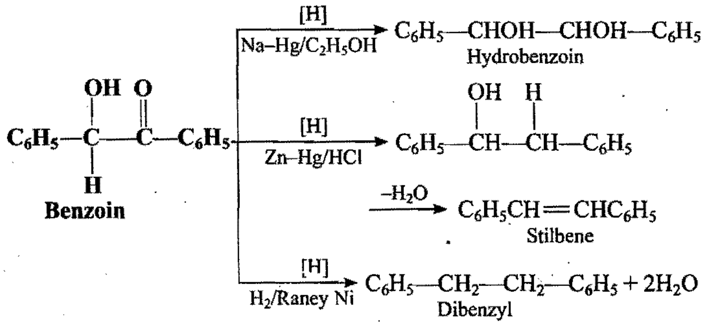
Two molecules of benzaldehyde Benzoin

Benzoin can be readily oxidized to a diketone, *i.e.*, benzil.



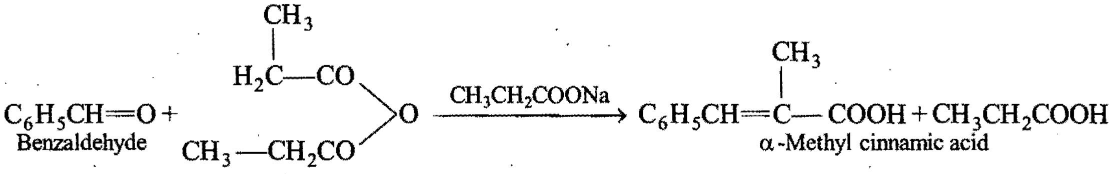
$$\underset{\text{Benzoin}}{C_6H_5-\underset{OH}{CH}-\underset{O}{\overset{\|}{C}}-C_6H_5} + [O] \xrightarrow[\text{Pyridine, } H_2O]{CuSO_4} \underset{\text{Benzil}}{C_6H_5-\underset{O}{\overset{\|}{C}}-\underset{O}{\overset{\|}{C}}-C_6H_5}$$

It can also be reduced to a number of products, *i.e.*,



6. Perkin's reaction : Benzaldehyde (or any other aromatic aldehyde), when heated with an anhydride of an aliphatic acid (containing two α-hydrogen atoms) and its sodium salt (base catalysed), condensation takes place and on hydrolysis an α-β unsaturated acid is formed. Benzaldehyde with acetic anhydride and sodium acetate yields cinnamic acid.

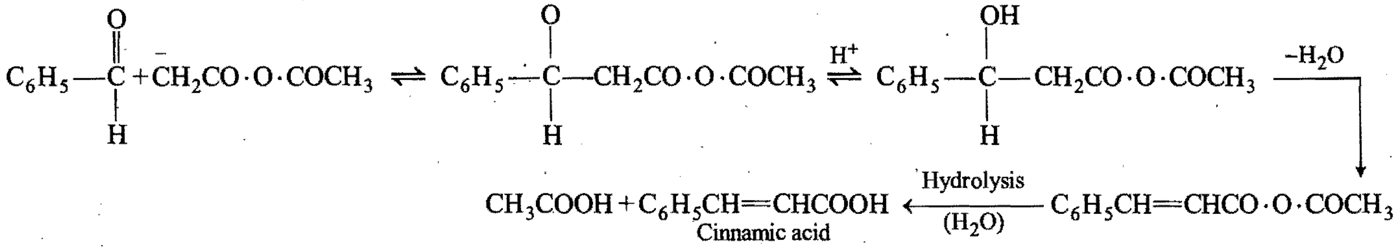
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Acetic anhydride}}{H_2CHCOOCOCH_3} \xrightarrow[-H_2O]{CH_3COONa} \underset{\text{Condensation product}}{C_6H_5CH{=}CHCOOCOCH_3} \xrightarrow[\text{Boil}]{H_2O} \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CHCOOH} + \underset{\text{Acetic acid}}{CH_3COOH}$$



$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + \underset{\text{Propionic anhydride}}{\begin{array}{l} H_2\overset{CH_3}{\overset{|}{C}}-CO \\ CH_3-CH_2CO \end{array}\!\!>O} \xrightarrow{CH_3CH_2COONa} \underset{\alpha\text{-Methyl cinnamic acid}}{C_6H_5CH{=}\overset{CH_3}{\overset{|}{C}}-COOH} + CH_3CH_2COOH$$

Mechanism : The reaction is believed to take place through the formation of a carbanion as follows :

$$CH_3CO\cdot O\cdot COCH_3 + CH_3COO^- \rightleftharpoons \bar{C}H_2CO\cdot O\cdot COCH_3 + CH_3COOH$$



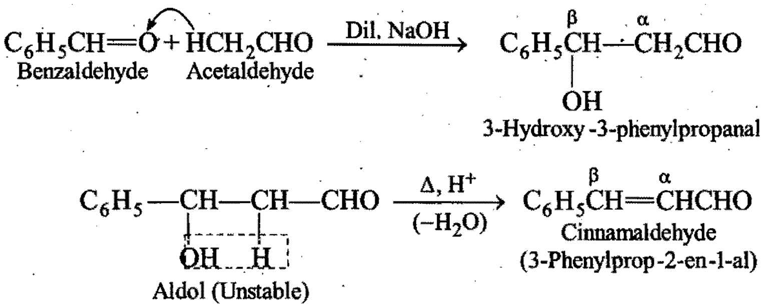
$$C_6H_5-\underset{H}{\overset{O}{\overset{\|}{C}}} + \bar{C}H_2CO\cdot O\cdot COCH_3 \rightleftharpoons C_6H_5-\underset{H}{\overset{\bar{O}}{\overset{|}{C}}}-CH_2CO\cdot O\cdot COCH_3 \overset{H^+}{\rightleftharpoons} C_6H_5-\underset{H}{\overset{OH}{\overset{|}{C}}}-CH_2CO\cdot O\cdot COCH_3 \xrightarrow{-H_2O}$$

$$CH_3COOH + \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CHCOOH} \xleftarrow[(H_2O)]{\text{Hydrolysis}} C_6H_5CH{=}CHCO\cdot O\cdot COCH_3$$

It is always that only the α-hydrogen atoms of the anhydride are involved in the condensation.

7. Claisen condensation (also known as Claisen-Schmidt reaction) : Benzaldehyde undergoes condensation with aldehydes and ketones having two α-hydrogen atoms in presence of dilute alkalies at room temperature to form unsaturated carbonyl compounds.

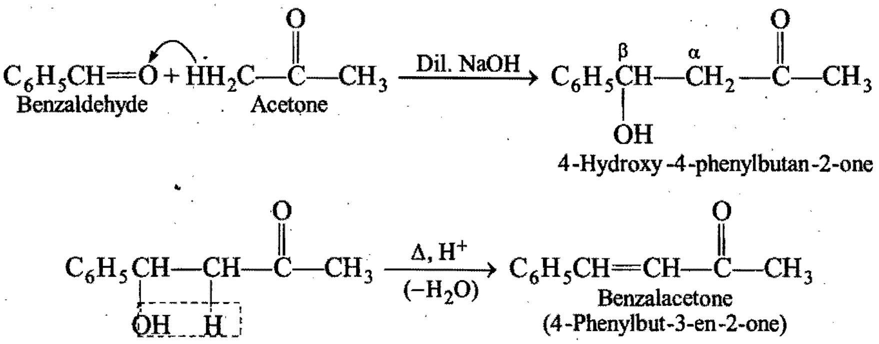
(i)



$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + \underset{\text{Acetaldehyde}}{HCH_2CHO} \xrightarrow{\text{Dil. NaOH}} \underset{\text{3-Hydroxy-3-phenylpropanal}}{C_6H_5\underset{OH}{\overset{\beta}{C}H}-\overset{\alpha}{C}H_2CHO}$$

$$\underset{\text{Aldol (Unstable)}}{C_6H_5-\underset{OH}{CH}-\underset{H}{CH}-CHO} \xrightarrow[(-H_2O)]{\Delta,\ H^+} \underset{\substack{\text{Cinnamaldehyde}\\ \text{(3-Phenylprop-2-en-1-al)}}}{C_6H_5\overset{\beta}{C}H{=}\overset{\alpha}{C}HCHO}$$

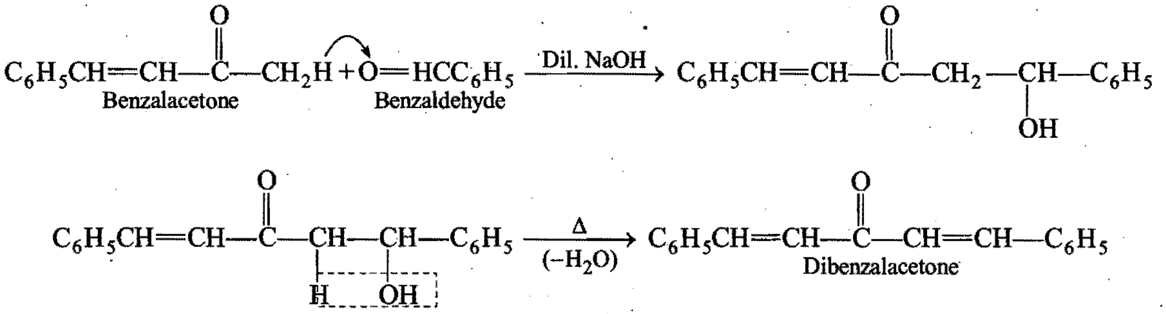
(ii)



$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + \underset{\text{Acetone}}{HH_2C-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{\text{Dil. NaOH}} \underset{\text{4-Hydroxy-4-phenylbutan-2-one}}{C_6H_5\underset{OH}{\overset{\beta}{C}H}-\overset{\alpha}{C}H_2-\overset{O}{\overset{\|}{C}}-CH_3}$$

$$C_6H_5\underset{OH}{CH}-\underset{H}{CH}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[(-H_2O)]{\Delta,\ H^+} \underset{\substack{\text{Benzalacetone}\\ \text{(4-Phenylbut-3-en-2-one)}}}{C_6H_5CH{=}CH-\overset{O}{\overset{\|}{C}}-CH_3}$$

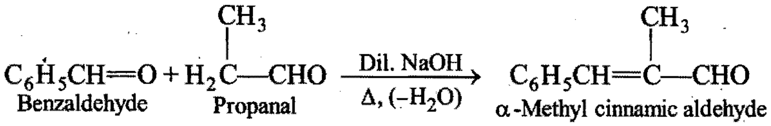
But, if benzaldehyde is taken in excess, the benzal-acetone so obtained condenses with another molecule of benzaldehyde to form dibenzal acetone.



$$\underset{\text{Benzalacetone}}{C_6H_5CH{=}CH-\overset{O}{\overset{\|}{C}}-CH_2H} + \underset{\text{Benzaldehyde}}{O{=}HCC_6H_5} \xrightarrow{\text{Dil. NaOH}} C_6H_5CH{=}CH-\overset{O}{\overset{\|}{C}}-CH_2-\underset{OH}{CH}-C_6H_5$$

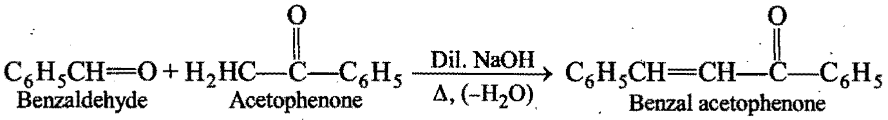
$$C_6H_5CH{=}CH-\overset{O}{\overset{\|}{C}}-\underset{H}{CH}-\underset{OH}{CH}-C_6H_5 \xrightarrow[(-H_2O)]{\Delta} \underset{\text{Dibenzalacetone}}{C_6H_5CH{=}CH-\overset{O}{\overset{\|}{C}}-CH{=}CH-C_6H_5}$$

(iii)



$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + \underset{\text{Propanal}}{H_2\overset{CH_3}{\overset{|}{C}}-CHO} \xrightarrow[\Delta,\ (-H_2O)]{\text{Dil. NaOH}} \underset{\alpha\text{-Methyl cinnamic aldehyde}}{C_6H_5CH{=}\overset{CH_3}{\overset{|}{C}}-CHO}$$

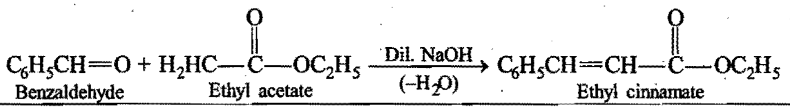
(iv)



$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + \underset{\text{Acetophenone}}{H_2HC-\overset{O}{\overset{\|}{C}}-C_6H_5} \xrightarrow[\Delta,\ (-H_2O)]{\text{Dil. NaOH}} \underset{\text{Benzal acetophenone}}{C_6H_5CH{=}CH-\overset{O}{\overset{\|}{C}}-C_6H_5}$$

Such crossed Aldol condensation reactions between an aromatic aldehyde (or ketone) and an aliphatic aldehyde or ketone in the presence of dilute alkali (base-catalysed) at room temperature to form unsaturated carbonyl compounds is called **Claisen-Schmidt reaction** or **Claisen condensation.**

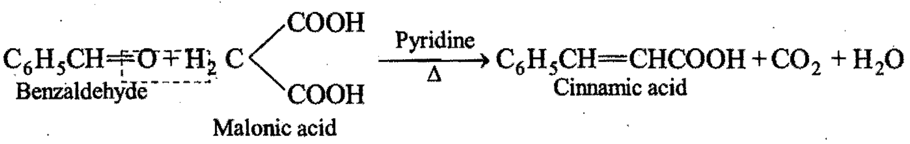
Note : Aliphatic esters (R—COOR') containing α-hydrogen atoms also undergo Claisen-Schmidt condensation with an aromatic aldehyde in presence of dilute alkali. For example,



$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + \underset{\text{Ethyl acetate}}{H_2HC-\overset{O}{\overset{\|}{C}}-OC_2H_5} \xrightarrow[(-H_2O)]{\text{Dil. NaOH}} \underset{\text{Ethyl cinnamate}}{C_6H_5CH{=}CH-\overset{O}{\overset{\|}{C}}-OC_2H_5}$$

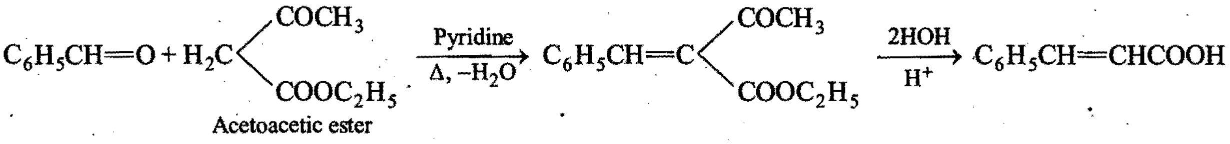
---

8. Knoevenagel reaction : Benzaldehyde on treatment with any reactive methylene compound, *e.g.*, malonic acid, malonic ester, acetoacetic ester, in the presence of pyridine base or ethanolic ammonia, forms cinnamic acid (α, β-unsaturated acid).



$$C_6H_5CH{=}O + H_2C(COOH)_2 \xrightarrow[\Delta]{\text{Pyridine}} C_6H_5CH{=}CHCOOH + CO_2 + H_2O$$

Benzaldehyde; Malonic acid; Cinnamic acid



$$C_6H_5CH{=}O + H_2C\begin{matrix}COCH_3\\COOC_2H_5\end{matrix} \xrightarrow[\Delta,\,-H_2O]{\text{Pyridine}} C_6H_5CH{=}C\begin{matrix}COCH_3\\COOC_2H_5\end{matrix} \xrightarrow[H^+]{2HOH} C_6H_5CH{=}CHCOOH$$

Acetoacetic ester

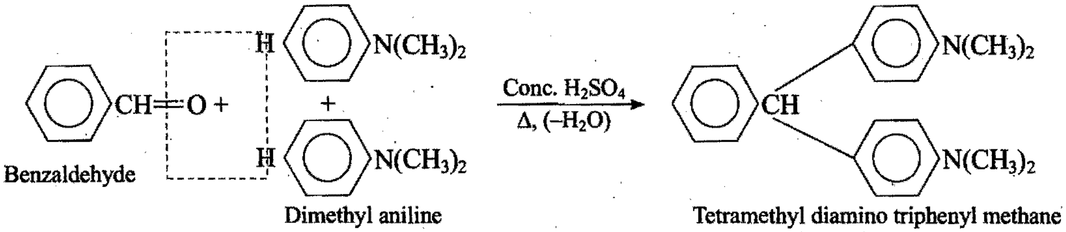
$$+ CH_3COOH + C_2H_5OH$$

9. Reaction with aniline : Benzaldehyde reacts with aniline and forms **Schiff base** (benzal aniline) or anils.

$$C_6H_5CH{=}O + H_2NC_6H_5 \xrightarrow[(-H_2O)]{H^+,\ \text{Warm}} C_6H_5CH{=}NC_6H_5$$

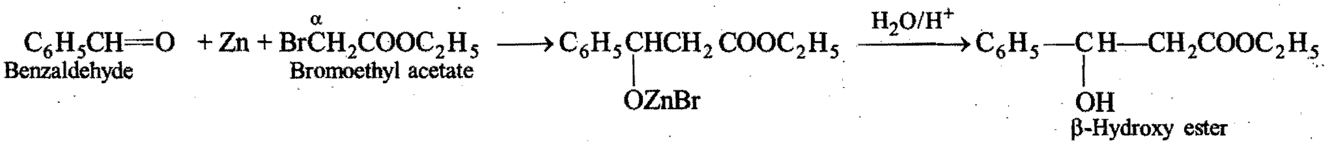
Benzaldehyde; Aniline; Benzylidene aniline (Schiff base)

10. Reaction of dimethyl aniline : Benzaldehyde condenses with tertiary aromatic amines in the presence of $ZnCl_2$ or H_2SO_4, forms triphenyl methane derivative, *i.e.*, **Malachite green.**



Tetramethyl diamino triphenyl methane (Malachite green)

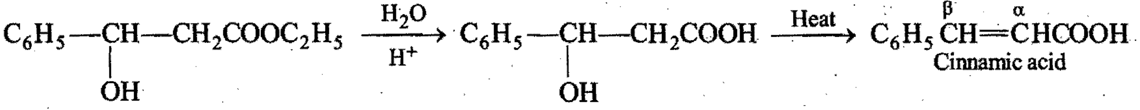
11. Reformatsky reaction : This reaction involves the treatment of aromatic aldehydes with α-halogenated ester in presence of metallic zinc to form β-hydroxy ester.



$$C_6H_5CH{=}O + Zn + \overset{\alpha}{Br}CH_2COOC_2H_5 \longrightarrow C_6H_5\underset{\displaystyle OZnBr}{\underset{|}{C}}HCH_2COOC_2H_5 \xrightarrow{H_2O/H^+} C_6H_5{-}\underset{\displaystyle OH}{\underset{|}{C}}H{-}CH_2COOC_2H_5$$

Benzaldehyde; Bromoethyl acetate; β-Hydroxy ester

β-hydroxy ester gives an acid on hydrolysis with dilute H_2SO_4, which on heating gives α, β-unsaturated acid.



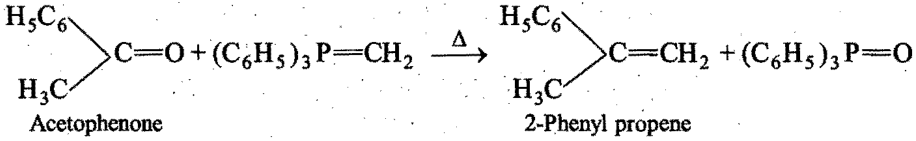
$$C_6H_5{-}\underset{\displaystyle OH}{\underset{|}{C}}H{-}CH_2COOC_2H_5 \xrightarrow[H^+]{H_2O} C_6H_5{-}\underset{\displaystyle OH}{\underset{|}{C}}H{-}CH_2COOH \xrightarrow{\text{Heat}} C_6H_5\overset{\beta}{C}H{=}\overset{\alpha}{C}HCOOH$$

Cinnamic acid

12. Wittig reaction : The reaction between a carbonyl compound and methylene triphenyl phosphorane (Wittig reagent) to give an alkene is known as Wittig reaction, *e.g.*,

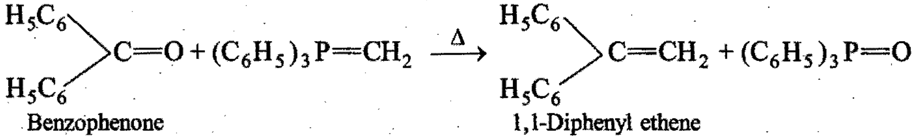
$$C_6H_5CH{=}O + (C_6H_5)_3P{=}CH_2 \xrightarrow{\Delta} C_6H_5CH{=}CH_2 + (C_6H_5)_3P{=}O$$

Benzaldehyde; Styrene; Triphenyl phosphine oxide



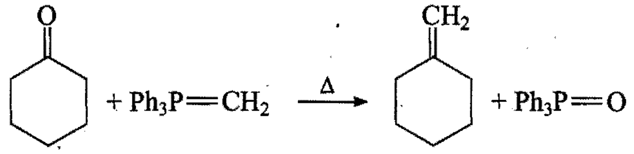
$$\begin{matrix}H_5C_6\\H_3C\end{matrix}\!\!>C{=}O + (C_6H_5)_3P{=}CH_2 \xrightarrow{\Delta} \begin{matrix}H_5C_6\\H_3C\end{matrix}\!\!>C{=}CH_2 + (C_6H_5)_3P{=}O$$

Acetophenone; 2-Phenyl propene

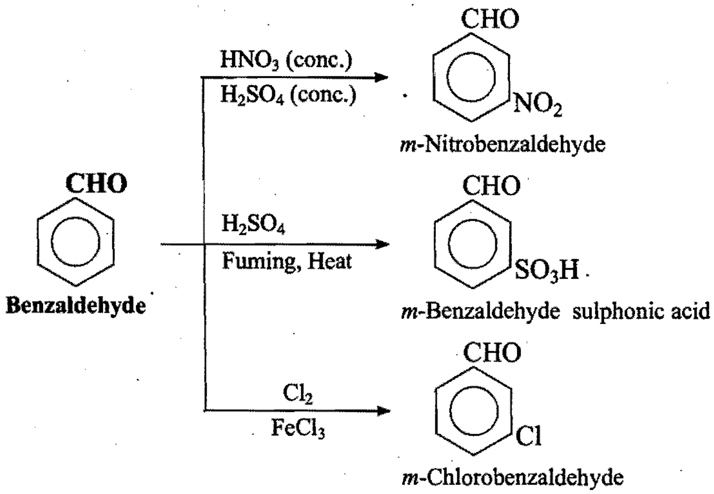


$$\begin{matrix}H_5C_6\\H_5C_6\end{matrix}\!\!>C{=}O + (C_6H_5)_3P{=}CH_2 \xrightarrow{\Delta} \begin{matrix}H_5C_6\\H_5C_6\end{matrix}\!\!>C{=}CH_2 + (C_6H_5)_3P{=}O$$

Benzophenone; 1,1-Diphenyl ethene



13. Substitution reactions of benzene nucleus : The benzene ring of benzaldehyde undergoes nitration, halogenation and sulphonation. The —CHO group is *meta*-directing and deactivating.



Uses : Benzaldehyde is used,

(i) in perfumery.

(ii) in manufacture of dyes.

(iii) in manufacture of benzoic acid, cinnamic acid, cinnamaldehyde, Schiff base, etc.

Tests : (i) Benzaldehyde forms a white precipitate with $NaHSO_3$ solution.

(ii) Benzaldehyde forms a yellow precipitate with 2 : 4 dinitrophenylhydrazine.

(iii) Benzaldehyde gives pink colour with Schiff reagent.

(iv) Benzaldehyde forms black precipitate or silver mirror with Tollens' reagent.

(v) Benzaldehyde on treatment with alkaline $KMnO_4$ and subsequent acidification gives a white precipitate of benzoic acid on cooling.

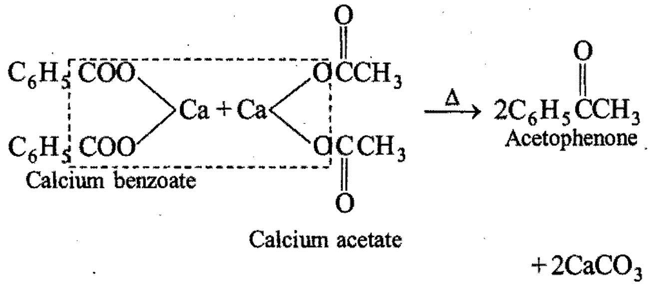
16.17 ACETOPHENONE (METHYL PHENYL KETONE); $C_6H_5COCH_3$, (ACETYL BENZENE)

Methods of Preparation

1. Friedel-Crafts reaction : Acetyl chloride reacts with benzene in presence of anhydrous aluminium chloride to form acetophenone.

$$\underset{\text{Benzene}}{C_6H_5H} + \underset{\text{Acetyl chloride}}{ClCOCH_3} \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

2. By distillation of a mixture of calcium benzoate and calcium acetate.



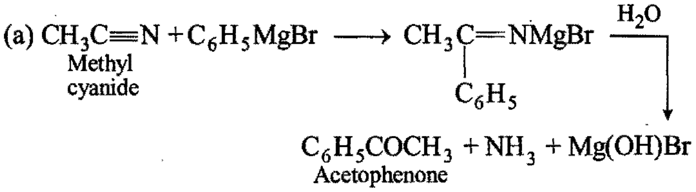
3. By methylation of benzaldehyde with diazomethane.

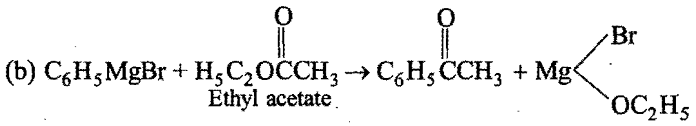
$$C_6H_5CHO + CH_2N_2 \longrightarrow C_6H_5COCH_3 + N_2$$

4. By treating benzoyl chloride with dimethyl cadmium.

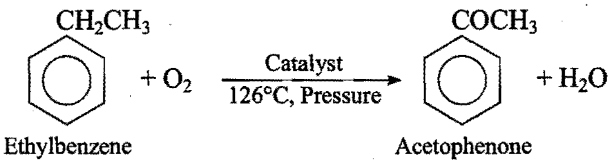
$$2C_6H_5COCl + (CH_3)_2Cd \longrightarrow 2C_6H_5COCH_3 + CdCl_2$$

5. By Grignard reagents:

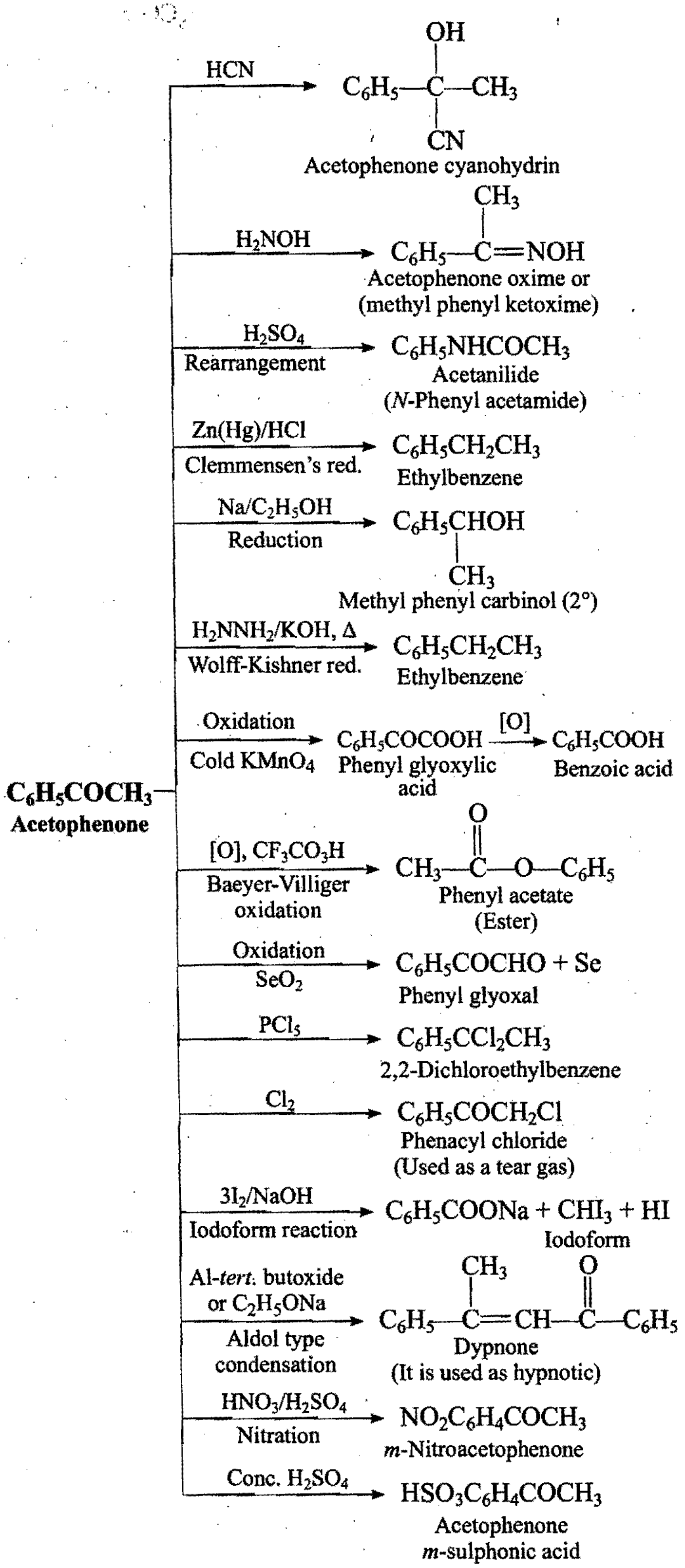




6. Commercial preparation : Ethylbenzene is oxidized with air at 126°C under pressure in presence of a catalyst manganese acetate.



Properties : It is a colourless crystalline compound with melting point 20°C and boiling point 202°C. It has characteristic pleasant odour. It is slightly soluble in water. Chemically, it is similar to acetone. However, it does not form addition compound with sodium bisulphite due to steric hindrance offered by the phenyl group. It gives usual **electrophilic substitution reactions** of the benzene ring (*i.e.*, halogenation, nitration and sulphonation) in *meta*-position. Its other important reactions are summarized as follows:

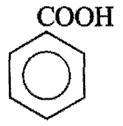


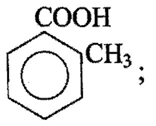
Acetophenone and benzophenone do not form bisulphite addition compound with $NaHSO_3$ due to steric factors.

Uses : It is used in perfumery and as a sleep producing drug.

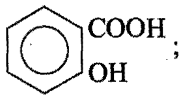
16.18 AROMATIC CARBOXYLIC ACIDS

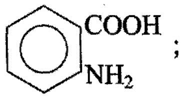
Aromatic acids are compounds in which one or more carboxyl groups (—COOH) are attached directly to the aromatic ring. Some acids are listed below:

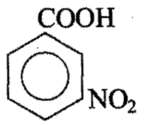

Benzoic acid


2-Methylbenzoic acid (o-Toluic acid)

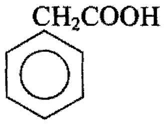

Benzene-1,2-dicarboxylic acid (Phthalic acid)

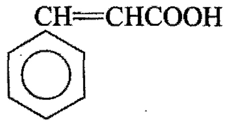

2-Hydroxy benzoic acid (Salicylic acid)


2-Aminobenzoic acid (Anthranilic acid)


3-Nitrobenzoic acid (m-Nitrobenzoic acid)

Aromatic acids containing —COOH group in the side-chain are considered as aryl substituted aliphatic acids. For example,


2-Phenylethanoic acid (Phenyl acetic acid)


3-Phenylprop-2-enoic acid (Cinnamic acid)

Benzoic acid, C_6H_5COOH or 

Benzoic acid is found in nature in combined state as ester in balsams and in free state in some resins like gum benzoin. It also occurs in urine of horses in the form of hippuric acid (benzoyl glycine).

Methods of Preparation

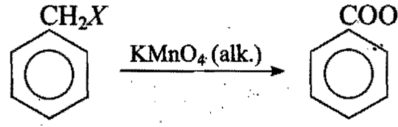
1. Laboratory method : In laboratory, benzoic acid is obtained by oxidation of benzyl chloride in presence of alkaline $KMnO_4$.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + 2KOH + 2[O] \longrightarrow C_6H_5COOK + KCl + 2H_2O$$

The reaction actually takes place in following stages:

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{H_2O} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow{[O]} \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

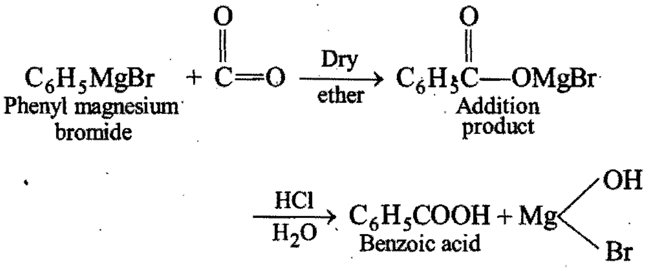
Side-chains, *e.g.*, $—CH_2Cl$, $—CH_2NH_2$ or $—CH_2OH$, etc., attached to benzene nucleus are oxidised to —COOH group by alkaline $KMnO_4$:



(X = —Cl, —NH₂, —OH, etc.)

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow[\text{(ii) Dil. } H_2SO_4]{\text{(i) } KMnO_4/KOH, \Delta} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

2. From Grignard reagent (Carbonation of Grignard reagent) : Grignard reagent, (C_6H_5MgBr), forms addition product with bubbled carbon dioxide (or dry ice is employed as a source of CO_2) which on hydrolysis with HCl yields benzoic acid.



$$\underset{\substack{\text{Phenyl magnesium}\\ \text{bromide}}}{C_6H_5MgBr} + O{=}C{=}O \xrightarrow[\text{ether}]{\text{Dry}} \underset{\substack{\text{Addition}\\ \text{product}}}{C_6H_5\overset{O}{\overset{\|}{C}}—OMgBr}$$

$$\xrightarrow[H_2O]{HCl} \underset{\text{Benzoic acid}}{C_6H_5COOH} + Mg\begin{cases}OH\\ Br\end{cases}$$

3. From phenyl cyanide : Phenyl cyanide (benzonitrile) on hydrolysis with mineral acid yields benzoic acid.

$$\underset{\text{Phenyl cyanide}}{C_6H_5CN} + 2H_2O \xrightarrow{H^+ \text{ or } OH^-} \underset{\text{Benzoic acid}}{C_6H_5COOH} + NH_3$$

Phenyl cyanide may be obtained either from chlorobenzene or sodium benzene sulphonate or benzene diazonium salts, etc.

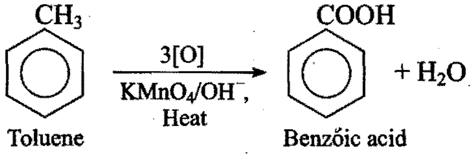
4. From benzene by Friedel-Crafts reaction : Benzene is converted into benzoyl chloride by action of carbonyl chloride in presence of anhydrous $AlCl_3$. Benzoyl chloride on hydrolysis gives benzoic acid.

$$C_6H_6 + COCl_2 \xrightarrow[\Delta]{\text{Anhyd. } AlCl_3} C_6H_5COCl + HCl$$

$$C_6H_5COCl + H_2O \longrightarrow C_6H_5COOH + HCl$$

$$\text{and } C_6H_5H + CO_2 \xrightarrow[\Delta]{\text{Anhyd. } AlCl_3} C_6H_5COOH$$

5. From toluene : Toluene on oxidation forms benzoic acid. The oxidation can be done with dilute nitric acid or alkaline potassium permanganate or chromic trioxide in glacial acetic acid or Co-Mn acetate, etc. The alkyl side-chain gets oxidized to —COOH group irrespective of the length of the chain.

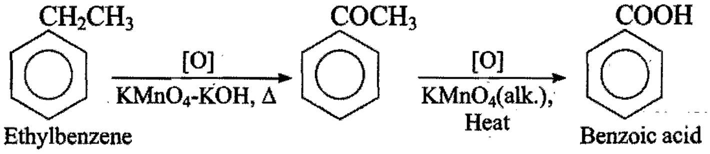


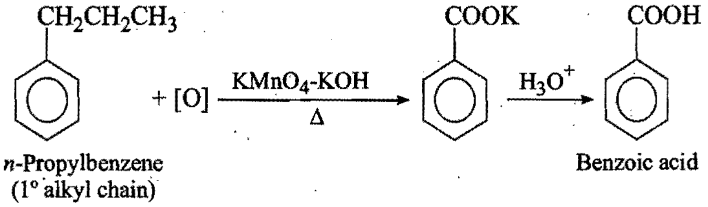
$$[—CH_3 \xrightarrow{[O]} —CH_2OH \xrightarrow{[O]} —CHO \xrightarrow{[O]} —COOH]$$

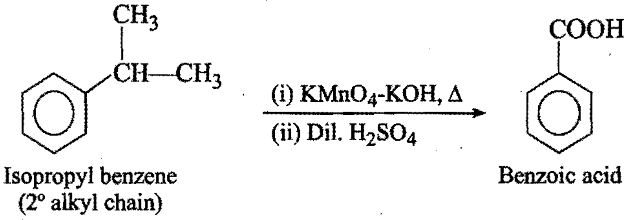
When a mixture of toluene and air vapours is passed over heated V_2O_5 catalyst, benzoic acid is formed.

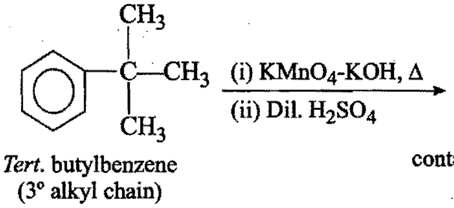
$$\underset{\text{Vapours}}{2C_6H_5CH_3} + 3[O]_2 \xrightarrow[300\text{-}400°C]{V_2O_5} 2C_6H_5COOH + 2H_2O$$

Homologues of benzene (irrespective of side-chain length) on oxidation with alkaline potassium permanganate finally gives benzoic acid. Initial attack is at α-carbon.





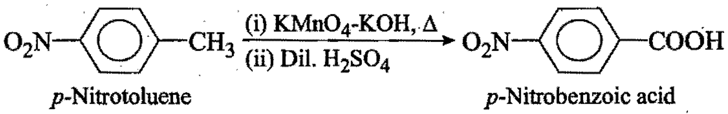




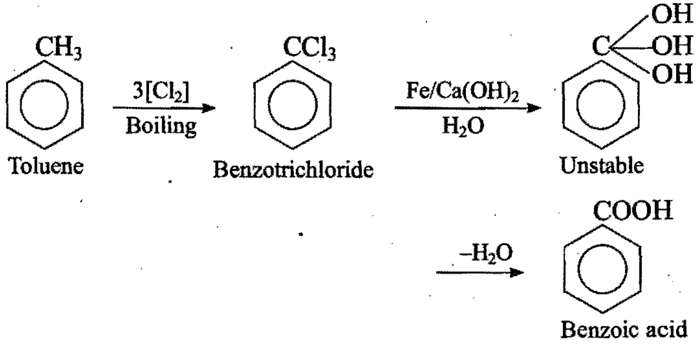
No action

(As 3° alkyl chain contains no benzylic hydrogen)

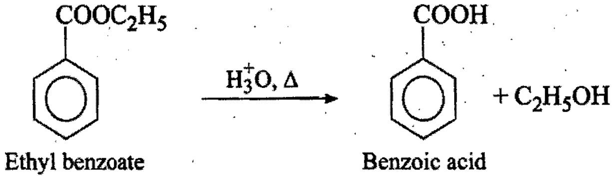
Presence of electron withdrawing groups ($—NO_2$, $—SO_3H$, $—X$, $—COOH$, $—OH$, ... etc.) in the benzene ring increases the reactivity of benzylic hydrogens and hence p-nitrotoluene is much more easily oxidised as compared to toluene.



6. By hydrolysis of benzotrichloride : Hydrolysis is done with aqueous NaOH or milk of lime in presence of iron as catalyst.



7. By hydrolysis of esters : Hydrolysis of esters with mineral acids gives directly carboxylic acids.

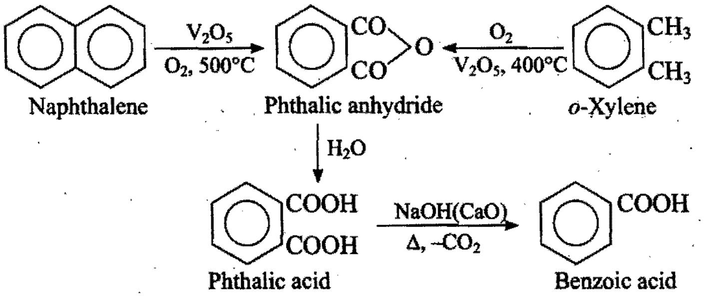


Manufacture or Industrial Preparation

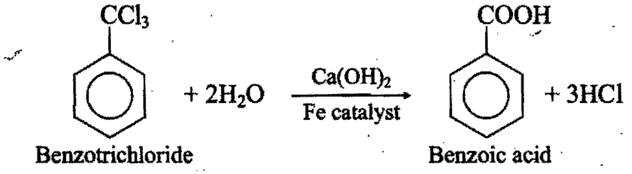
1. Oxidation of toluene, naphthalene or *o*-xylene : Oxidation of toluene is done with air in presence of vanadium pentoxide as a catalyst or cobalt and manganese acetate as catalyst at 170°C.

$$\underset{\text{Toluene}}{2C_6H_5CH_3} + 3O_2 \xrightarrow[170°C]{\text{Co-Mn acetate}} \underset{\text{Benzoic acid}}{2C_6H_5COOH} + 2H_2O$$

Oxidation of naphthalene or *o*-xylene with air using V_2O_5 as catalyst, yields phthalic acid which by partial decarboxylation yields benzoic acid.



2. By hydrolysis of benzotrichloride : Benzotrichloride obtained by passing chlorine through boiling toluene at 110°C in presence of light is hydrolysed with milk of lime in presence of iron catalyst when benzoic acid is obtained.



Physical properties : (i) Benzoic acid is a colourless crystalline compound. It melts at 121°C.

(ii) It is sparingly soluble in cold water but fairly soluble in hot water. It is also soluble in alcohol and ether.

(iii) It readily sublimes and is volatile in steam.

(iv) Its vapours are irritating and cause coughing and sneezing.

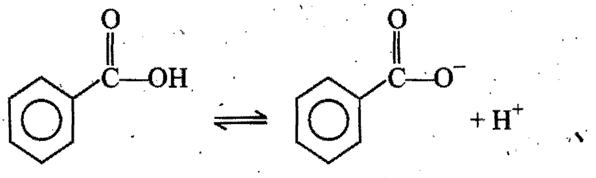
Comparison of Acidic Character of Carboxylic Acids with Alcohols and Phenols

(a) Carboxylic acids and alcohols : Alkoxide anion from alcohol does not show resonance and is not stabilized since, the alkyl group has electron repelling inductive effect. This lack of stabilization is responsible for a very weak acidity of alcohols than carboxylic acids.

$$\underset{\text{Alcohol}}{R—OH} \rightleftharpoons \underset{\substack{\text{No resonance}\\\text{hybrid}}}{R—O^-} + H^+$$

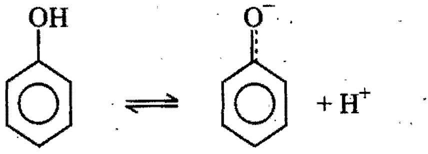
For example, acetic acid is about ten times stronger acid than ethyl alcohol though both contain an —OH group. Both carboxylic acid and the carboxylate ions are resonance stabilized and carboxylic acids have tendency to give H^+ ions forming more stable carboxylate ion. However, neither the alcohols (R—OH) nor their alkoxide ions ($R—O^-$) are stabilized by resonance.

(b) Carboxylic acids and phenols : *Carboxylic acids are stronger acids than phenols.* The difference in their relative acidic strengths can be explained by considering the resonating structures of carboxylate ion and phenoxide ion.



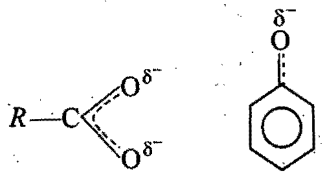
Carboxylate ion

$$(R—COOH \rightleftharpoons R—COO^- + H^+)$$



Phenoxide ion

The resonance hybrid structures may be represented as:

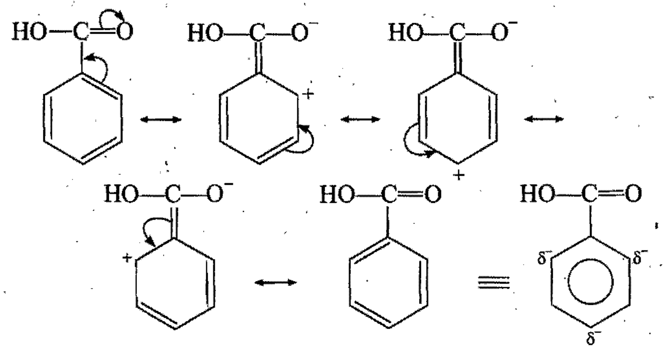


In carboxylate ion, the negative charge is equally distributed over two electronegative oxygen atoms while in phenoxide ion it is present only on one oxygen. Therefore, carboxylate ion is much more resonance stabilized than phenoxide ion. Thus, the release of proton (H^+) from carboxylic acids is much easier than from phenols. In other words, carboxylic acids are stronger acids than phenols.

Chemical properties : Benzoic acid exhibits the reactions of —COOH group and benzene nucleus. The main reactions of benzoic acid are :

(i) Salt formation : Benzoic acid is a weak acid. However, it is slightly stronger than acetic acid due to presence of benzene nucleus and being resonance stabilized.

Carboxylic group (—COOH) attached to benzene nucleus is *m*-directing and deactivating group. Electrophile can attack only at the *meta* (*m*-) positions with decreased reactivity.



Benzoic acid forms salts with strong alkalies and decomposes metal carbonates and bicarbonates, giving effervescence of CO_2 (a laboratory test of —COOH group).

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaOH \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + H_2O$$

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2$$

$$2C_6H_5COOH + Na_2CO_3 \longrightarrow 2C_6H_5COONa + CO_2 + H_2O$$

It combines with ammonia to form ammonium benzoate.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NH_3 \longrightarrow \underset{\text{Ammonium benzoate}}{C_6H_5COONH_4}$$

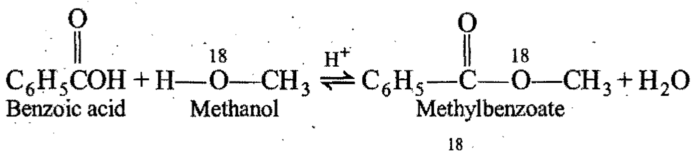
[Ammonium benzoate on heating forms benzamide and then phenyl cyanide.

$$C_6H_5COONH_4 \xrightarrow[(-H_2O)]{\text{Heat}} \underset{\text{Benzamide}}{C_6H_5CONH_2}$$

$$\xrightarrow[\Delta,\,(-H_2O)]{P_2O_5 \text{ or } POCl_3} \underset{\text{Benzonitrile}}{C_6H_5CN]}$$

(ii) Ester formation : Benzoic acid reacts with alcohols to form esters in presence of small amount of conc. H_2SO_4 on heating (Esterification).

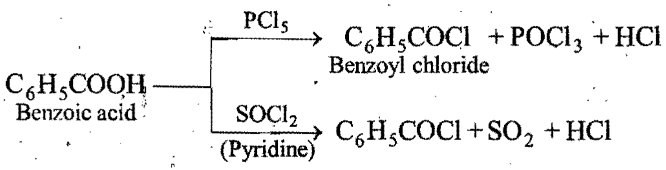
$$C_6H_5COOH + \underset{\text{Ethanol}}{HOC_2H_5} \xrightarrow[\Delta,\,(-H_2O)]{\text{Conc. } H_2SO_4} \underset{\text{Ethylbenzoate}}{C_6H_5COOC_2H_5}$$



$$\underset{\text{Benzoic acid}}{C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}OH} + \underset{\text{Methanol}}{H—\overset{18}{O}—CH_3} \overset{H^+}{\rightleftharpoons} \underset{\text{Methylbenzoate}}{C_6H_5—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{18}{O}—CH_3} + H_2O$$

($\overset{18}{O}$-Labelled)

(iii) Reaction with PCl_5 or thionyl chloride : Benzoic acid reacts with phosphorus pentachloride or thionyl chloride to form benzoyl chloride.



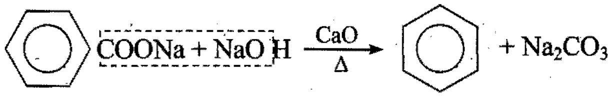
$$\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow{PCl_5} \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + POCl_3 + HCl$$

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow[\text{(Pyridine)}]{SOCl_2} C_6H_5COCl + SO_2 + HCl$$

(iv) Reduction with $LiAlH_4$: Benzoic acid undergoes reduction with $LiAlH_4$. It is converted into benzyl alcohol.

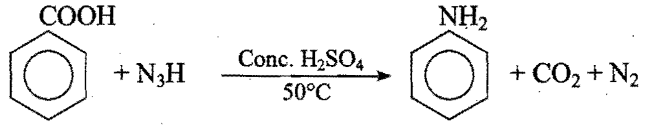
$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + 2H_2 \xrightarrow{LiAlH_4} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + H_2O$$

(v) Decarboxylation : Benzoic acid or its sodium salt when heated with soda lime yields benzene. This reaction is termed as decarboxylation.



Sodium benzoate Benzene

(vi) Schmidt reaction : When heated with hydrazoic acid in presence of cold, concentrated H_2SO_4 in chloroform at 50°C, aniline is formed.



Benzoic acid Aniline

(vii) Heating of calcium benzoate :

(a) Benzophenone is formed when calcium benzoate is heated alone.

$$\underset{\text{Calcium benzoate}}{(C_6H_5COO)_2Ca} \xrightarrow{\text{Heat}} \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + CaCO_3$$

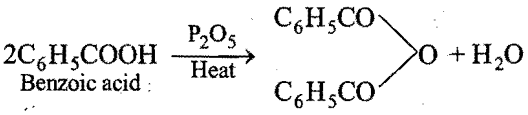
(b) When mixture of calcium benzoate and calcium formate is heated, benzaldehyde is formed.

$$\underset{\text{Calcium benzoate}}{(C_6H_5COO)_2Ca} + (HCOO)_2Ca \xrightarrow{\text{Heat}} \underset{\text{Benzaldehyde}}{2C_6H_5CHO} + 2CaCO_3$$

(c) When a mixture of calcium benzoate and calcium acetate is heated, acetophenone is formed.

$$\underset{\text{Calcium benzoate}}{(C_6H_5COO)_2Ca} + \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\text{Heat}} \underset{\text{Acetophenone}}{2C_6H_5COCH_3} + 2CaCO_3$$

(viii) Anhydride formation : When benzoic acid is heated with P_2O_5 or acetic anhydride, benzoic anhydride is formed (dehydration).



$$\underset{\text{Benzoic acid}}{2C_6H_5COOH} \xrightarrow[\text{Heat}]{P_2O_5} \begin{matrix} C_6H_5CO \\ C_6H_5CO \end{matrix}\!\!\!>O + H_2O$$

Benzoic anhydride

(ix) Hunsdiecker reaction : When silver salt of acid (in xylene solution) is heated with halogens (Br_2 or Cl_2) in CCl_4, aryl halide is formed.

$$\underset{\text{Silver benzoate}}{C_6H_5COOAg} + \underset{(Br_2 \text{ or } Cl_2)}{X_2} \xrightarrow[\text{Heat}]{\text{in } CCl_4} \underset{\text{Phenyl halide}}{C_6H_5—X} + CO_2\uparrow + AgX$$

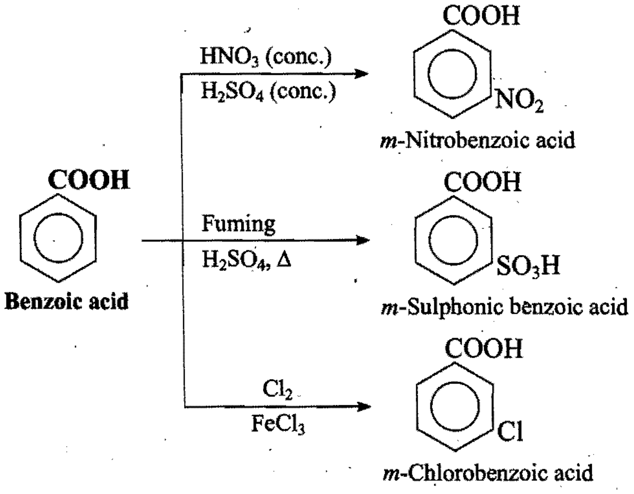
(x) Action of manganous oxide (MnO) : Aromatic aldehydes and ketones can be obtained by decarboxylation and dehydration of aromatic acids.

$$C_6H_5COOH + \underset{\text{Formic acid}}{HCOOH} \xrightarrow[300°C]{MnO} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + H_2O + CO_2$$

$$C_6H_5COOH + \underset{\text{Acetic acid}}{HOOCCH_3} \xrightarrow[300°C]{MnO} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + H_2O + CO_2$$

$$\underset{\text{Benzoic acid (2 moles)}}{C_6H_5COOH + HOOCC_6H_5} \xrightarrow[300°C]{MnO} \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + H_2O + CO_2$$

(xi) Substitution reactions of benzene ring : The benzene ring of benzoic acid undergoes the usual electrophilic substitution reactions. The —COOH group is *meta*-directing and deactivates the benzene ring.



Uses : Benzoic acid is used,

(i) in medicine in the form of its salts especially as urinary antiseptic.

(ii) as sodium benzoate for preservation of food such as fruit juices, tomato ketchup, pickles, etc.

(iii) in the preparation of aniline blue.

(iv) in treatment of skin diseases like eczema.

Tests : (i) Benzoic acid dissolves in hot water but separates out in the form of white shining flakes on cooling.

(ii) It evolves CO_2 with sodium bicarbonate, *i.e.*, it gives effervescence with sodium dicarbonate.

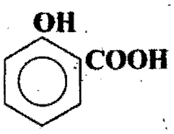
(iii) Neutral ferric chloride gives a buff coloured (pale dull yellow) precipitate.

(iv) When warmed with ethyl alcohol and a little conc. H_2SO_4, a fragrant odour of ethylbenzoate is obtained.

(v) When heated strongly with soda lime, benzene vapours are evolved which are inflammable.

16.19 SOME IMPORTANT AROMATIC ACIDS

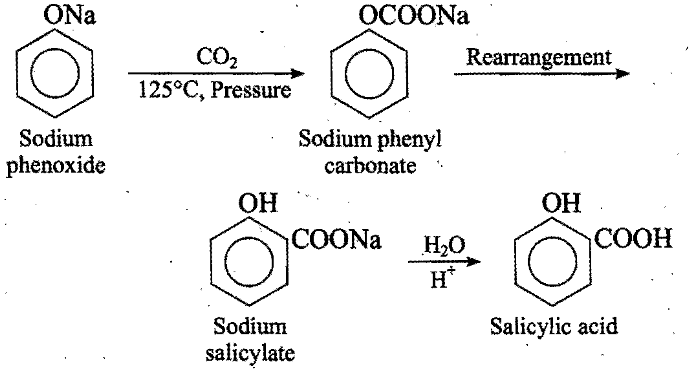
1. Salicylic Acid (*o*-Hydroxy benzoic acid) or



Salicylic acid is present in many essential oils in the form of esters. Oil of winter green is a methyl ester of salicylic acid.

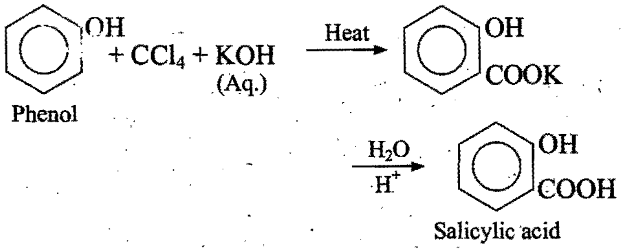
Methods of Preparation

1. Kolbe-Schmidt reaction : Carbon dioxide is passed over dry sodium phenoxide in a sealed tube at 125°C under pressure.



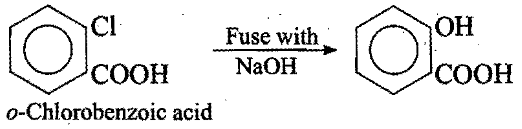
It is a commercial method. In fact, the reaction yields both *o*- and *p*-isomers. Salicylic acid being more volatile is separated by steam distillation.

2. Reimer-Tiemann reaction : Phenol on refluxing with carbon tetrachloride and alkali solution, gives a mixture of *o*- and *p*-hydroxy benzoic acids.

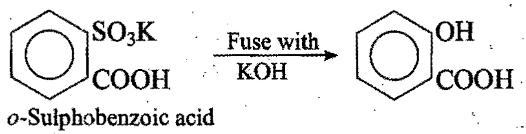


3. The following benzene derivatives can be used to prepare salicylic acid.

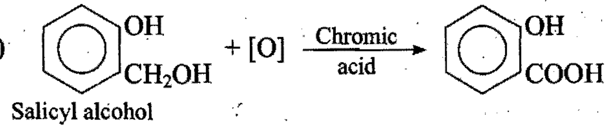
(a)



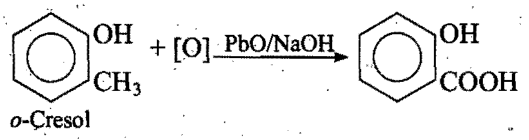
(b)



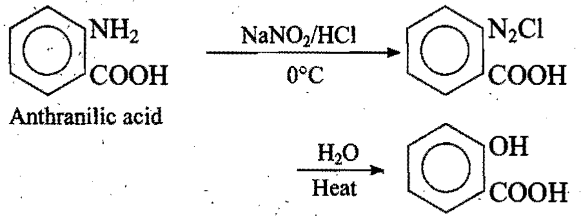
(c)



(d)

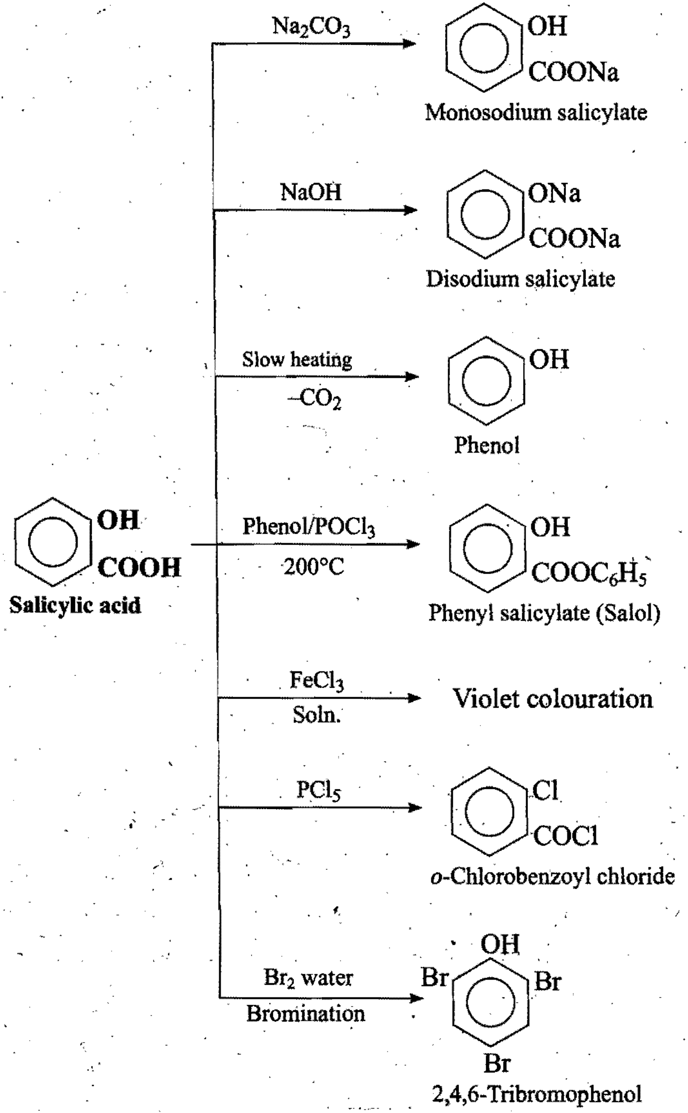


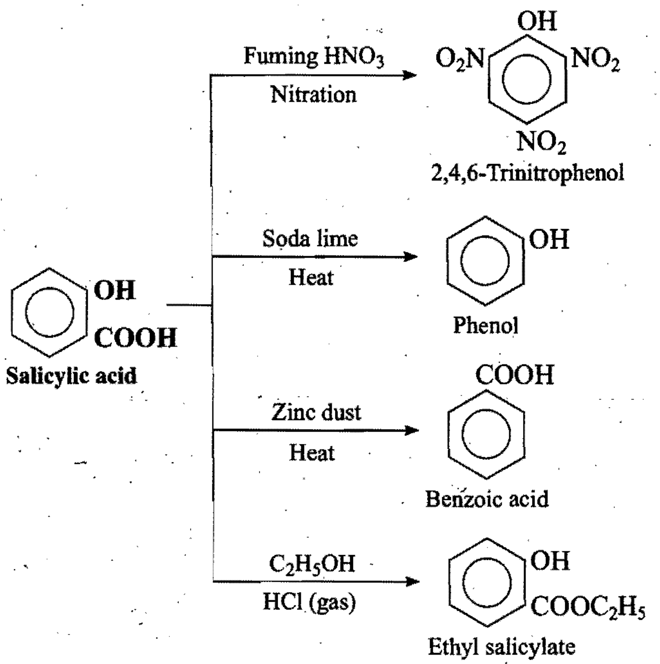
(e)



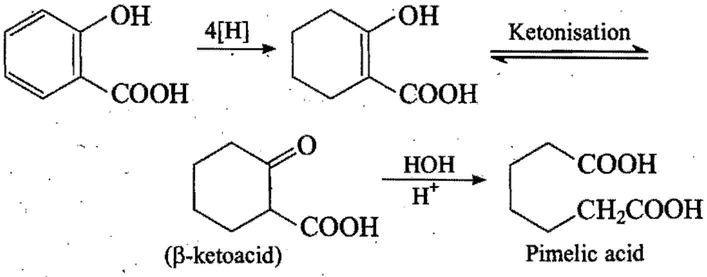
Properties : It is a colourless needle shaped crystalline compound and its melting point is 156°C. It is sparingly soluble in cold water but readily soluble in hot water, alcohol, ether and chloroform. It is steam volatile. It is poisonous in nature. However, it is used in medicine internally and externally as antipyretic and antiseptic.

Chemically, it exhibits the properties of both phenol and acid.



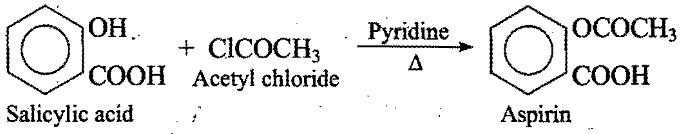


Reduction : On reduction with sodium and isopentanol, salicylic acid yields pimelic acid.



Salicylic acid forms the following important compounds:

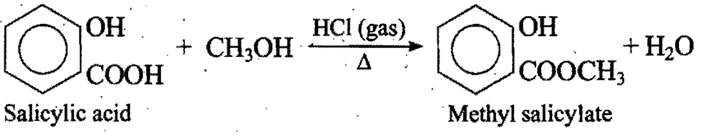
(i) Acetyl salicylic acid (Aspirin) : It is obtained by heating salicylic acid with acetyl chloride or acetic anhydride and glacial acetic acid or sodium acetate or a few drops of conc. H_2SO_4 or in presence of phosphoric acid.



It is a white solid, m.pt. 135°C.

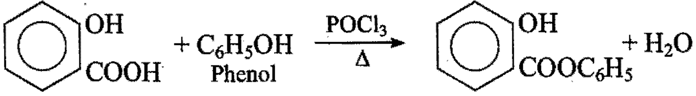
It is used as antipyretic and pain killer (analgesic action).

(ii) Methyl salicylate : It is formed by direct esterification of salicylic acid with methyl alcohol in presence of HCl gas or conc. H_2SO_4.



It is an oily liquid (**oil of winter green**) with pleasant odour b.pt. 224°C. It is used in perfumery and as a flavouring material. It is also used in medicine in the treatment of rheumatic pain and as a remedy for aches, sprains and bruises. It is used for making of **iodex.**

(iii) Phenyl salicylate (Salol): It is obtained by heating salicylic acid alone at 200°C or with phenol in presence of $POCl_3$



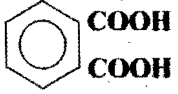
Salicylic acid Phenyl salicylate

It is a white solid, m.pt. 43°C.

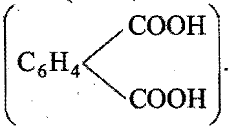
It is a good internal antiseptic. It is used in making of toothpastes. Salol absorbs ultraviolet light and its main use now is as sun-screening agent and stabilizer of plastics.

2. Phthalic acid (1,2-Benzene dicarboxylic acid)

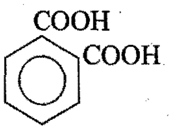
or



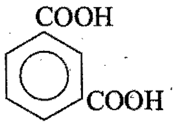
There are three (*ortho, meta* and *para*) benzene dicarboxylic acids



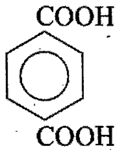
$$\left(C_6H_4\begin{matrix}COOH\\COOH\end{matrix}\right).$$



Benzene-1,2-dicarboxylic acid (Phthalic acid),



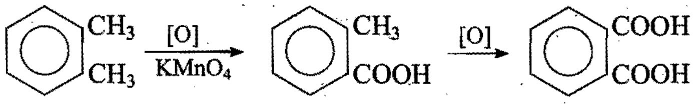
Benzene-1,3-dicarboxylic acid (Isophthalic acid),



Benzene-1,4-dicarboxylic acid (Terephthalic acid)

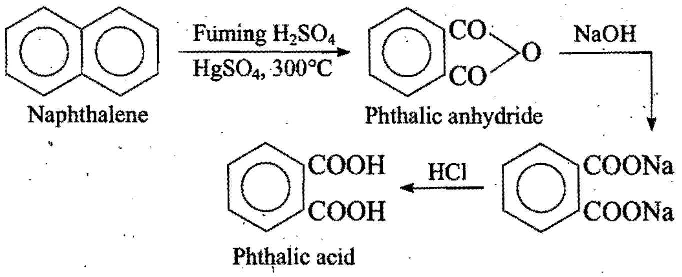
Phthalic acid is distinguished from the *meta* and *para* isomers, as it forms phthalic anhydride on heating (*meta* and *para* do not).

Preparation : Phthalic acid is formed by oxidation of *o*-xylene or *o*-toluic acid with dilute HNO_3 or potassium permanganate.



o-Xylene *o*-Toluic acid Phthalic acid

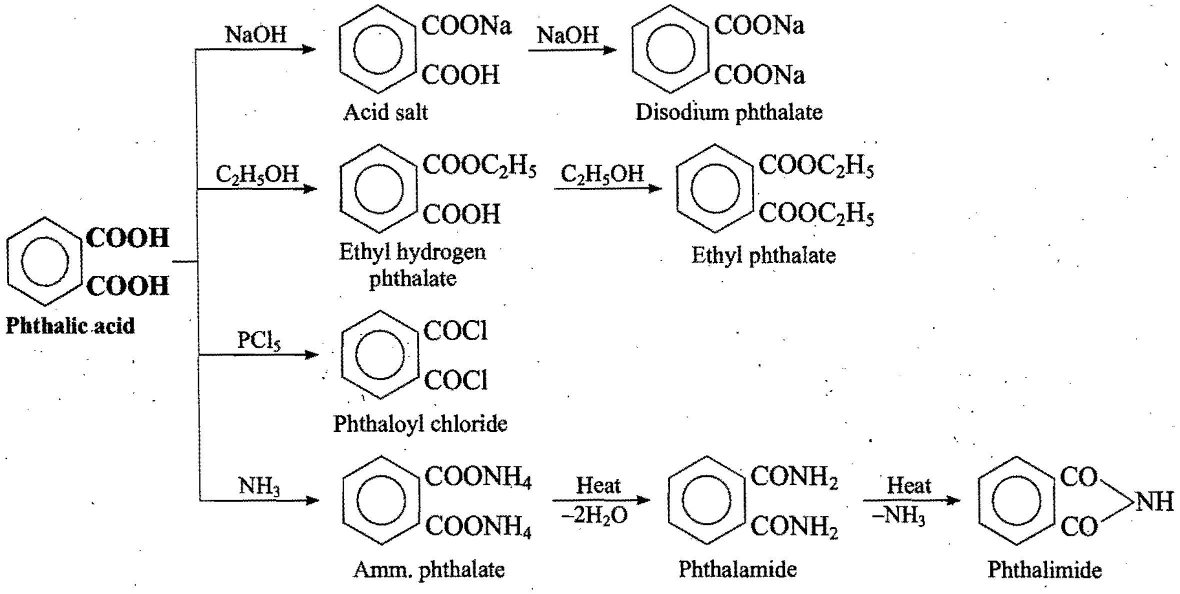
In laboratory, it is prepared by oxidation of naphthalene with fuming sulphuric acid in presence of mercuric sulphate at 300°C. The product is phthalic anhydride which on boiling with alkali and acidification gives free phthalic acid.



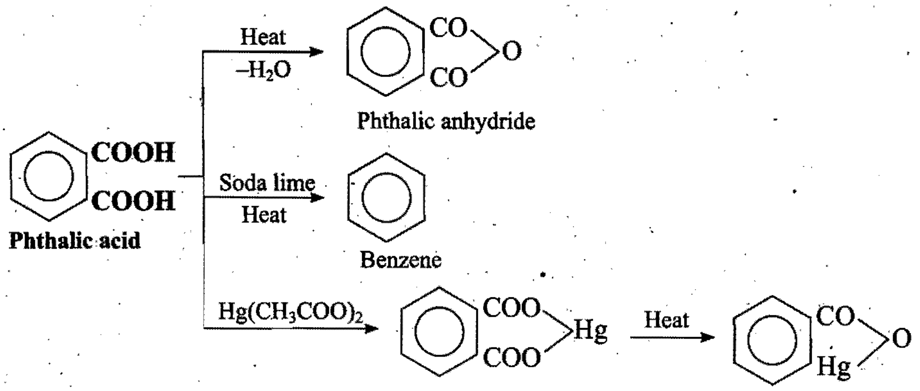
Naphthalene Phthalic anhydride Phthalic acid

Industrially, phthalic acid is obtained by passing vapours of naphthalene with excess of air over heated vanadium pentoxide at 400°C. Phthalic anhydride is formed which is converted into phthalic acid.

Properties : It is a colourless crystalline compound. Its melting point is not sharp (195 – 213°C). It is sparingly soluble in cold water but soluble in hot water, alcohol, ether, benzene, etc. It is a dibasic acid and gives usual reactions of two —COOH groups.



Phthalic acid Acid salt Disodium phthalate Ethyl hydrogen phthalate Ethyl phthalate Phthaloyl chloride Amm. phthalate Phthalamide Phthalimide



It is used in the manufacture of plastics, dyes and other compounds such as phthalic anhydride, phthalimide, anthraquinone and fluorescein, etc.

3. Cinnamic acid (β-Phenyl acrylic acid), $C_6H_5CH{=}CHCOOH$

Methods of Preparation

It is prepared from benzaldehyde by the following three methods:

1. By Perkin's reaction : It involves the treatment of benzaldehyde with acetic anhydride in presence of sodium acetate at 180°C.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + (CH_3CO)_2O \xrightarrow[180°C]{CH_3COONa} \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CHCOOH} + CH_3COOH$$

2. By Claisen condensation : It involves the treatment of benzaldehyde with ethyl acetate in presence of sodium ethoxide followed by hydrolysis.

$$C_6H_5CHO + \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} \xrightarrow{C_2H_5ONa}$$

$$\underset{\text{Ester}}{C_6H_5CH{=}CHCOOC_2H_5} \xrightarrow[H^+]{H_2O} \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CHCOOH} + C_2H_5OH$$

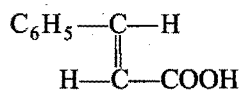
3. By Knoevenagel reaction : It involves the treatment of benzaldehyde with malonic acid in alcoholic ammonia or in the presence of pyridine.

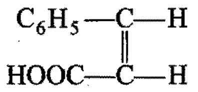
$$C_6H_5CHO + \underset{\text{Malonic acid}}{CH_2(COOH)_2} \xrightarrow[Heat]{NH_3} C_6H_5CH{=}CHCOOH + CO_2 + H_2O$$

On commercial scale, it is prepared by heating benzal chloride with sodium acetate at 200°C.

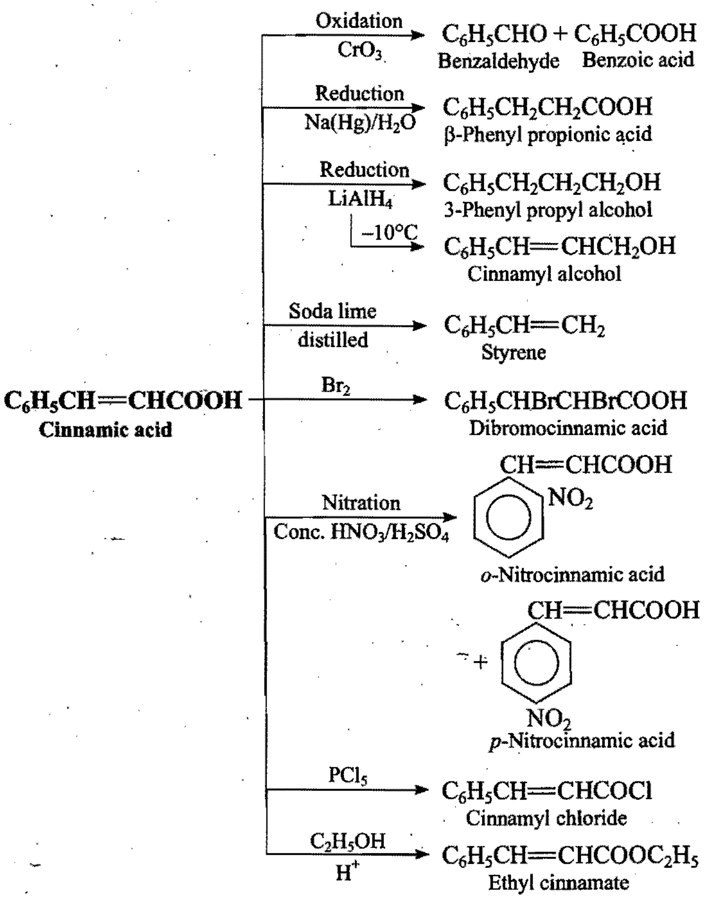
$$\underset{\text{Benzal chloride}}{C_6H_5CHCl_2} + H_2CHCOONa \longrightarrow \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CHCOOH} + NaCl + HCl$$

Properties : Cinnamic acid is a colourless crystalline compound. Its melting point is 133°C. It is almost insoluble in water. It exhibits geometrical isomerism.


Trans-form
(Cinnamic acid)

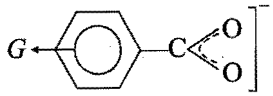

Cis-form
(Allocinnamic acid)

It behaves as an unsaturated acid and the *trans*-form is named as cinnamic acid (stable form) which occurs in nature both free and as esters in balsams and resins. It also gives reactions of benzene nucleus.

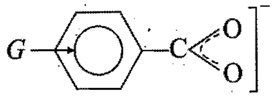


16.20 EFFECT OF SUBSTITUENTS ON ACID STRENGTH OF SUBSTITUTED AROMATIC ACIDS

As discussed earlier that an electron withdrawing substituent decreases electron density, stabilize the anion and thus, increases the acidity of carboxylic acid. An electron releasing substituent increases electron density (negative charge) destabilize the anion and thus, decreases acidity.

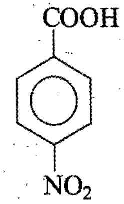


G-electron withdrawing group, increases acidity (—NO_2, —CN, —COOH, —Cl)



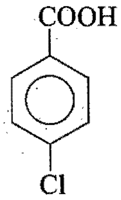
G-electron releasing group, decreases acidity (—CH_3, —OCH_3, —NH_2, —OH)

(i) The effect of substituent on aromatic acid, infact, is determined by their inductive and resonance effect. Inductive effect affects all positions, *i.e.*, *o*-, *m*-, and *p*-, however resonance effect affects only *o*- and *p*- positions. Some examples are,



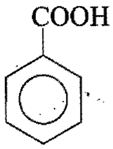
p-Nitro benzoic acid (pK_a 3.44)

>



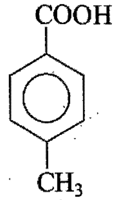
p-Chloro benzoic acid (pK_a 3.99)

>



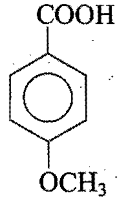
Benzoic acid (pK_a 4.19)

>



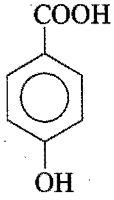
p-Toluic acid (pK_a 4.38)

>

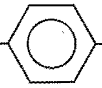


p-Anisic acid (pK_a 4.48)

>



p-Hydroxy benzoic acid (pK_a 4.58)

The substituent effects on acid strength of *p*- substituted benzoic acid, G——COOH is given below:

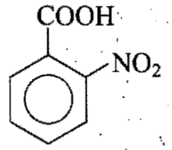
Electron withdrawing groups (*G*)

	—NO_2 >	—CN >	—CHO >	Br >	Cl
pK_a	3.44	3.55	3.75	3.96	4.0

Electron releasing groups (*G*)

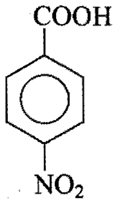
	—CH_3 >	—OCH_3 >	—OH >	—NH_2
pK_a	4.38	4.48	4.58	4.80

(ii) In case of *o*-, *m*-, and *p*-nitro benzoic acids, the —NO_2 group exerts greater **electron withdrawing effect** when present in the *o*- and *p*- positions. So, *o*- and *p*- nitro benzoic acids are stronger than *m*-nitro benzoic acid which is, of course, stronger than benzoic acid.



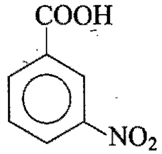
o-Nitro benzoic acid (pK_a 2.17)

>



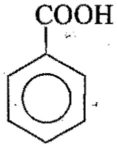
p-Nitro benzoic acid (pK_a 3.41)

>



m-Nitro benzoic acid (pK_a 3.45)

>

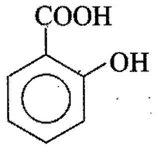


Benzoic acid (pK_a 4.19)

(iii) In case of *o*-substituted benzoic acids, they are usually stronger acid than benzoic acid irrespective of the nature of the substituent (whether electron withdrawing or electron releasing). This is called ***ortho* effect** and is probably due to intramolecular H-bonding or a combination of steric and electronic factors.

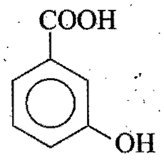
In case, both resonance and inductive effects operate in the molecule, the resonance effect being stronger dominates over inductive effect. For example, the nitro group exerts greater electron withdrawing effect when present in the *o*- and *p*-positions. So *o*- and *p*-nitro benzoic acids are stronger than *m*-nitrobenzoic acid which is, ofcourse, stronger than benzoic acid.

In case of hydroxy (or methoxy) benzoic acids, they display both kinds of effect and there is a decrease in electron density at all positions due to inductive effect, but increase in electron density at *o*- and *p*-positions due to resonance effect. So, *o*- and *p*-hydroxy benzoic acids should be weaker than benzoic acid, but actually *o*-isomer is strongest among the three hydroxy benzoic acids due to intramolecular H-bonding. Hence, the following sequences are observed in order of acidity.



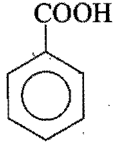
o-Hydroxy benzoic acid (pK_a 2.98)

>



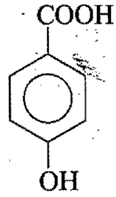
m-Hydroxy benzoic acid (pK_a 4.08)

>

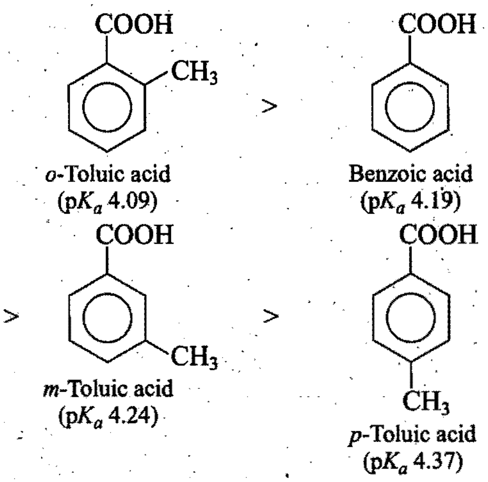


Benzoic acid (pK_a 4.19)

>



p-Hydroxy benzoic acid (pK_a 4.58)



In such cases *m*- isomer is stronger than *p*- isomer.

Hence, the following sequences are observed in order of acidity.

(a) Nitro benzoic acids : *o*- > *p*- > *m*- > benzoic acid
(b) Hydroxy benzoic acids : *o*- > *m*- > benzoic acid > *p*-
(c) Chloro benzoic acids : *o*- > *m*- > *p*- > benzoic acid
(d) Methyl benzoic acids : *o*- > benzoic acid > *m*- > *p*-
(e) $p\text{-}NO_2—C_6H_4COOH > p\text{-}Cl—C_6H_4COOH > C_6H_5COOH > p\text{-}CH_3—C_6H_4COOH > p\text{-}OH—C_6H_4COOH$
(f) $C_6H_5SO_3H > C_6H_5COOH > C_6H_5OH > C_6H_5CH_2OH$

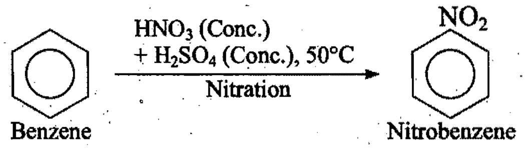
SOME TYPICAL AROMATIC CONVERSIONS

1. Lime to benzene.

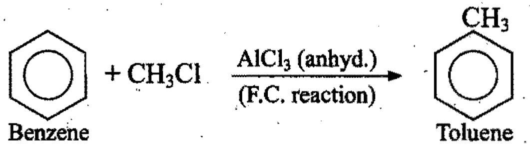
$$\underset{\text{Lime}}{CaO} \xrightarrow[\text{Electric furnace}]{\text{Coke, 2000°C}} \underset{\substack{\text{Calcium}\\ \text{carbide}}}{CaC_2} \xrightarrow{H_2O} \underset{\text{Acetylene}}{C_2H_2}$$

$$\xrightarrow[\text{Red hot tube}]{\text{Polymerization}} \underset{\text{Benzene}}{C_6H_6}$$

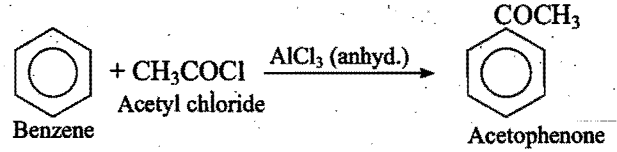
2. Benzene to nitrobenzene.



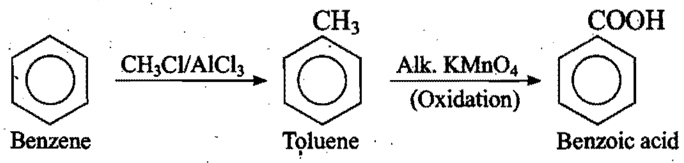
3. Benzene to toluene.



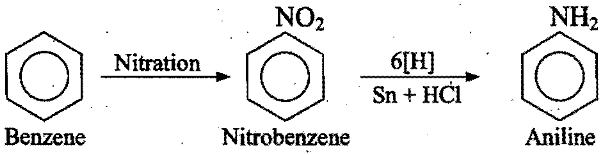
4. Benzene to acetophenone.



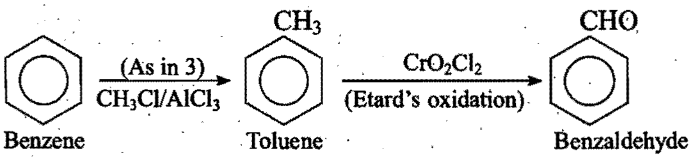
5. Benzene to benzoic acid.



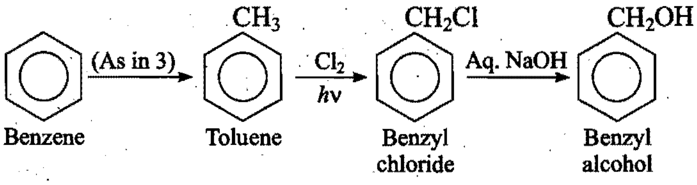
6. Benzene to aniline.



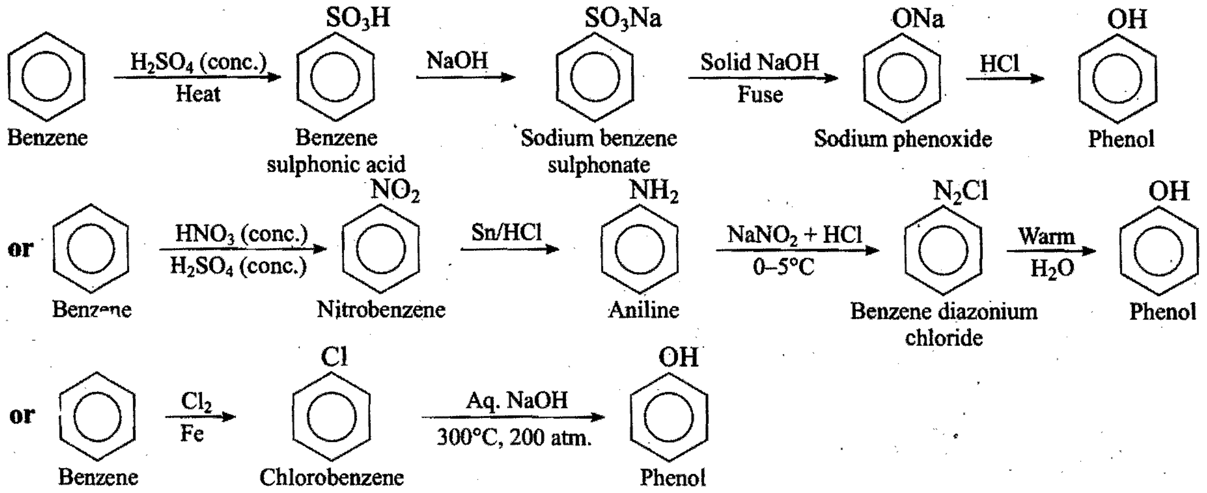
7. Benzene or toluene to benzaldehyde.



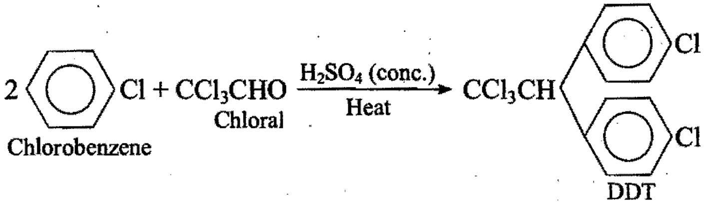
8. Benzene or toluene to benzyl alcohol.



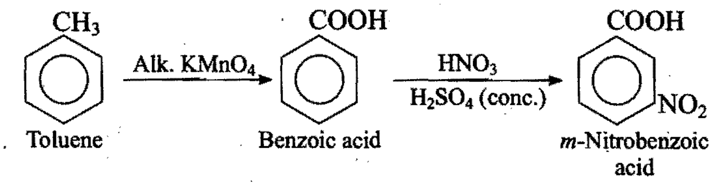
9. Benzene to phenol.



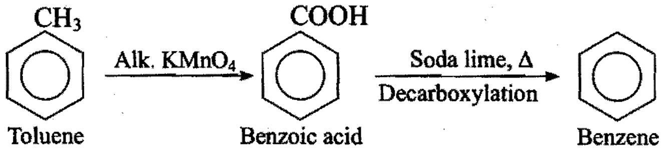
10. Chlorobenzene to DDT.



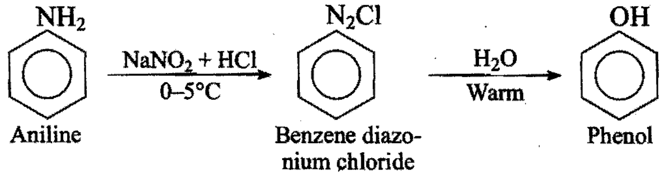
11. Toluene to *m*-nitrobenzoic acid.



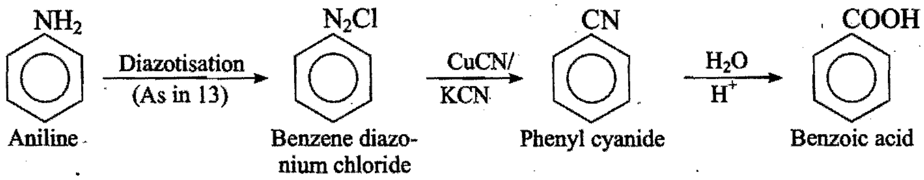
12. Toluene to benzene.



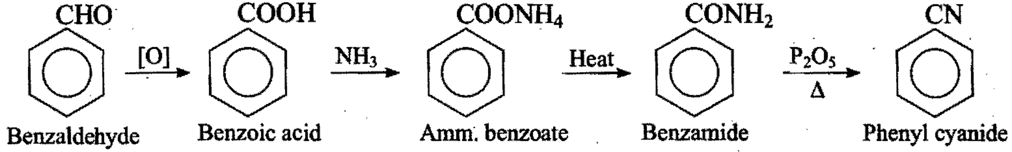
13. Aniline to phenol.



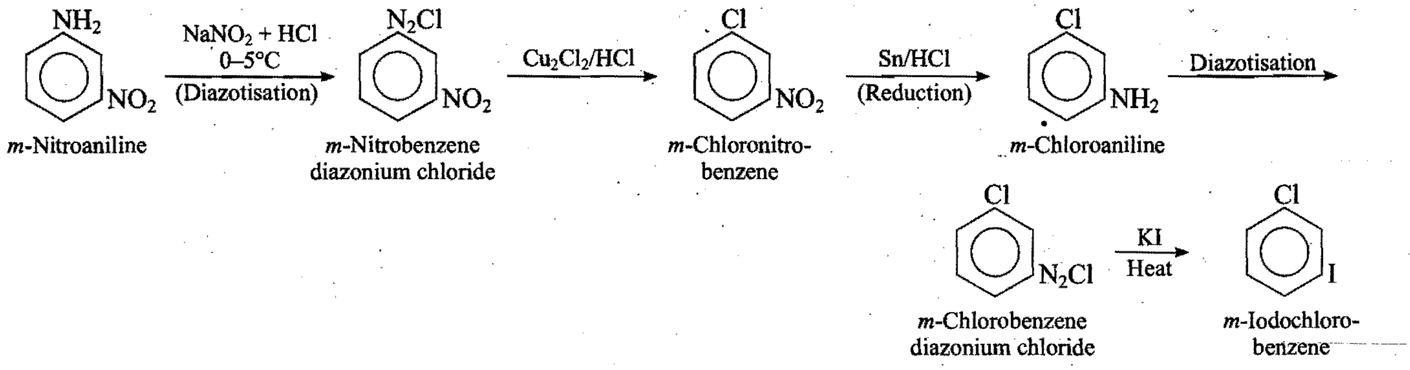
14. Aniline to benzoic acid.



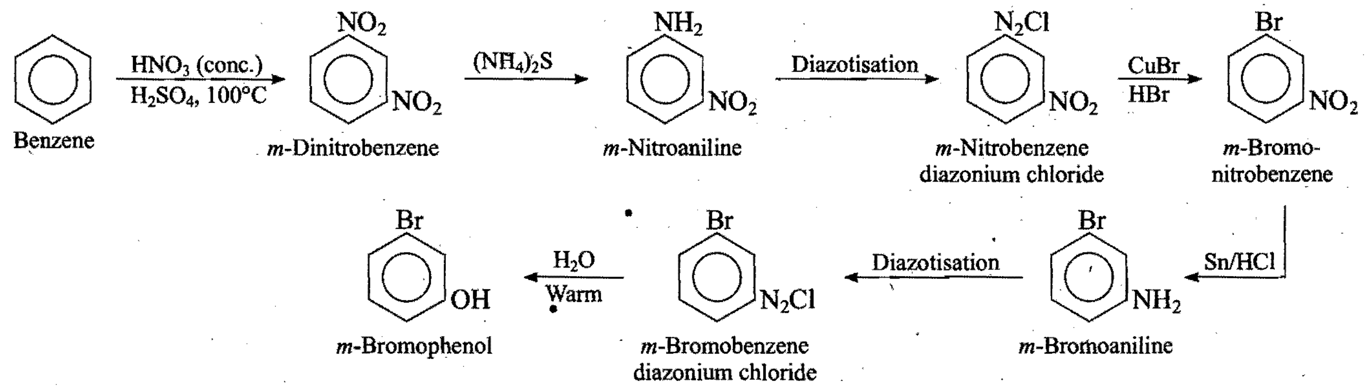
15. Benzaldehyde to phenyl cyanide.



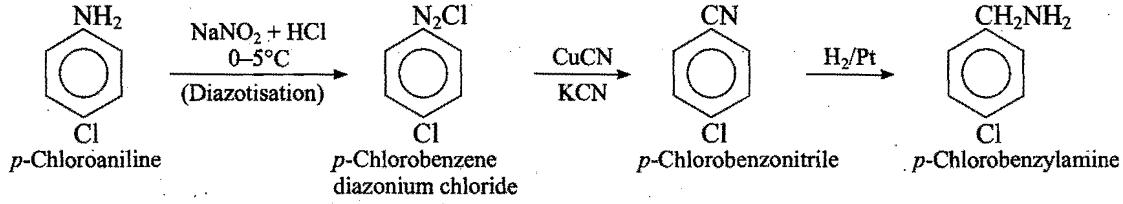
16. *m*-Nitroaniline to *m*-iodochlorobenzene.



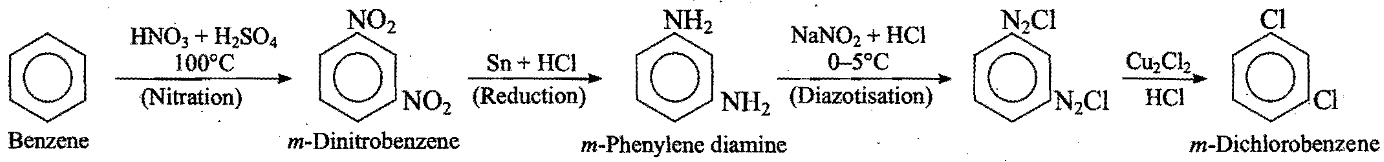
17. Benzene to *m*-bromophenol.



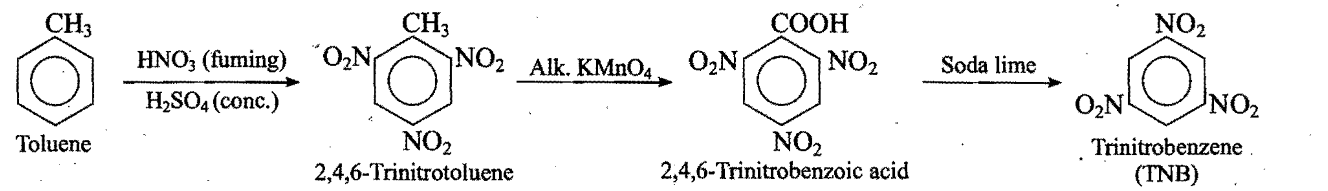
18. *p*-Chloroaniline to *p*-chlorobenzylamine.



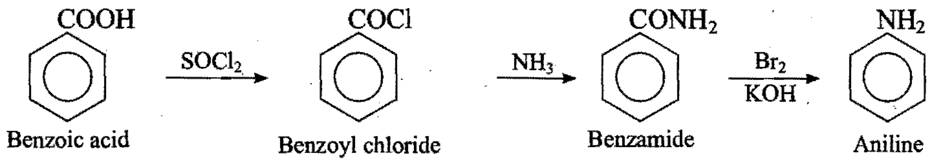
19. Benzene to *m*-dichlorobenzene.



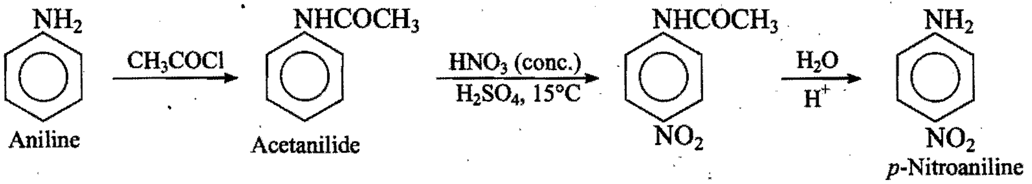
20. Toluene to trinitrobenzene (TNB).



21. Benzoic acid to aniline.

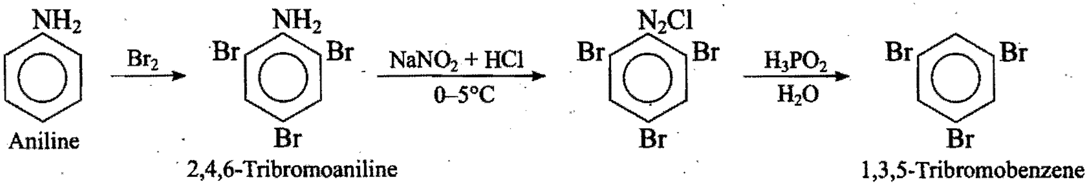


22. Aniline to *p*-nitroaniline.



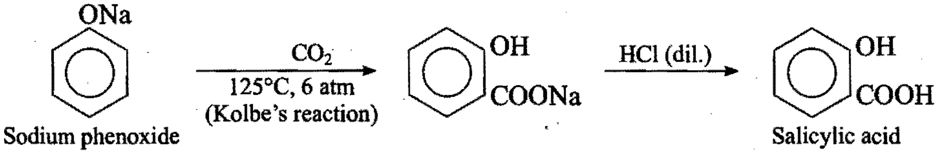
—NH_2 group protection is done by acetylation.

23. Aniline to 1,3,5-tribromobenzene.



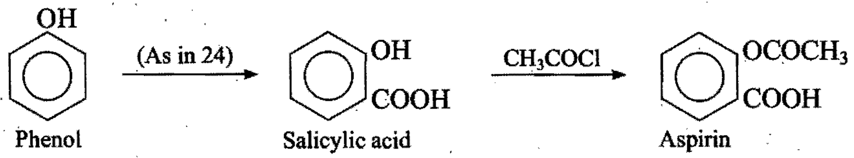
24. Benzene to salicylic acid.

First benzene is converted into phenol according to conversion 9.

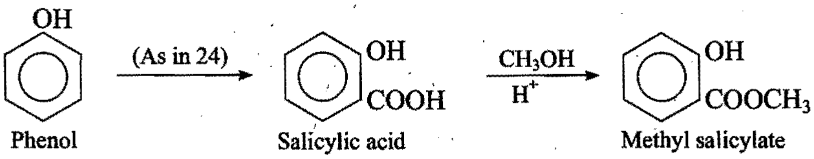


25. Phenol to aspirin. **[IIT 2003]**

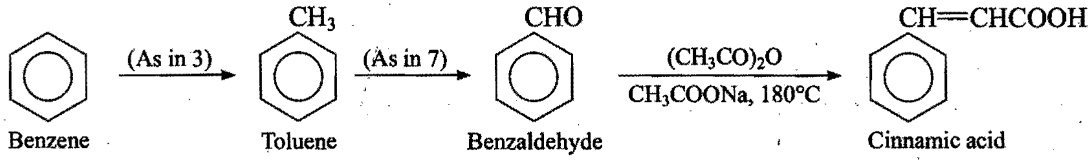
Aspirin is acetyl derivative of salicylic acid.



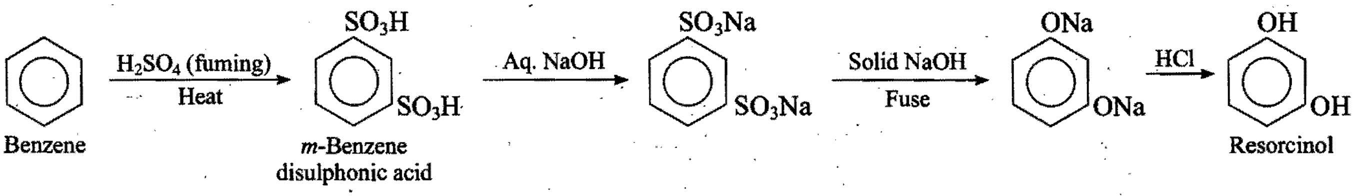
26. Phenol to oil of winter-green (Methyl salicylate).



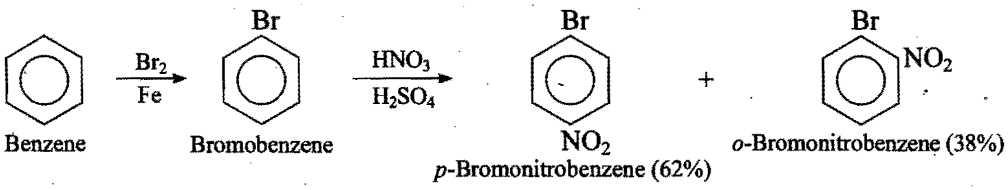
27. Benzene to cinnamic acid.



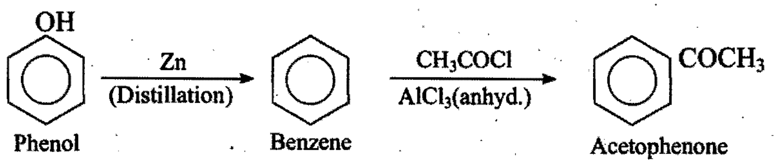
28. Benzene to resorcinol.



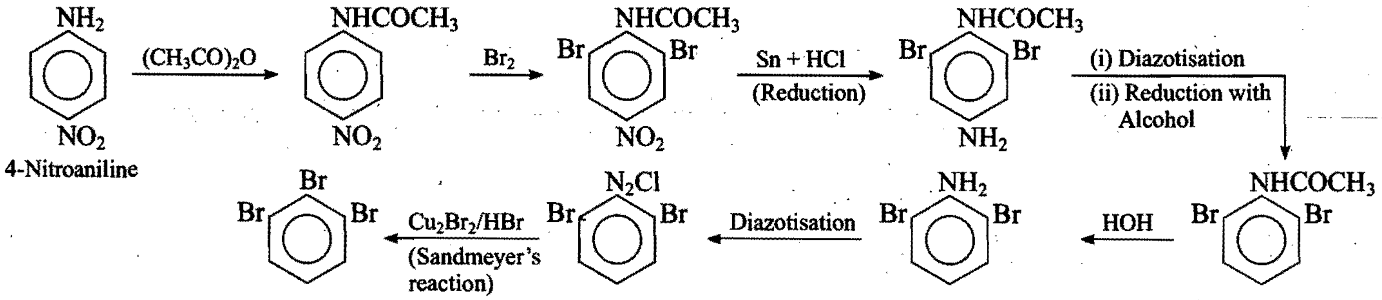
29. Benzene to *p*-bromonitrobenzene.



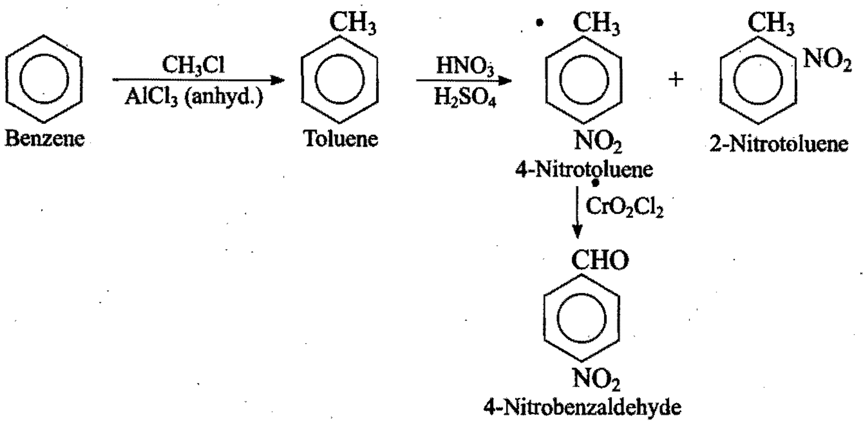
30. Phenol to acetophenone.



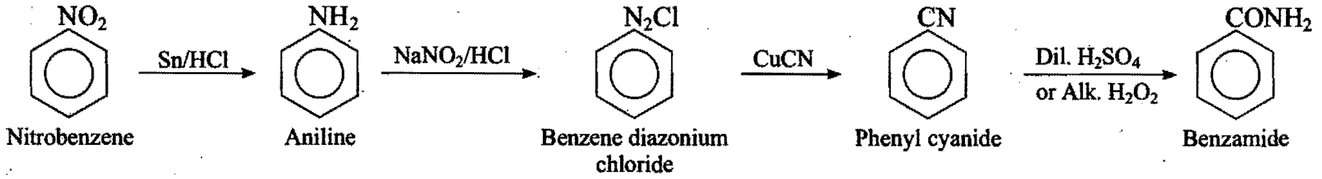
31. 4-Nitroaniline to 1,2,3-tribromobenzene.



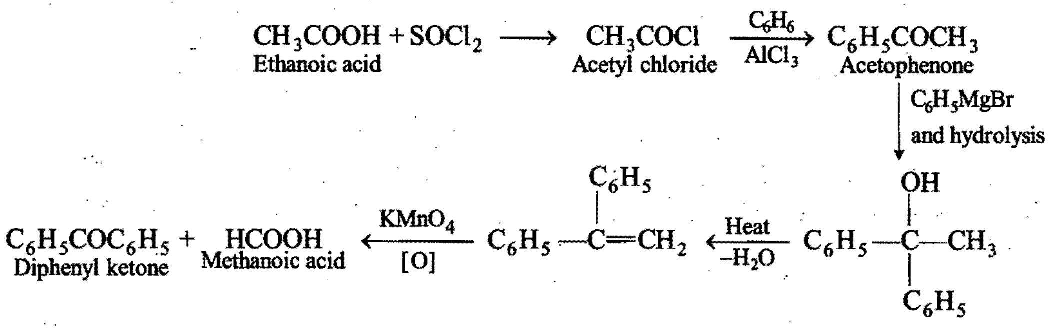
32. Benzene to 4-nitrobenzaldehyde.



33. Nitrobenzene to benzamide.



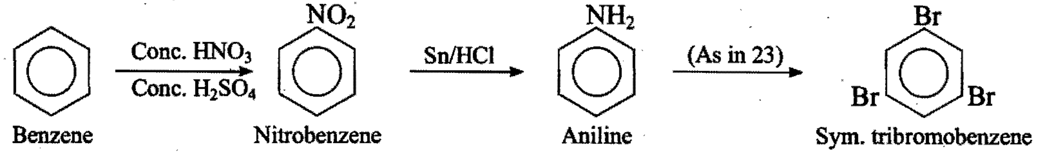
34. Ethanoic acid to a mixture of methanoic acid and diphenyl ketone.



$$\underset{\text{Ethanoic acid}}{CH_3COOH} + SOCl_2 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow[AlCl_3]{C_6H_6} \underset{\text{Acetophenone}}{C_6H_5COCH_3} \xrightarrow{C_6H_5MgBr \text{ and hydrolysis}} C_6H_5-\overset{OH}{\underset{C_6H_5}{C}}-CH_3$$

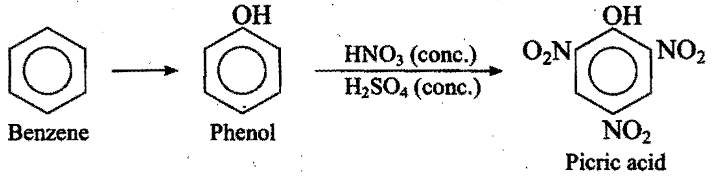
$$C_6H_5-\overset{OH}{\underset{C_6H_5}{C}}-CH_3 \xrightarrow[-H_2O]{\text{Heat}} C_6H_5-\overset{C_6H_5}{C}{=}CH_2 \xrightarrow[{[O]}]{KMnO_4} \underset{\text{Diphenyl ketone}}{C_6H_5COC_6H_5} + \underset{\text{Methanoic acid}}{HCOOH}$$

35. Benzene to Sym. tribromobenzene.



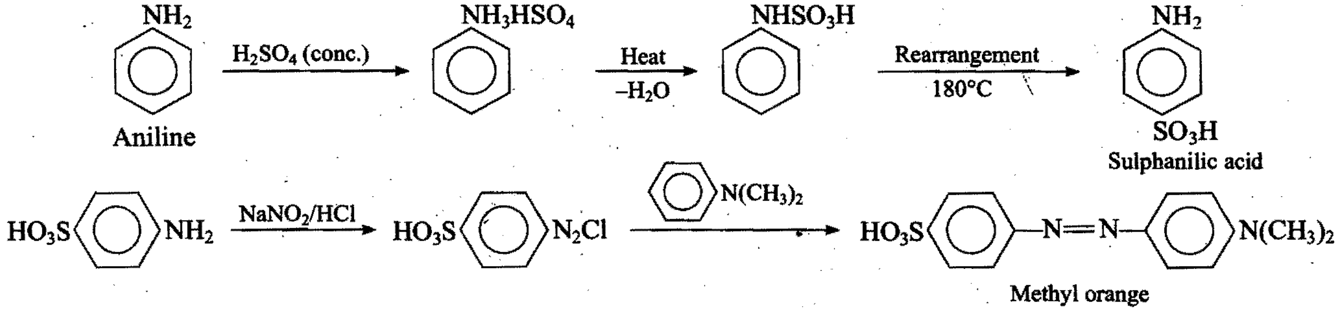
36. Benzene to picric acid.

Convert benzene into phenol as done in conversion 9.



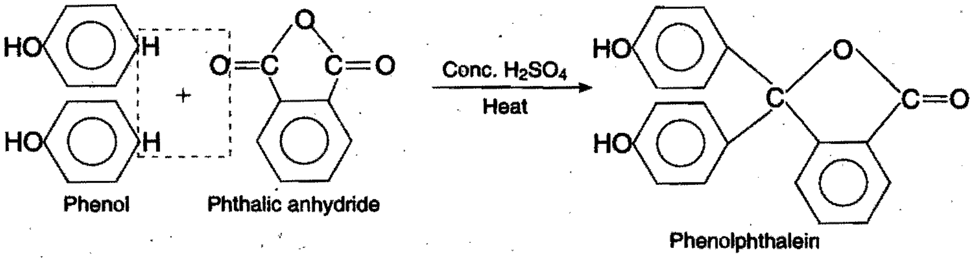
37. Benzene to methyl orange.

Benzene is first converted into aniline (Follow conversion 6). Aniline is then converted into sulphanilic acid.

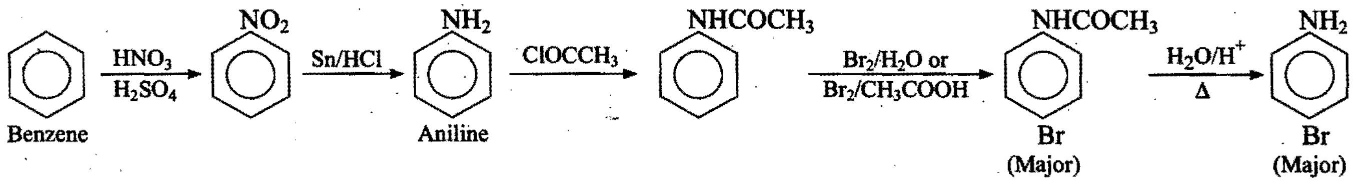


38. Benzene to phenolphthalein.

Benzene is first converted into phenol as done in conversion 9. Phenol on condensation with phthalic anhydride in presence of conc. H_2SO_4 gives phenolphthalein.

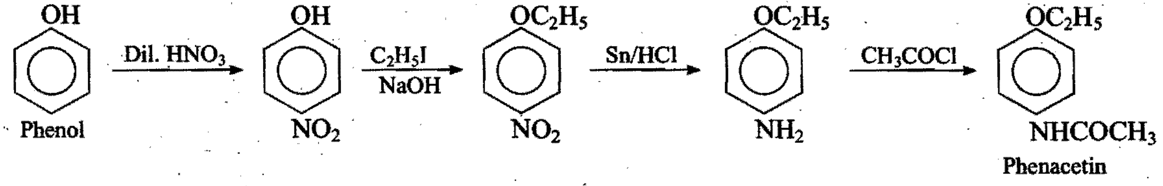


39. Benzene to aniline to *p*-bromoaniline. **[AIPMT (Mains) 2009]**

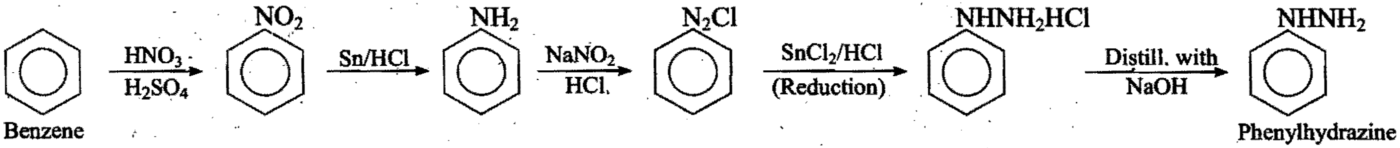


40. Benzene to phenacetin.

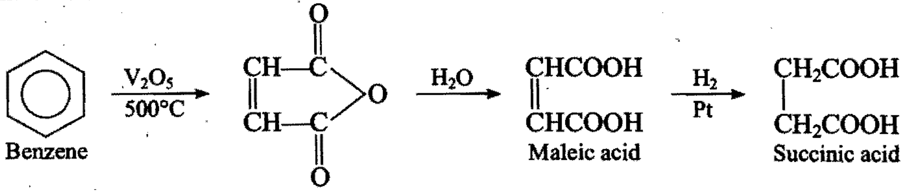
Benzene is first converted into phenol (follow conversion 9).



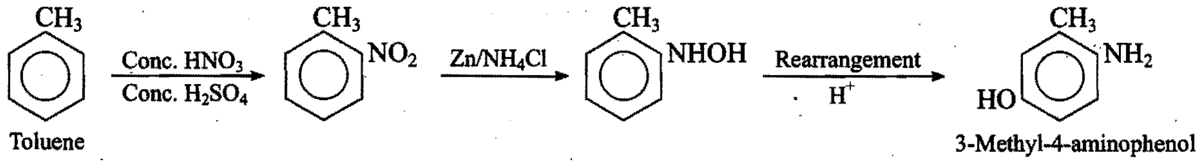
41. Benzene to phenylhydrazine.



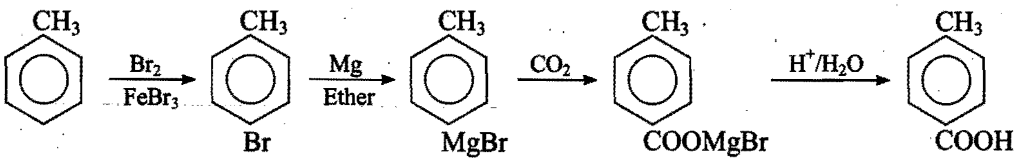
42. Benzene to succinic acid.



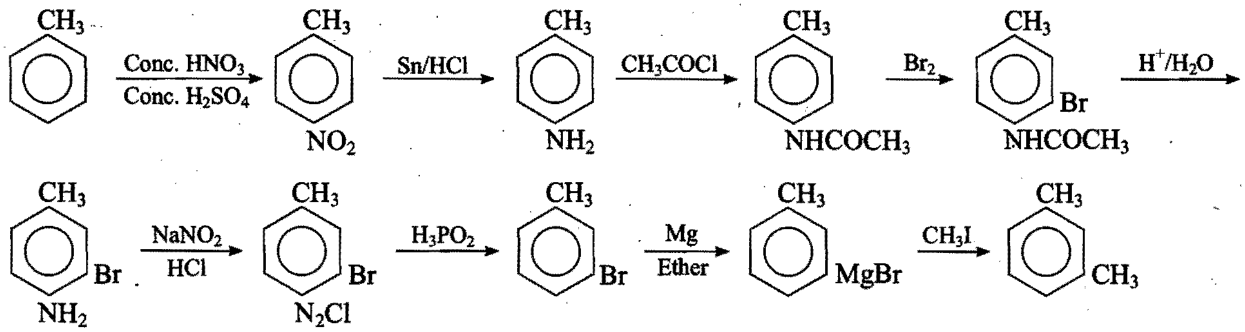
43. Toluene to 3-methyl-4-aminophenol.



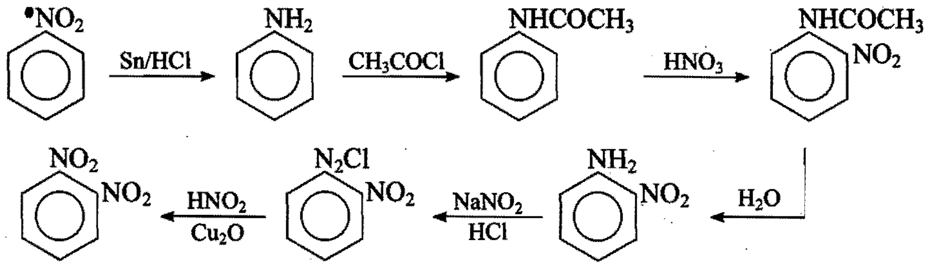
44. Toluene to *p*-methyl benzoic acid.



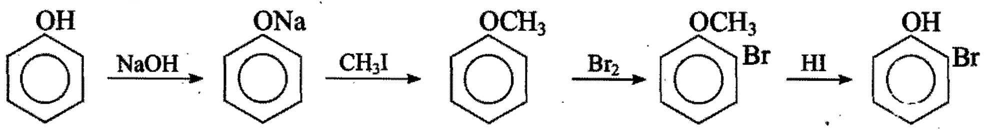
45. Toluene to *m*-xylene.



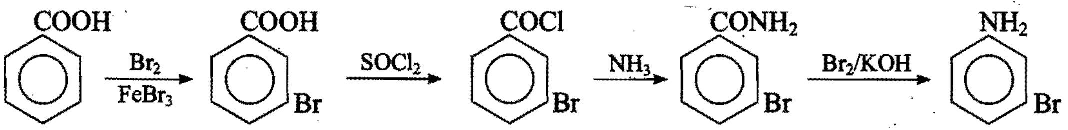
46. Nitrobenzene to *o*-dinitrobenzene.



47. Phenol to *o*-bromophenol.

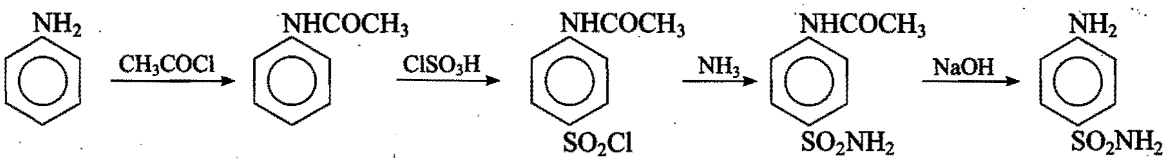


48. Benzoic acid to *m*-bromoaniline.



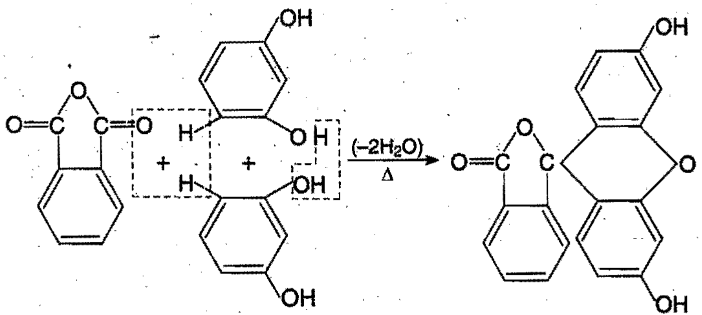
49. Benzene to sulphanilamide.

Benzene is first converted into aniline as done in conversion 6.



50. Benzene to fluorescein.

Benzene is first converted into resorcinol as done in conversion 28. Resorcinol is then fused with phthalic anhydride in presence of conc. H_2SO_4.



Fluorescein

Problem 25. *Answer the following :*

(*a*) *Why benzene cannot be iodated with iodine directly ?*

(*b*) *Why fluoroarenes cannot be prepared by direct reaction of fluorine ?*

(*c*) *How benzene can be iodated ?*

(*d*) *Why iodation of an arene occurs with* ICl *?*

(*e*) *Why nitrobenzene and not benzene is a suitable solvent for Friedel-Crafts alkylation of bromobenzene ?*

Solution : (a) Iodation with iodine is slow and somewhat reversible.

$$C_6H_6 + I_2 \rightleftharpoons C_6H_5I + HI$$

(b) Fluorine is too reactive in nature. Both addition and polysubstitution occur.

(c) The presence of I^- reverses the reaction. Iodation can occur smoothly if an oxidising agent such as HNO_3, HIO_3, H_2O_2, etc., is present which can convert I^- to I_2.

(d) ICl is more reactive than iodine. The aromatic ring can displace Cl^- more easily from $I^{\delta+}\ Cl^{\delta-}$ than it can displace I^- from the non-polar I_2.

(e) Benzene is more reactive than bromobenzene in Friedel-Crafts reaction and would alkylate more rapidly. Nitrobenzene may be used as a solvent because it does not undergo Friedel-Crafts reaction owning to deactivating effect of NO_2 group.

Problem 26. *Explain the following with proper reasoning:*

(*i*) *Oxidation of toluene with chromyl chloride to get benzaldehyde is carried out in presence of acetic anhydride.*

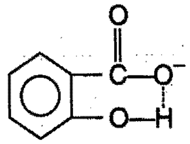
Solution : Oxidation of benzaldehyde to benzoic acid is prevented because benzaldehyde reacts with acetic anhydride to form benzylidene acetate. The benzylidene acetate on treatment with HCl regenerates benzaldehyde.

$$C_6H_5CH_3 \xrightarrow[CrO_2Cl_2]{[O]} C_6H_5CHO \xrightarrow{(CH_3CO)_2O}$$

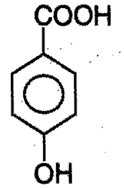
$$C_6H_5CH(OOCCH_3)_2 \xrightarrow{HCl} C_6H_5CHO + 2CH_3COOH$$

(*ii*) *Although p-hydroxy benzoic acid is less acidic than benzoic acid but o-hydroxy benzoic acid (salicylic acid) is* 15 *times more acidic than benzoic acid.*

Solution : Presence of —OH group (electron withdrawing) on benzoic acid decreases the acidic nature because negative charge on carboxylate ion increases thereby making carboxylate ion less stable. The resonance effect being stronger as compared to inductive effect, there is net increase in electron density at *o*- and *p*- positions, *p*-hydroxy benzoic acid is, therefore, less acidic than benzoic acid. However, in *o*-hydroxy benzoic acid, there is intramolecular hydrogen bonding which stabilizes *o*-hydroxy benzoate ion (Conjugated base) to greater extent and thereby increasing acidic nature.



Conjugate base of *ortho*-isomer
($pK_a = 2.98$)



Para-isomer
($pK_a = 4.58$)

This anomalous behaviour of groups when present in *ortho*-position is termed ***ortho* effect.**

(*iii*) *The melting point of para dihalobenzenes are much higher than those of the corresponding ortho and meta isomers.*

Solution : This is because the *para* isomer is more symmetrical than *ortho* and *meta* isomers and hence can fit better in the crystal lattice of the solid forms.

(*iv*) *Oxidation of toluene by acidic* $KMnO_4$ *gives poor yield of benzoic acid while oxidation of* p-$O_2NC_6H_4CH_3$ *gives good yield of p-nitrobenzoic acid.*

Solution : Oxidant is an electrophile, it can destroy the ring in case of toluene. But in *para*-nitrotoluene, the $—NO_2$ group deactivates the benzene ring and thus increases the yield of *p*-nitrobenzoic acid.

(*v*) *Why the* C—O *bond in phenol is shorter than in alcohol?*

Solution : In phenol, carbon uses sp^2-hybrid orbital to form C—O bond (more *s*-character) while in alcohol, carbon uses sp^3-hybrid orbital (less *s*-character). Also the delocalization of electron density from O to the ring by extended π-bonding brings double bond character in phenolic C—O bond making it shorter.

(*vi*) *The dipole moment of p-nitrophenol* (5.0 *D*) *is greater than phenol or nitrobenzene* (4.0 *D*).

Solution : The electron-donation of the OH reinforces the electron withdrawal of NO_2. Thus, dipole moment of *p*-nitrophenol becomes higher.

(*vii*) *Why are the following conditions unsatisfactory for diazo coupling?*

(*a*) *Strong base* (*b*) *Strong acid.*

Solution :

$$Ar\overset{+}{N}\equiv N\colon \overset{OH^-}{\rightleftharpoons} \underset{\text{A diazoic acid}}{Ar\ddot{N}=\ddot{N}—OH} \overset{-H^+}{\rightleftharpoons} \underset{\text{A diazotate ion}}{Ar\ddot{N}=\ddot{N}—O^-}$$

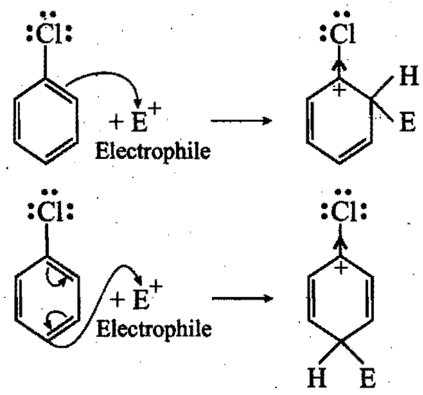
Neither the diazoic acid nor its ion couple.

(*viii*) *Benzaldehyde does not undergo aldol condensation on treatment with* NaOH *whereas acetaldehyde does so.*

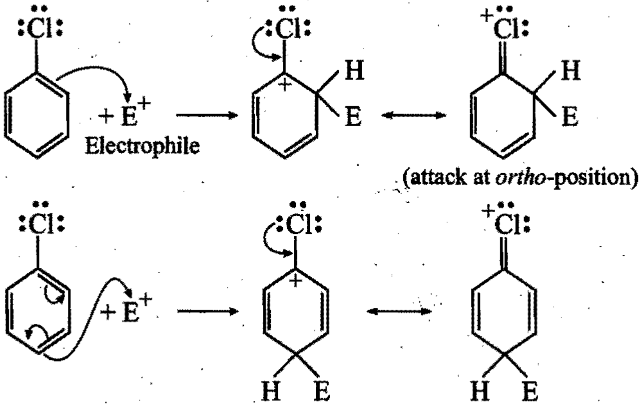
Solution : Those aldehydes undergo aldol condensation which possess α-hydrogen atoms. As benzaldehyde does not possess α-hydrogen atoms, it does not undergo aldol condensation.

Problem 27. Although chlorine is an electron withdrawing group, yet it is *ortho-para* directing in electrophilic aromatic substitution reactions. Why?

Solution : Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution. Through resonance, chlorine tends to stabilise the carbocation and the effect is more pronounced at *o*- and *p*-positions.



[Inductive (–*I*) effect of Cl destabilises the intermediate carbocation.]

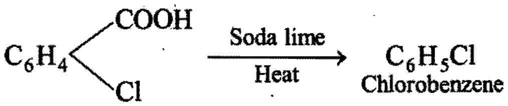


(Resonance effect of Cl stabilises the intermediate carbocation)

The inductive effect is stronger than resonance and causes net deactivation due to net electron withdrawl. The resonance effect tends to oppose the inductive effect for the attack at *o*- and *p*-positions and hence makes the deactivation less for *o*- and *p*- attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

Problem 28. *Compound (A), with empirical formula* C_7H_9N *on diazotization, gives a product which undergoes Sandmeyer's reaction with* Cu_2Cl_2 *and* HCl *to give a compound (B). (B) on oxidation gives a compound (C) which when heated with soda lime gives chlorobenzene. Give the structural formulae of (A), (B) and (C) and explain the reactions involved.*

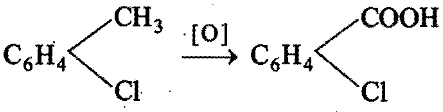
Solution : Chlorobenzene is formed from (*C*) on heating with soda lime. Hence, it consists of —COOH group. The (*C*) is chlorobenzoic acid.



$$C_6H_4\!<\!\begin{smallmatrix}COOH\\ Cl\end{smallmatrix} \xrightarrow[\text{Heat}]{\text{Soda lime}} \underset{\text{Chlorobenzene}}{C_6H_5Cl}$$

(*C*)

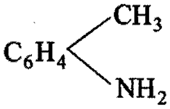
(*C*) is obtained by oxidation of (*B*), *i.e.*, one CH_3 group is present.



$$C_6H_4\!<\!\begin{smallmatrix}CH_3\\ Cl\end{smallmatrix} \xrightarrow{[O]} C_6H_4\!<\!\begin{smallmatrix}COOH\\ Cl\end{smallmatrix}$$

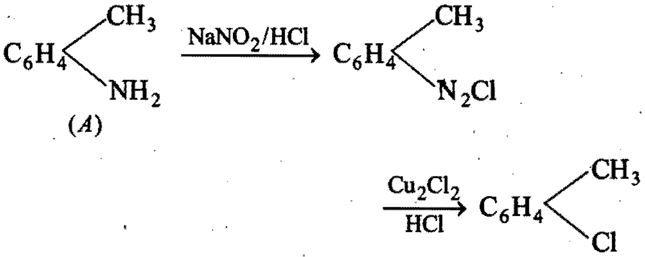
(*B*) (*C*)

(*B*) is formed after doing diazotization of (*A*) followed by Sandmeyer's reaction. Thus, (*A*) is,



$$C_6H_4\!<\!\begin{smallmatrix}CH_3\\ NH_2\end{smallmatrix} \qquad (C_7H_9N)$$

(*o*-, *m*- or *p*-toludine)



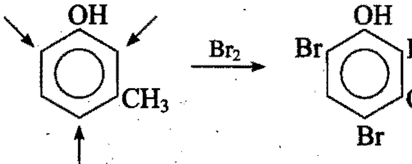
$$\underset{(A)}{C_6H_4\!<\!\begin{smallmatrix}CH_3\\ NH_2\end{smallmatrix}} \xrightarrow{NaNO_2/HCl} C_6H_4\!<\!\begin{smallmatrix}CH_3\\ N_2Cl\end{smallmatrix} \xrightarrow[HCl]{Cu_2Cl_2} C_6H_4\!<\!\begin{smallmatrix}CH_3\\ Cl\end{smallmatrix}$$

Problem 29. *Compound (A)* C_7H_8O *is insoluble in* $NaHCO_3$ *solution but dissolves in sodium hydroxide and gives a characteristic colour with aqueous ferric chloride. When treated with bromine (A) forms a compound (B)* $C_7H_5OBr_3$.

(*i*) *Give the structural formulae of (A) and (B).*

(*ii*) *What would be the structure of (A) if it neither dissolves in sodium hydroxide solution nor gives a characteristic colour with* $FeCl_3$?

Solution : (i) (*A*) gives characteristic colour with $FeCl_3$ solution, so it is a phenol. (*A*) forms tribromoproduct, thus it is *meta*-cresol.

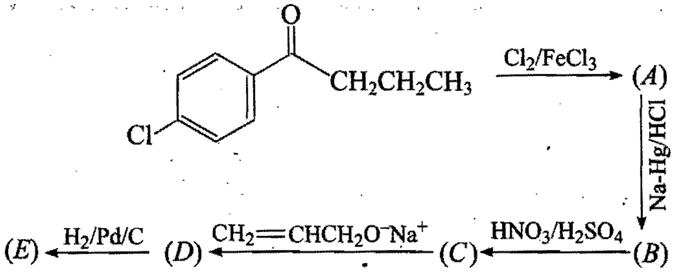


($C_7H_5OBr_3$)

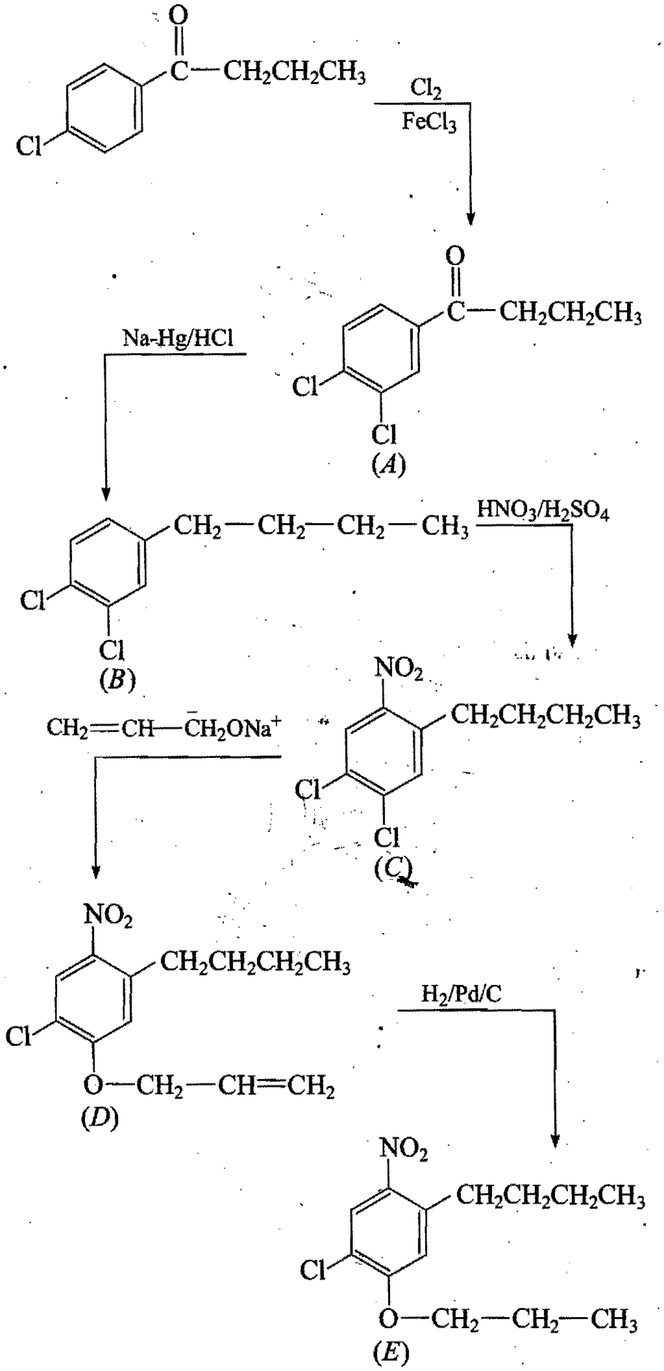
Meta-cresol (*A*) (*B*)

(ii) If the compound does not dissolve in aqueous NaOH and does not give characteristic colour with $FeCl_3$, it should be a neutral compound, *i.e.*, either anisole (C_6H_5—O—CH_3) or benzyl alcohol ($C_6H_5CH_2OH$).

Problem 30. *Write the structures of the products (A), (B), (C), (D) and (E) in the following scheme :* **[IIT 2002]**



Solution :



Problem 31. *Five isomeric para-disubstituted aromatic compounds (A) to (E) with molecular formula* $C_8H_8O_2$ *were given for identification. Based on the following observations, give structures of the compounds.*

(i) Both (A) and (B) form a silver mirror with Tollens' reagent; also, (B) gives a positive test with $FeCl_3$ *solution.*

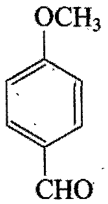
(ii) (C) gives positive iodoform test.

(iii) (D) is readily extracted in aqueous $NaHCO_3$ *solution.*

(iv) (E) on acid hydrolysis gives 1,4-dihydroxy benzene.

Solution : Structural formulae of the five isomers (*A* to *E*) with molecular formula $C_8H_8O_2$ are given below :

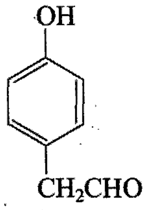
(i) (*A*)



p-Methoxy benzaldehyde

It gives silver mirror test with Tollens' reagent because it has aldehydic group.

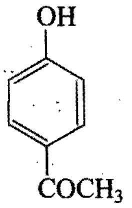
(*B*)



p-Hydroxy phenyl acetaldehyde

It has both aldehydic and phenolic groups; therefore, it gives silver mirror test and positive test with $FeCl_3$ solution.

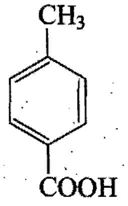
(ii) (*C*)



p-Hydroxy acetophenone

This isomer has $(-\overset{O}{\overset{\|}{C}}-CH_3)$ group; therefore it gives positive test with $NaOH/I_2$, *i.e.*, iodoform test.

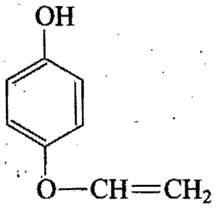
(iii) (*D*)



p-Methyl benzoic acid

It can be extracted with aqueous $NaHCO_3$ because it has carboxylic group.

(iv) (*E*)



p-Hydroxy phenyl vinyl ether

It will give 1,4-dihydroxy benzene on acid hydrolysis.

QUESTIONS

❖ Very Short Answer Type

1. Fill in the blanks:
   - (a) Benzene and toluene are present in ...... fraction of coal-tar.
   - (b) All the carbon atoms in benzene are ...... hybridised.
   - (c) The ring structure of benzene was proposed by ....
   - (d) Benzene shows ...... substitution reactions.
   - (e) Nitro group in benzene nucleus is ...... directing. It ...... the reactivity of benzene nucleus.
   - (f) Friedel-Crafts reaction occurs in presence of ....
   - (g) The two aromatic halogen derivatives used as insecticides are ...... and ....
   - (h) Benzyl alcohol and phenol can be distinguished by using reagent ....
   - (i) Benzene reacts with ...... in presence of aluminium chloride to form acetophenone.
   - (j) Chloral and chlorobenzene in presence of conc. H_2SO_4 forms an insecticide called as ....
   - (k) Oil of Mirabane is chemically called as ....
   - (l) Aniline when treated with sodium nitrite and HCl at 0°C forms benzene diazonium chloride. This reaction is termed as ....
   - (m) Benzene is formed when ...... is distilled with zinc dust.
   - (n) Phenol is ...... while C_2H_5OH is ....
   - (o) In the formation of salicylic acid by Reimer-Tiemann's reaction, phenol is heated with ...... in presence of an alkali.
   - (p) Oxidation of toluene into ...... using chromyl chloride is commonly called Etard's reaction.
   - (q) Benzaldehyde undergoes Cannizzaro's reaction to form ...... and ....
   - (r) Benzoin is formed when benzaldehyde is treated with ......
   - (s) Toluene is converted into benzaldehyde by reaction with ....
   - (t) Aniline forms ...... when heated with chloroform and alcoholic KOH.
   - (u) Aniline is ...... base than ammonia.
   - (v) Liebermann's reaction is given by ....
   - (w) Phenol is acidic because of resonance stabilization of its conjugate base namely ....
   - (x) Sulphonation of benzoic acid yields ....
   - (y) When salicylic acid is heated with soda lime, the product obtained is ....
   - (z) The active species in the nitrating mixture is ....

2. Fill in the blanks:
   - (i) In the presence of UV light, benzene reacts with chlorine forming ....
   - (ii) Toluene is more reactive than benzene for ...... attack.
   - (iii) 2,4,6-Trinitrophenol is also known as ....
   - (iv) Dipole moment of benzene is ....
   - (v) The bond dissociation energy needed to form the benzyl radical from toluene is ...... than the formation of methyl radical from methane.
   - (vi) The structure of the intermediate product formed by the oxidation of toluene with CrO_3 and acetic anhydride, whose hydrolysis gives benzaldehyde is ....
   - (vii) Amongst the three isomers of nitrophenol, the one that is least soluble in water is ....
   - (viii) Formation of phenol from chlorobenzene is an example of ...... aromatic substitution.
   - (ix) The high melting point and insolubility in organic solvents of sulphanilic acid are due to its ...... structure.
   - (x) Compound formed on distilling sodium benzoate with soda lime is ....
   - (xi) Benzene diazonium chloride with cuprous chloride and HCl gives ....
   - (xii) Phenol when distilled with zinc gives ....
   - (xiii) On sulphonation of toluene, the sulphonic acid group will enter in ...... position.
   - (xiv) On nitration of nitrobenzene, the second nitro group will enter in ...... position.
   - (xv) Benzene on catalytic oxidation at 500°C with V_2O_5 as catalyst gives ....
   - (xvi) Haloarenes are ...... reactive than haloalkanes.
   - (xvii) Condensation of phenol with ...... in presence of conc. H_2SO_4 gives phenolphthalein.
   - (xviii) Benzoic acid is ...... than acetic acid.
   - (xix) Aspirin is an ...... derivative of ....
   - (xx) Before carrying out nitration of aniline, NH_2 is ...... by ....

3. State, whether the following statements are **True or False** :
   - (a) Benzene has a planar structure.
   - (b) Benzene is an unsaturated hydrocarbon and it shows addition reactions like alkenes.
   - (c) Chlorobenzene is more reactive than benzene as chlorine is o-,p-directing group.
   - (d) Aniline forms phenol when treated with nitrous acid.
   - (e) Phenol gives violet colouration with neutral ferric chloride.
   - (f) Aniline is obtained by reduction of nitrobenzene with tin and HCl.
   - (g) Benzoic acid is steam volatile.
   - (h) Both benzaldehyde and nitrobenzene have smell of bitter almonds.
   - (i) Picric acid is 2,4,6-trinitrotoluene.
   - (j) Phenol evolves carbon dioxide from sodium bicarbonate.
   - (k) Aniline with conc. HNO_3 and conc. H_2SO_4 forms o- and p-nitroaniline.
   - (l) Phenol can be converted into salicylaldehyde on treatment with $CHCl_3$/KOH.

(m) Aniline is weaker base than methyl amine.
(n) Benzene molecule has two different C—C bond lengths corresponding to alternate single and double bonds.
(o) If the number of π-electrons is equal to $4n+2$, the system is aromatic (n can have values 0, 1, 2...).
(p) Phenolphthalein is obtained when phenol is heated with phthalic anhydride in the presence of conc. H_2SO_4.
(q) Benzamide on treatment with NaOH and Br_2 forms benzoic acid.
(r) TNT and TNB are insecticides.
(s) Aniline gives foul smell when heated with chloroform and KOH.
(t) In Friedel-Crafts reaction, $AlCl_3$ is an electrophile.
(u) All the bond angles in benzene are of 60°.
(v) Benzaldehyde gives red precipitate with Fehling's solution.
(w) *m*-Chlorobromobenzene is an isomer of *m*-Bromochlorobenzene.
(x) 2,4-Dinitrochlorobenzene is less reactive than chlorobenzene towards nucleophilic substitution.
(y) Phenol is more acidic than cresol.
(z) Both aliphatic and aromatic primary amines respond to carbylamine test.

4. State, whether the following statements are **True** or **False**:
   (i) In benzene, carbon uses all the three p-orbitals for hybridization.
   (ii) An electron donating substituent in benzene orients the incoming electrophile to the *meta*-position.
   (iii) Chlorobenzene is inert to ammoniacal silver nitrate but *t*-butyl chloride gives a white precipitate.
   (iv) Phenol forms 2,4,6-Tribromophenol with bromine water but form only monobromophenol with Br_2/CS_2.
   (v) Phenol gives salicylic acid on treatment with $CHCl_3$/KOH.
   (vi) Benzaldehyde undergoes aldol condensation in alkaline medium.
   (vii) Nitrogen is evolved when aniline is treated with HNO_2 at 0°C.
   (viii) Benzene diazonium chloride when warmed with dilute H_2SO_4 gives phenol.
   (ix) For the synthesis of fluorobenzene, benzene diazonium chloride is heated with HBF_4.
   (x) Aniline is more basic than ethylamine.
   (xi) Phenols having electron withdrawing group or groups attached to benzene ring are more acidic than phenol itself.
   (xii) All the common meta directing groups deactivate the benzene nucleus towards electrophilic substitution.
   (xiii) Nitrobenzene undergoes Friedel-Crafts reaction.
   (xiv) 2,4,6-Trinitrotoluene is more powerful explosive than 1,3,5-Trinitrobenzene.
   (xv) A side chain attached on benzene ring is oxidised to —COOH group.
   (xvi) Aromatic compounds contain low percentage of carbon, hence burn with sooty flame.
   (xvii) When Cl_2 is passed through boiling toluene in presence of sunlight, substitution in the side chain takes place.
   (xviii) Toluene forms benzaldehyde with dil. HNO_3.
   (xix) Nitrobenzene when reduced with zinc dust and aqueous NH_4Cl, forms mainly phenyl hydroxylamine.
   (xx) Aniline with carbon disulphide forms diphenyl thio urea in presence of alkali.

5. Match the following:

[A]

1. C_6H_6, CH_3Cl, anhyd. $AlCl_3$	(a) Electrophilic substitution
2. Insecticides	(b) C_6H_5COONa + Soda lime
3. Explosive	(c) Phenol + $CHCl_3$ + NaOH
4. Benzene, nitric acid and sulphuric acid	(d) Conversion of toluene to benzaldehyde
5. Decarboxylation	(e) Aniline
6. Reimer-Tiemann reaction	(f) Phenols
7. Etard's reaction	(g) TNT
8. Diazotisation	(h) Friedel-Crafts reaction
9. $FeCl_3$ solution	(i) BHC
10. Dye test	(j) Aniline, $NaNO_2$ and HCl

[B]

1. Picric acid	(a) *o*- and *p*-directing
2. —COOH	(b) $C_6H_5N_2Cl + Cu_2Cl_2 + HCl$
3. —OH	(c) Manufacture of chlorobenzene
4. Sandmeyer's reaction	(d) Benzanilide
5. Phenolic acid	(e) 2,4,6-Trinitrophenol
6. Raschig's process	(f) Cinnamic acid
7. Schotten-Baumann's reaction	(g) Phenol
8. Carbolic acid	(h) Bromobenzene + Sodium + Methyl bromide
9. Wurtz-Fittig reaction	(i) *Meta*-directing
10. Unsaturated acid	(j) Salicylic acid

[C]

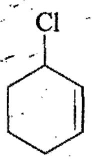
1. BHC	(a) *o*-Sulphobenzoic imide
2. Sym. trinitrobenzene	(b) *p*-$H_2NC_6H_4SO_3H$
3. Oil of Mirabane	(c) Benzaldehyde
4. Picric acid	(d) Acetyl salicylic acid
5. Sulphanilic acid	(e) Sym. $C_6H_3(CH_3)_3$
6. Anisole	(f) $C_6H_6Cl_6$
7. Aspirin	(g) $C_6H_5OCH_3$
8. Oil of bitter almonds	(h) Nitrobenzene
9. Mesitylene	(i) $(OH)C_6H_2(NO_2)_3$
10. Saccharin	(j) TNB

(A) Classify the following groups as *ortho*, *para* or *meta* directing when present on benzene nucleus.
(i) $—CH_3$, (ii) $—NH_2$, (iii) $—NO_2$, (iv) —COOH, (v) —OH, (vi) $—SO_3H$, (vii) —*X* (halogen), (viii) $—OCH_3$, (ix) —CHO, (x) —CN.

(B) Classify the following groups as activating or deactivating with respect to further electrophilic substitution of the aromatic ring.
(i) $—NH_2$, (ii) $—NO_2$, (iii) $—SO_3H$, (iv) $—CH_3$, (v) —Cl, (vi) —CN.

(C) Write the IUPAC names of the following:

(i)



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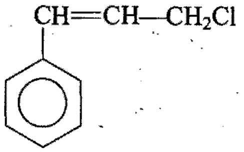

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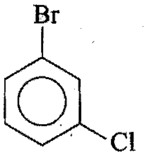

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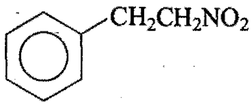

(v)

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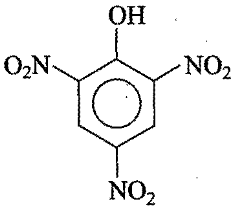

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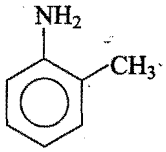

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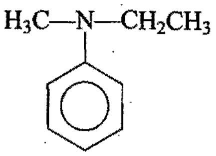

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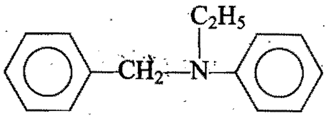

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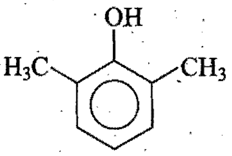

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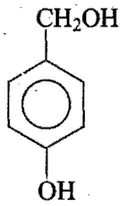

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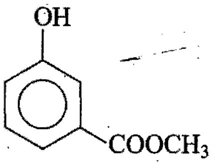

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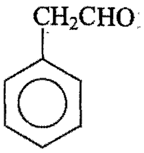

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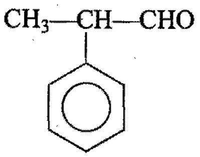

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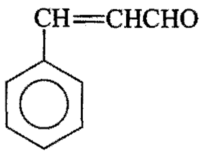


7. Complete the following equations:

(i) $2C_6H_5Cl + Na \xrightarrow{\text{Ether}}$

(ii) $C_6H_6 + Cl_2 \xrightarrow{FeCl_3}$

(iii) $C_6H_5OH + Br_2 \xrightarrow{H_2O}$

(iv) $C_6H_5OH + CHCl_3 \xrightarrow[70°C]{\text{NaOH (aq.)}}$

(v) $C_6H_5OH + HNO_3 \xrightarrow{H_2SO_4\text{(conc.)}}$

(vi) $C_6H_5CH_3 \xrightarrow{\text{Air}/V_2O_5}$

(vii) $C_6H_5NH_2 + CH_3COCl \xrightarrow{\text{Base}}$

(viii) $C_6H_5CONH_2 + Br_2/KOH \longrightarrow$

(ix) $C_6H_5NH_2 \xrightarrow{Br_2,\text{ water}}$

(x) $C_6H_5NO_2 \xrightarrow{Sn/HCl}$

(xi) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(xii) $C_6H_5N_2Cl \xrightarrow{Cu_2Cl_2/HCl}$

(xiii) $C_6H_5COOH + NaHCO_3 \longrightarrow$

(xiv) $C_6H_5N_2Cl + C_6H_5OH \longrightarrow$

(xv) $C_6H_5NH_2 \xrightarrow{H_2SO_4\text{(conc.)}}$

(xvi) $C_6H_5ONa + CO_2 \xrightarrow[4\text{–}7\text{ atm}]{125°C}$

(xvii) $C_6H_6 + CO + HCl \xrightarrow{AlCl_3}$

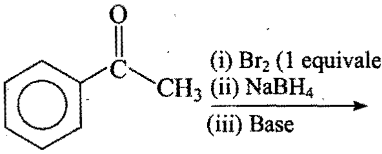
(xviii) $C_6H_5OH + NH_3 \xrightarrow[300°C]{ZnCl_2}$

(xix) $C_6H_6 + (CH_3)_3C—CH_2Br \xrightarrow{AlCl_3}$

[CBSE (Med.) 2006]

(xx) $C_6H_5OH + FeCl_3 \longrightarrow$

(xxi)



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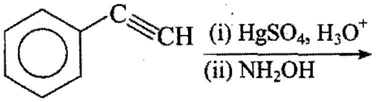

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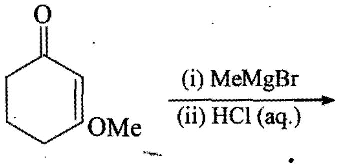

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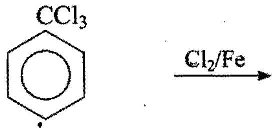


(xxv) $ClCH_2CH_2CH_2COPh + KOH + MeOH \longrightarrow$

(xxvi) $H_3CCOCOC_6H_5 + NaOH/H_3O^+ \longrightarrow$

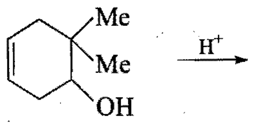
(xxvii) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$

(xxviii) $C_6H_5CH_2COOCH_3 \xrightarrow[\text{(ii) } H^+]{\text{(i) } CH_3MgBr \text{ (excess)}}$

(xxix) $C_6H_5C_2H_5 \xrightarrow[\text{(ii) NaCN}]{\text{(i) } Br_2\text{, heat, light}}$

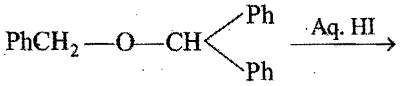
[CBSE (Med.) 2005]

(xxx)



[AIPMT (Mains) 2009]

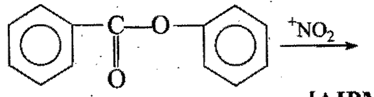
(xxxi)



$PhCH_2—O—CH(Ph)_2 \xrightarrow{\text{Aq. HI}}$

[AIPMT (Mains) 2009]

(xxxii)



[AIPMT (Mains) 2009]

8. Identify the final product in each reaction :

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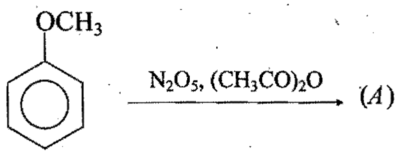

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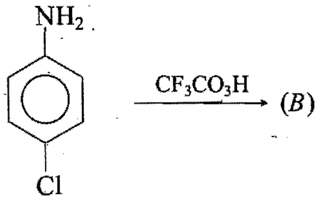

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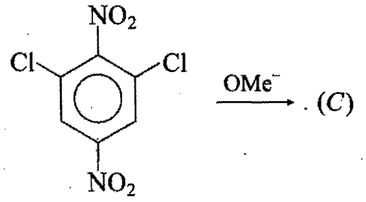

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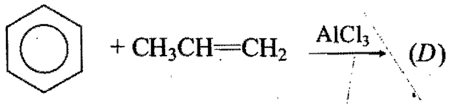

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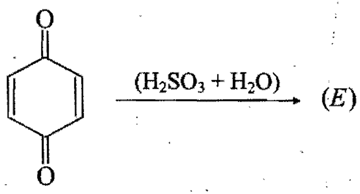

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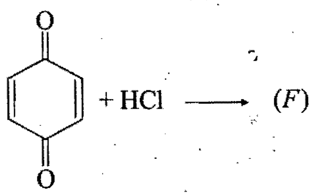

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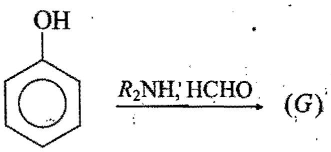

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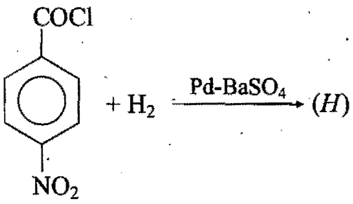

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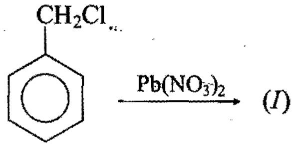

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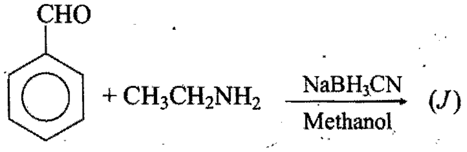

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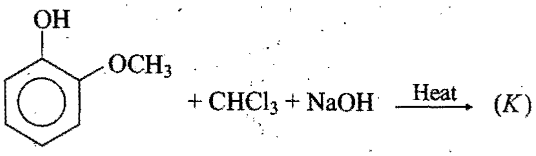

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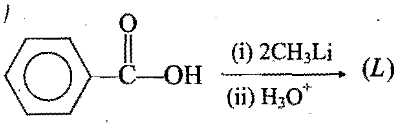

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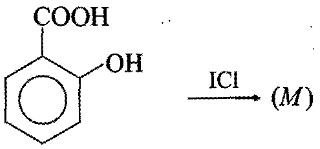

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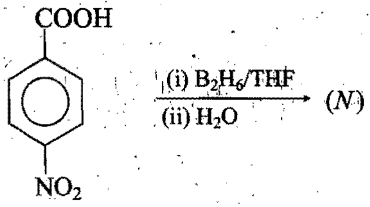

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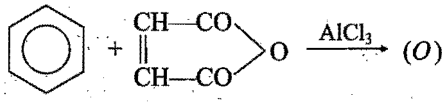

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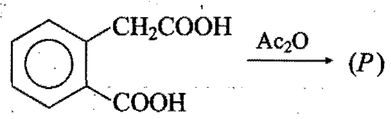

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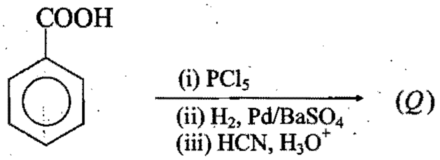

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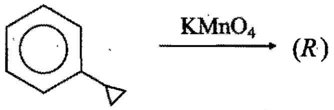

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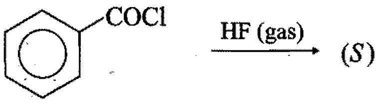

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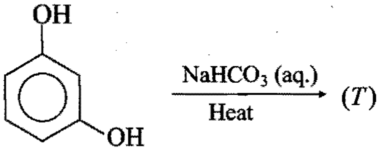

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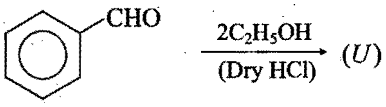

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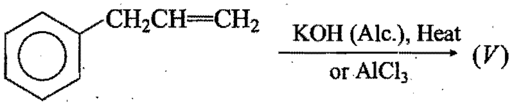

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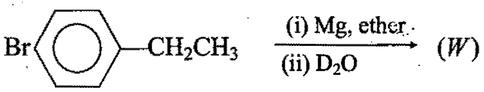

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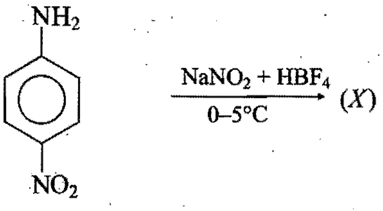

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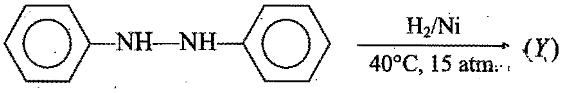

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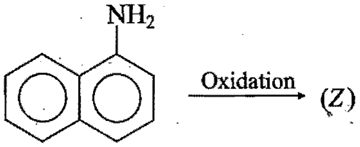


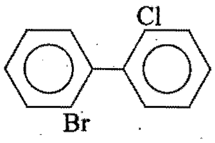
9. Name the final product of the following reactions :
   - (i) Benzene is treated with methyl chloride in the presence of anhydrous aluminium chloride.
   - (ii) Benzene is treated with acetyl chloride in the presence of anhydrous aluminium chloride.
   - (iii) Phenol is heated with zinc.
   - (iv) Sodium benzoate is heated with soda lime.
   - (v) Benzene is treated with fuming nitric acid in presence of conc. H_2SO_4.
   - (vi) Benzene is catalytically hydrogenated.
   - (vii) Benzaldehyde is heated with ammonia.
   - (viii) Toluene is treated with a mixture of conc. HNO_3 and conc. H_2SO_4.
   - (ix) Chlorine is passed through boiling toluene.
   - (x) Toluene is heated with acidic potassium permanganate solution.
   - (xi) Toluene in carbon tetrachloride is oxidised by chromyl chloride.
   - (xii) Aniline reacts with sodium nitrite and hydrochloric acid at 0°C.
   - (xiii) Phenol is treated with nitric acid in presence of H_2SO_4.
   - (xiv) Bromine is added to phenol.
   - (xv) Ammonia is added to benzoic acid and product is heated.
   - (xvi) Benzamide is heated with phosphorus pentoxide.
   - (xvii) Ozone reacts with benzene.
   - (xviii) Benzaldehyde reacts with hydroxylamine.
   - (xix) Phthalic anhydride is condensed with phenol in presence of conc. H_2SO_4.
   - (xx) Benzaldehyde reacts with hydrogen cyanide.

10. The following names are inconsistent with the prevalent rules. Rename these compounds in accordance with the accepted conventions:
   - (a) 1-Hydroxy-2-nitrobenzene
   - (b) 2,4,6-Trimethylbenzene
   - (c) 2-Ethyl-1-methylbenzene
   - (d) 2-Phenyl-3-butanol
   - (e) 3-Bromo-1-chlorobenzene.

11. Give the structure and names of the following substances : (a) TNT, (b) DDT, (c) PABA, (d) Picric Acid, (e) Saccharin, (f) Aspirin, (g) Mesitylene, (h) Pyrogallol, (i) Phenacetin, (j) Sulphanilic acid.

12. Write the structures and names of all the (a) dichlorinated and (b) trichlorinated derivatives of benzene.

13. Name each of the following substituted biphenyls:

(a)


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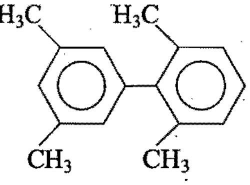

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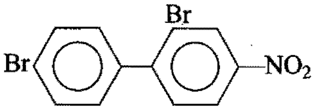
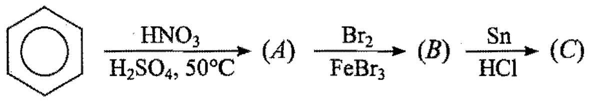


14. Write the structures and names for all the possible isomers of benzene derivatives having the following molecular formulae: (a) C_8H_{10}, (b) C_9H_{12} and (c) $C_6H_2F_4$.

15. Arrange the following:
   (a) Benzene, toluene, methoxybenzene and chlorobenzene in the order of reactivity towards sulphonation with fuming sulphuric acid.
   (b) $-\ddot{\underset{\cdot\cdot}{O}}H$, $-\ddot{\underset{\cdot\cdot}{O}}:^-$ and $-\ddot{O}COCH_3$ in decreasing order of activating effect towards electrophilic substitution.
   (c) $C_6H_5CH_2CH_2Cl$, $C_6H_5CHClCH_3$ and $C_6H_5CH{=}CHCl$ in the order of their decreasing activities with alcoholic silver nitrate.
   (d) CH_3CH_2Br, C_6H_5Br and $C_6H_5CH_2Br$ in order of their decreasing activities with KCN.
   (e) C_6H_5OH, m-ClC_6H_4OH and p-ClC_6H_4OH in decreasing order of their acidity.
   (f) m-$NO_2C_6H_4OH$, C_6H_5OH and p-$NO_2C_6H_4OH$ in decreasing order of their acidity.
   (g) *o*-, *m*- and *p*-bromophenol in order of increasing basicity.
   (h) *o*-, *m*- and *p*-nitrophenol in order of increasing basicity.
   (i) Carbonic acid, phenol, *p*-nitrophenol and benzoic acid in order of increasing acidity.
   (j) *m*-Cresol, phenol, *m*-chlorophenol and *m*-nitrophenol in order of increasing acidity.
   (k) C_6H_5COOH, p-OHC_6H_4COOH, p-$CH_3C_6H_4COOH$, p-ClC_6H_4COOH, p-BrC_6H_4COOH, p-$NO_2C_6H_4COOH$ in decreasing order of acidity.
   (l) *p*-Toluidine, *N,N*-dimethyl *p*-toluidine, *p*-nitroaniline, aniline in order of decreasing basicity.
   (m) Methylamine, dimethylamine, aniline, *N*-methyl aniline in order of decreasing basicity.
   (n) NH_3, CH_3NH_2, $C_6H_5NH_2$, $(C_6H_5)_2NH$, $(C_6H_5)_3N$ in order of decreasing basicity.

❖ Short Answer Type

16. Identify the unknown compounds:

(a)


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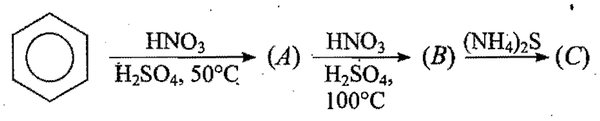

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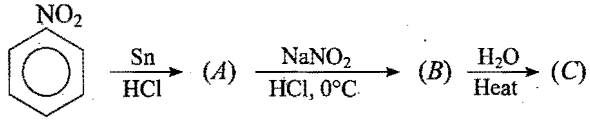

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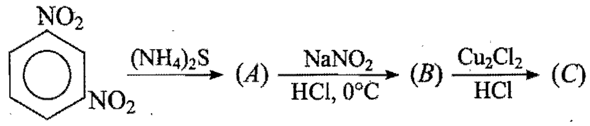

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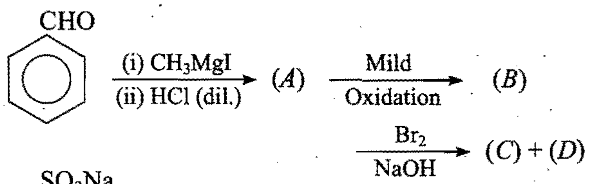

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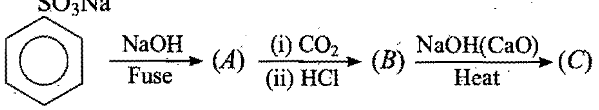
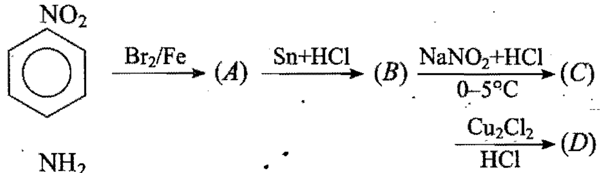


(g)


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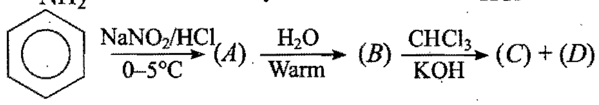
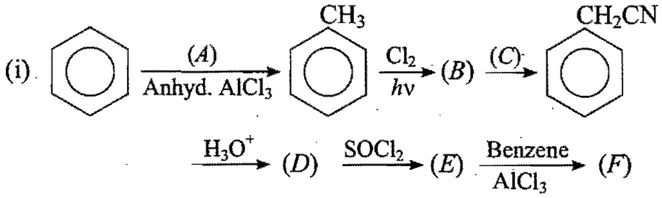
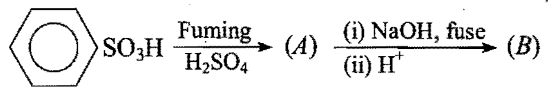


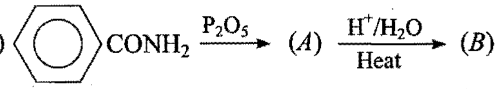
(i)


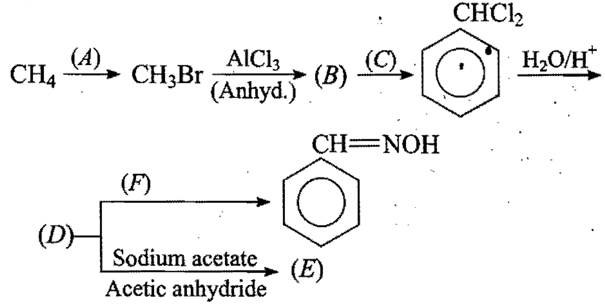
(j) $C_6H_5COOH \xrightarrow{(A)} C_6H_5COCl \xrightarrow{NH_3} (B) \xrightarrow{(C)} C_6H_5CN$

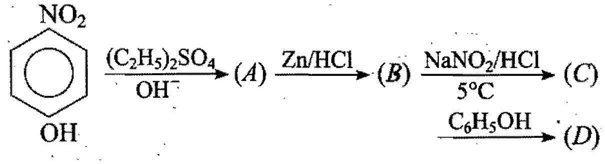
(k) $C_6H_5COOH \xrightarrow{PCl_5} (A) \xrightarrow{NH_3} (B) \xrightarrow{P_2O_5} C_6H_5CN$

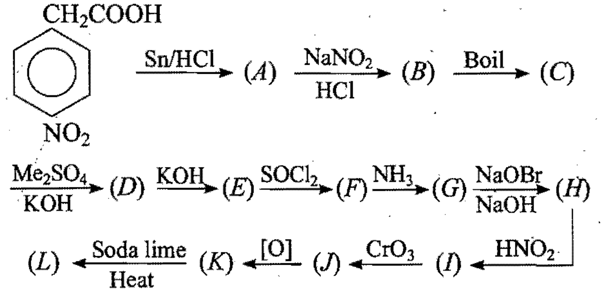
$\xrightarrow{H_2/Ni} (C)$

(l)


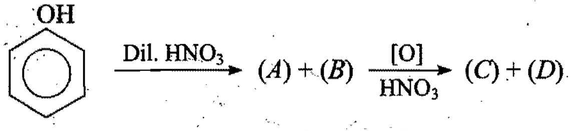
(m)


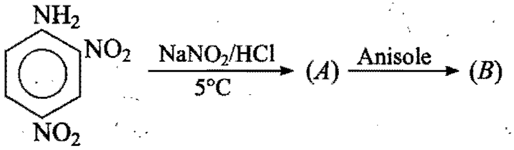
(n)


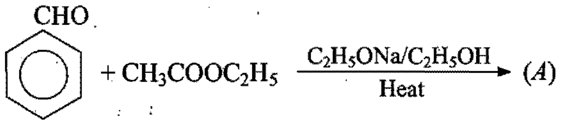
(o)


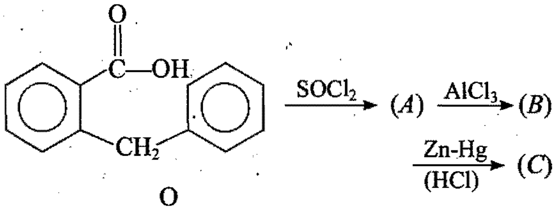
(p)


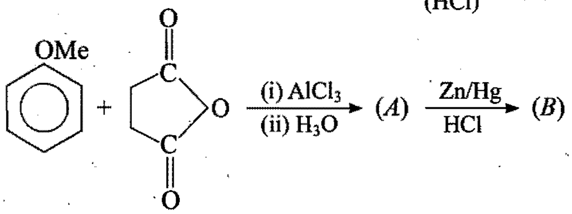
(q) $(A) \xrightarrow{PCl_5} C_6H_5COCl \xrightarrow{NH_3} (B) \xrightarrow{(C)} C_6H_5CN \xrightarrow{H_2/Ni} (D) \xrightarrow{COCl_2} (E)$

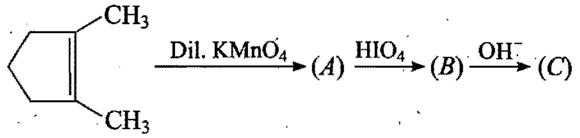
(r)


(s)


(t)


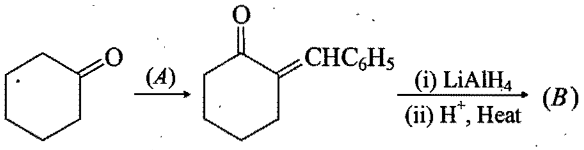
(u)


(v)


(w)


(x) $C_6H_5C{\equiv}CH \xrightarrow{NaNH_2,\ MeI} (A) \xrightarrow{Na/NH_3(l)} (B)$

(y) $C_6H_5CH{=}CH_2 \xrightarrow{Br_2} (A) \xrightarrow[\text{(ii) } CH_3I]{\text{(i) } NaNH_2 \text{ (3 equiv.)}} (B)$

(z)


How will you prepare benzene from?
(i) Phenol, (ii) Benzoic acid, (iii) Benzene sulphonic acid, (iv) Acetylene, (v) Aniline, (vi) Nitrobenzene, (vii) Toluene.

[**Hint :** (v) and (vi)

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Sn/HCl} \underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow{NaNO_2/HCl} \underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} \xrightarrow[NaOH]{SnCl_2} \underset{\text{Benzene}}{C_6H_6}$$

(vii) $C_6H_5CH_3 \xrightarrow[{[O]}]{\text{Alk. } KMnO_4} C_6H_5COOH \xrightarrow[\text{Heat}]{\text{Soda lime}} C_6H_6$]

18. How will you obtain toluene from?
(a) Toluic acid, (b) Cresol, (c) Bromobenzene, (d) Benzene.

19. How is chlorobenzene prepared from?
(a) Benzene, (b) Benzene diazonium chloride, (c) Aniline.

20. Give the method of preparation and important properties and uses of following compounds:
(a) Aniline, (b) Phenol, (c) Benzaldehyde, (d) Benzoic acid.

21. Answer the following:

(i) Prove that benzene molecule has three double bonds.

(ii) Give two examples which prove that benzene behaves differently than aliphatic unsaturated hydrocarbons.

(iii) Give the resonance structure of benzene.

(iv) Discuss the molecular orbital structure of benzene.

(v) Give the general mechanism of electrophilic substitution.

(vi) Give the mechanism of nitration of benzene.

(vii) Give the mechanism of halogenation of benzene.

(viii) Give the mechanism of Friedel-Crafts reaction.

(ix) Why —NH_2 group acts as *ortho-para*-directing ?

(x) Why —NO_2 group acts as *meta*-directing ?

(xi) State the conditions under which chlorination of toluene occurs in benzene ring and in the side chain.

(xii) Chlorobenzene is less reactive as compared to ethyl chloride.

[**Hint :** The lower reactivity of chlorobenzene is due to partial double bond character of C—Cl bond, *i.e.*, it is shorter and stronger bond in comparison to C—Cl bond in ethyl chloride.]

(xiii) Phenol is more acidic than ethyl alcohol.

[**Hint :** Phenoxide ion in phenol undergoes resonance stabilization.]

(xiv) Phenol is an acid but does not react with $NaHCO_3$.

[**Hint :** Phenol is weaker acid than carbonic acid.]

(xv) Aniline is less basic than ammonia.

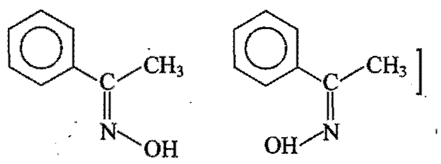
[**Hint :** Aniline has resonance structure and the lone pair of electrons on nitrogen atom is less available for coordination.]

(xvi) Aniline is always acetylated before nitration with acid mixture.

[**Hint :** Aniline is easily oxidised by oxidising agents. It is thus necessary to protect NH_2 group by acetylation.]

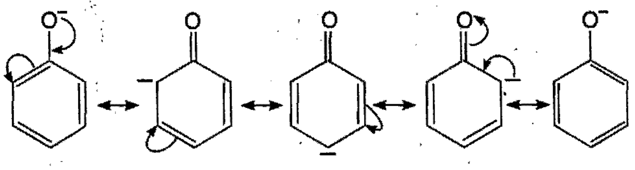
(xvii) Acetophenone or reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write the structures of the oximes.

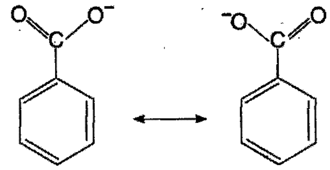
[**Hint :** The structures of two isomeric oximes are:


]

(xviii) Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is stronger acid than phenol. Why?

[**Hint :** The resonating structures are:





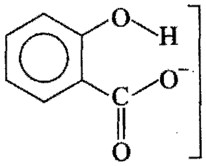
The benzoate ion is more stabilised because the negative charge is on the more electronegative oxygen atom, whereas in phenoxide ion, it is on the less electro negative carbon atoms. This causes benzoic acid to be a stronger acid than phenol.]

(xix) Nitrobenzene does not undergo Friedel-Crafts alkylation.

[**Hint :** The nitro group in nitrobenzene strongly deactivates the benzene ring. This decreases the reactivity of benzene towards Friedel-Crafts alkylation.]

(xx) *o*-Hydroxy benzoic acid is stronger than *p*-hydroxy benzoic acid. Why?

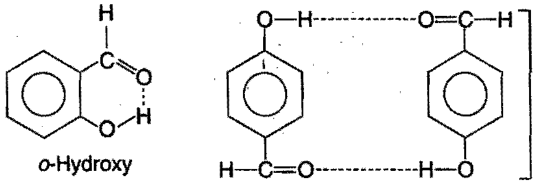
[**Hint :** The anion from salicylic acid is stabilized by intramolecular hydrogen bonding which does not exist in *p*-isomer.



Salicylate ion

(xxi) Why *o*-hydroxy benzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid?

[**Hint :** *o*-hydroxy benzaldehyde involves intramolecular hydrogen bonding hence it is a liquid because its intermolecular forces is low. On the other hand, *p*-hydroxy benzaldehyde involves intermolecular hydrogen bonding and therefore it is solid.

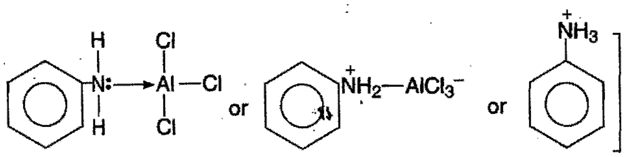


o-Hydroxy benzaldehyde

p-Hydroxy benzaldehyde

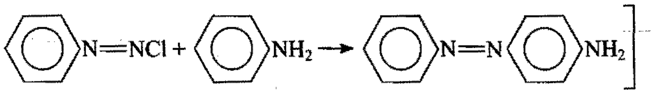
(xxii) Aniline does not undergo Friedel-Crafts reaction.

[**Hint :** Because lone pair of —NH_2 group undergoes coordintaion with Lewis acid catalyst ($AlCl_3$), *i.e.*, the group becomes electron withdrawing (m-directing and deactivating).



(xxiii) Mineral acid is added in excess in diazotisation of aryl amines.

[**Hint :** To keep the mixture strongly acidic which is necessary to prevent coupling of benzene diazonium chloride with excess of aryl amine.



22. How will you prepare the following compounds from benzene?
(i) Chlorobenzene, (ii) Nitrobenzene, (iii) Benzene sulphonic acid, (iv) Phenol, (v) Toluene, (vi) Acetophenone, (vii) Aniline, (viii) BHC, (ix) Glyoxal, (x) Trinitrotoluene, (xi) Resorcinol, (xii) Salicylic acid, (xiii) *m*-Nitrophenol, (xiv) Benzaldehyde, (xv) Benzoic acid.

23. How will you obtain the following from toluene?
(a) Benzaldehyde, (b) TNT, (c) TNB, (d) Benzoic acid, (e) Benzene, (f) Saccharin.

24. What products are obtained by reduction of nitrobenzene under different conditions ?

25. What happens when aniline reacts with following?
(i) Acetyl chloride, (ii) Bromine water, (iii) Nitrous acid, (iv) Benzaldehyde, (v) Fuming sulphuric acid.

26. How will you obtain the following from phenol?
(i) Benzene, (ii) Chlorobenzene, (iii) Picric acid, (iv) Aniline, (v) Phenolphthalein, (vi) Salicylaldehyde.

27. How will you obtain the following from benzaldehyde?
(a) Cinnamic acid, (b) Cinnamaldehyde, (c) Benzene, (d) Benzyl alcohol.

28. How will you obtain the following from benzoic acid?
(a) Benzamide, (b) Benzaldehyde, (c) Aniline, (d) Benzene, (e) Benzoyl chloride.

29. How will you obtain?
(a) *p*-Chlorobenzaldehyde from benzene.
(b) *o*-Bromobenzoic acid from toluene.
(c) Adipic acid from benzene.
(d) *o*-Chlorotoluene from toluene.
(e) *m*-Iodophenol from benzene (via diazonium salt reaction).
(f) Benzyl alcohol from benzene (via Grignard reaction).

30. How may benzoic acid be prepared from each of the following substances?
(i) Toluene, (ii) Benzene, (iii) Phenyl cyanide, (iv) Benzaldehyde, (v) Benzyl alcohol, (vi) Benzoyl chloride, (vii) Benzotrichloride.

31. With specific compounds write equations for the reactions involved in the following conversions:
(i) An aromatic hydrocarbon to its hydroxy derivative.
(ii) An aromatic hydrocarbon to its next higher homologue.
(iii) An aromatic hydrocarbon to its next lower homologue.
(iv) An aromatic hydroxy compound to an aromatic hydrocarbon.

32. How the following pairs can be distinguished?
(i) Benzene and ethanol.

[Ans. (a) Ethanol gives iodoform test benzene does not.
(b) Benzene burns with sooty flame while ethanol burns with non-luminous flame.]

(ii) Phenol and benzoic acid.

[Ans. (a) Phenol gives violet colour with ferric chloride solution, benzoic acid does not.
(b) Benzoic acid gives effervescence with aqueous $NaHCO_3$ solution, phenol does not.]

(iii) Phenol and glycerol.

[Ans. (a) Phenol gives violet colour with aqueous ferric chloride solution while glycerol does not.
(b) Glycerol on heating with $KHSO_4$ gives a pungent odour compound, acrolein, the aqueous solution of which gives Schiff's reagent test while phenol does not.]

(iv) Phenol and ethyl alcohol.

[Ans. (a) Phenol gives violet colouration with $FeCl_3$ aqueous solution, ethyl alcohol does not.
(b) Ethyl alcohol gives iodoform test, phenol does not.]

(v) Chlorobenzene and benzyl chloride.

[Ans. Benzyl chloride gives white precipitate with ethanolic silver nitrate solution while chlorobenzene does not.]

(vi) Styrene and ethyl benzene.

[Ans. (a) Styrene decolourises purple colour of dilute cold $KMnO_4$ solution. Ethylbenzene does not react.
(b) Styrene rapidly decolourises red colour of Br_2 in CCl_4. Ethylbenzene does not react under ordinary conditions.]

(vii) Ethylbenzene and *o*-xylene.

[Ans. Ethylbenzene gives benzoic acid (m.pt. 122°C) on oxidation with $KMnO_4$ while *o*-xylene gives phthalic acid (m.pt. 184°C)]

(viii) *p*-Bromotoluene and benzylbromide.

[Ans. Benzyl bromide produces a light yellow precipitate with alcoholic silver nitrate solution while *p*-bromotoluene does not.]

(ix) Aniline and ethylamine.

[Ans. Aniline reacts with nitrous acid (from $NaNO_2$ + HCl) at 0–5°C to form a diazonium salt which gives a red dye with alkaline solution of β-naphthol while ethylamine reacts with nitrous acid to produce nitrogen gas (seen as bubbles.)]

(x) Benzaldehyde and acetophenone.

[Ans. (a) Benzaldehyde forms silver mirror with an ammoniacal silver nitrate solution while acetophenone does not.
(b) Acetophenone forms yellow precipitate of iodoform with an alkaline solution of I_2. Benzaldehyde does not react.]

(xi) Benzaldehyde and acetaldehyde.

[Ans. (a) Acetaldehyde gives iodoform test, benzaldehyde does not.
(b) Acetaldehyde gives red precipitate with Fehling's solution while benzaldehyde does not react.]

(xii) Benzoic acid and cinnamic acid.

[Ans. Cinnamic acid being unsaturated compound decolourises bromine water in CCl_4. Benzoic acid does not react.]

(xiii) Phenol and salicylic acid.

[Ans. Phenol when heated with phthalic anhydride in presence of 2–3 drops of conc. H_2SO_4 forms phenolphthalein which gives pink colour with NaOH solution. This test is not given by salicylic acid.
Salicylic acid gives effervescences with $NaHCO_3$ solution while phenol does not.]

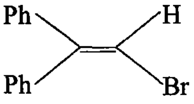
(xiv) Benzaldehyde and nitrobenzene.

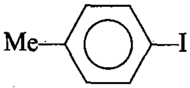
[Ans. (a) Benzaldehyde reduces Tollens' reagent while nitrobenzene does not.
(b) Benzaldehyde gives pink colour with Schiff's reagent but nitrobenzene does not.
(c) Nitrobenzene on reduction gives aniline which exhibits dye test. Benzaldehyde does not give dye test.]

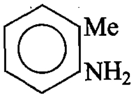
33. Explain the following with at least one example :
(i) Wurtz-Fittig reaction
(ii) Diazotisation
(iii) Sandmeyer's reaction
(iv) Reimer-Tiemann's reaction
(v) Friedel-Crafts reaction
(vi) Kolbe's reaction
(vii) Cannizzaro's reaction
(viii) Perkin reaction
(ix) Liebermann's nitroso reaction
(x) Claisen condensation

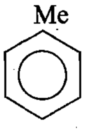
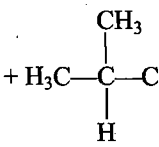
34. How will you prepare *m*-bromo iodo benzene from benzene?

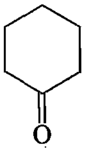
35. (i) Complete the following, giving the structures of the principal organic products:

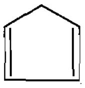
(a)

+ KNH_2 ⟶

(b)

+ Cu + Heat ⟶

(c)

+ $(COOEt)_2$ + EtONa ⟶

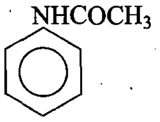
(d)

+

$H_3C-\overset{CH_3}{\underset{H}{C}}-CH_2Br$ + Anhy. $AlCl_3$ ⟶

(e)

+ $Ph_3P{=}CH_2$ ⟶

(f)

+ $CHBr_3$ + *t*-BuOK ⟶

(ii) Each of the following reactions gives two products. Write the structures of the products.

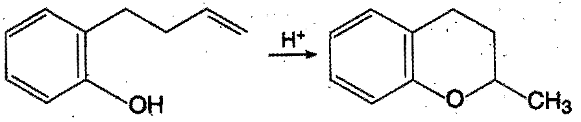
(g) $C_6H_5CH_2CH(Cl)C_6H_5 \xrightarrow{\text{Alc. KOH, heat}}$

(h)

$\xrightarrow{Br_2,Fe}$

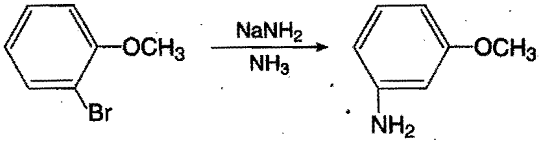
36. Show the steps to carry out the following transformations:
(i) Ethylbenzene ⟶ benzene
(ii) Ethylbenzene ⟶ 2-phenyl propionic acid

37. (a) Write the intermediate steps for each of the following reactions:

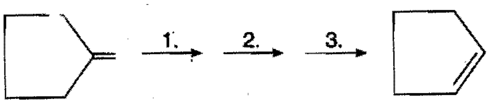
(i) $C_6H_5CH(OH)C{\equiv}CH \xrightarrow{H_3O^+} C_6H_5CH{=}CHCHO$

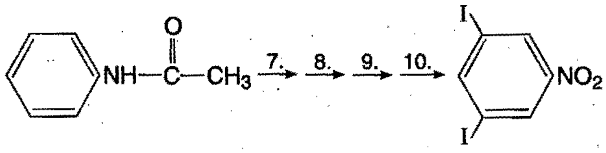
(ii)


(b) Explain briefly the formation of the products giving the structures of the intermediate.

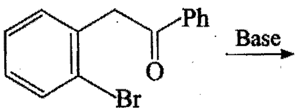
(iii)


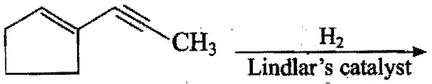
38. Complete the following reactions with appropriate reagents:

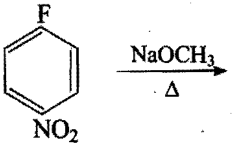
(a)


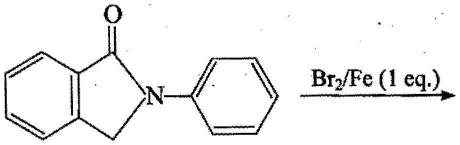
(b)


39. What would be the major product in each of the following reactions? **[IIT 2000]**

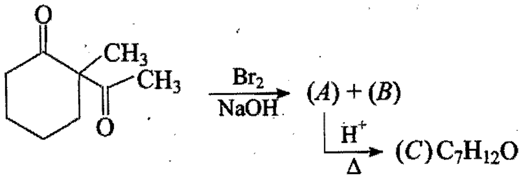
(i)


(ii)


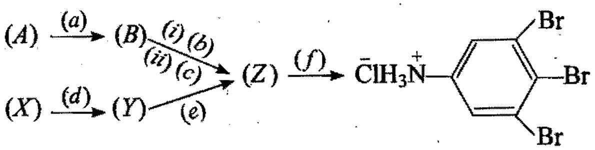
(iii)


(iv)


40. Identify the unknown compounds:

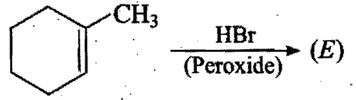
(i)


[IIT 2000]

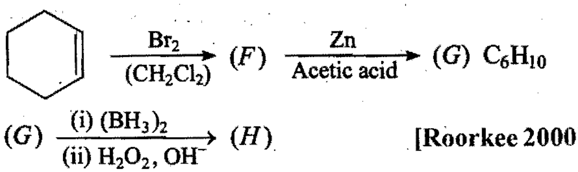
(ii)


[Roorkee 2001]

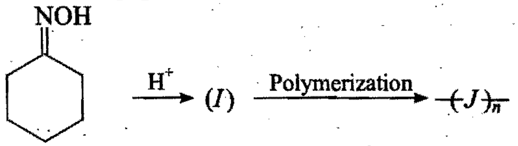
Give the structures of $(A), (B), (X), (Y)$ and (Z) if reagents a, b, c, d, e and f are Br_2/CH_3COOH, $NaNO_2/H_2SO_4$, Cu, HNO_3/H_2SO_4, Br_2/Fe and Sn/HCl respectively.

(iii)


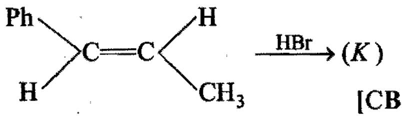
[Roorkee 2000]

(iv)


[Roorkee 2000]

(v)


[IIT 2000]

(vi)


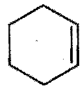
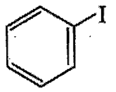
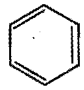
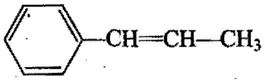
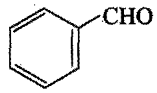
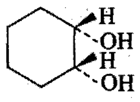
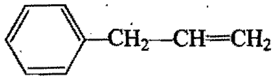
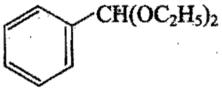
[CBSE (Med.) 2008]

41. How would you bring about the following conversions?

(i) Aniline into benzylamine (in three steps). **[IIT 2000]**

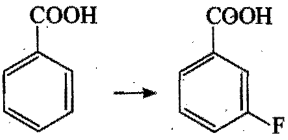
(ii) 4-Methoxy phenol from bromobenzene (in not more than five steps). **[IIT 2001]**

42. Structure of some reactants and products are given in column I and II respectively. First match the appropriate reactant-product pair from column I and II and then suggest another suitable reagent for each pair:

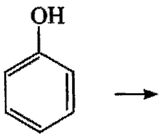
Column I		**Column II**	
(i)		(a)	
(ii)		(b)	
(iii)		(c)	
(iv)		(d)	

[Roorkee 2001]

43. Convert:

(a)


(not more than 3 steps)

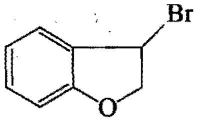
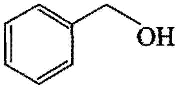
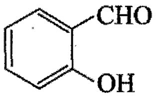
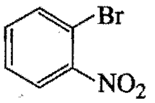
(b)


→ Aspirin

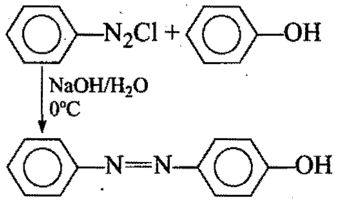
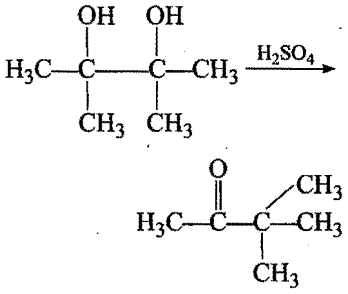
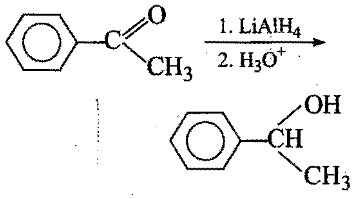
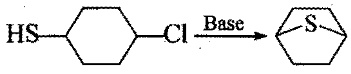
(c) PhCN to PhCOPh **[IIT 2003]** **[AIPMT (Mains) 2009]**

44. There is a solution of *p*-hydroxy benzoic acid and *p*-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory tests of the functional groups. **[IIT 2003]**

45. Match each of the compounds given in **Column I** with the reaction(s), that they can undergo with one or more statement(s), given in **Column II.** **[IIT 2009]**

Column I	**Column II**
(i) 	(p) Nucleophilic substitution
(ii) 	(q) Elimination
(iii) 	(r) Nucleophilic addition
(iv) 	(s) Esterification with acetic anhydride
	(t) Dehydrogenation

46. Match the reactions in **Column I** with one or more appropriate options in **Column II.** **[IIT 2010]**

Column I	**Column II**
(A) 	(p) Racemic mixture
(B) 	(q) Addition reaction
(C) 	(r) Substitution reaction
(D) 	(s) Coupling reaction
	(t) Carbocation intermediate

ANSWERS

1. (a) light oil; (b) sp^2; (c) Kekule; (d) electrophilic; (e) *meta*, decreases; (f) anhydrous aluminium chloride; (g) DDT and BHC; (h) ferric chloride or Br_2 water; (i) acetyl chloride; (j) *p, p'*-Dichlorodiphenyl trichloroethane, DDT; (k) nitrobenzene; (l) diazotisation; (m) phenol; (n) acidic, neutral; (o) carbontetrachloride; (p) benzaldehyde; (q) benzyl alcohol, benzoic acid; (r) potassium cyanide; (s) chromyl chloride; (t) phenyl isocyanide; (u) weaker; (v) phenol; (w) phenoxide ion; (x) *m*-sulphobenzoic acid; (y) phenol; (z) NO_2^+.

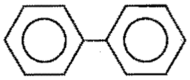
2. (i) Benzene hexachloride; (ii) electrophilic; (iii) picric acid; (iv) zero; (v) greater; (vi) benzylidene diacetate, $C_6H_5CH(OOCCH_3)_2$; (vii) *o*-nitrophenol; (viii) nucleophilic; (ix) dipolar ionic; (x) benzene; (xi) chlorobenzene; (xii) benzene; (xiii) *ortho* and *para*; (xiv) *meta;* (xv) maleic anhydride; (xvi) less; (xvii) phthalic anhydride; (xviii) stronger; (xix) acetyl, salicylic acid; (xx) protected, acetylation.

3. (a) True; (b) False—it does not show addition reactions like alkenes; (c) False—chlorobenzene is less reactive than benzene; (d) False— aniline forms diazonium compound with nitrous acid; (e) True; (f) True; (g) True; (h) True; (i) False—2,4,6-trinitrophenol is picric acid while 2,4,6-trinitrotoluene is TNT.; (j) False—does not decompose; (k) False—oxidation occurs; (l) True; (m) True; (n) False—same C—C bond lengths due to resonance; (o) True; (p) True; (q) False—benzamide on treatment with NaOH and Br_2 forms aniline; (r) False—explosives; (s) True; (t) False—$AlCl_3$ is a catalyst, produces electrophile when reacts with one of the reactants; (u) False—120°; (v) False—benzaldehyde does not reduce Fehling's solution; (w) False—same compound; (x) False—more reactive than chlorobenzene; (y) True; (z) True.

4. (i) False—in benzene carbon uses only two *p*-orbitals for hybridization; (ii) False—electron donating group orients the incoming electrophilic group to *ortho*- and *para*-positions; (iii) True; (iv) True; (v) False—phenol gives salicylaldehyde; (vi) False—does not undergo aldol condensation; (vii) False—forms diazonium salt; (viii) True; (ix) True; (x) False—aniline is less basic than ethylamine; (xi) True; (xii) True; (xiii) False—nitrobenzene does not undergo Friedel-Crafts reaction; (xiv) False—TNT is less powerful explosive than TNB; (xv) True; (xvi) False—aromatic compounds contain high percentage of carbon and hence, burn with sooty flame; (xvii) True; (xviii) False—toluene forms benzoic acid with dil. HNO_3; (xix) True; (xx) True.

5. [A] (1—h), (2—i), (3—g), (4—a), (5—b), (6—c), (7—d), (8—j), (9—f), (10—e).
[B] (1—e), (2—i), (3—a), (4—b), (5—j), (6—c), (7—d), (8—g), (9—h), (10—f).
[C] (1—f), (2—j), (3—h), (4—i), (5—b), (6—g), (7—d), (8—c), (9—e), (10—a).

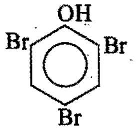
6. (A) (i), (ii), (v), (vii) and (viii) are *o*- and *p*-directing groups.
(iii), (iv), (vi), (ix) and (x) are *meta*-directing groups.
(B) (i) and (iv) are activating groups.
(ii), (iii), (v) and (vi) are deactivating groups.
(C) (i) 3-Chlorocyclohex-1-ene; (ii) 3-Chloro-1-phenylprop-1-ene; (iii) 1-Bromo-3-chlorobenzene; (iv) 2-Phenylnitroethane; (v) 4-Nitrobenzamine; (vi) 2,4,6-Trinitrophenol; (vii) 2-Methyl-benzamine; (viii) *N*-Ethyl-*N*-methylbenzamine; (ix) *N*-Benzyl-*N*-ethylbenzamine; (x) 2,6-Dimethylphenol; (xi) 4-(Hydroxy methyl) phenol; (xii) Methyl-3-hydroxy benzoate; (xiii) 2-Phenylethanal; (xiv) 2-Phenylpropanal; (xv) 3-Phenylprop-2-en-1-al.

7. (i) $2C_6H_5Cl + 2Na \longrightarrow$  $+ 2NaCl$

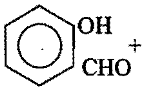
Diphenyl

(ii) $C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$

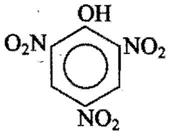
Chlorobenzene

(iii) $C_6H_5OH + 3Br_2 \xrightarrow{H_2O}$  $+ 3HBr$

2,4,6-Tribromophenol

(iv) $C_6H_5OH + CHCl_3 \xrightarrow[70°C]{3NaOH(aq.)}$  $+ 3NaCl + 2H_2O$

Salicylaldehyde

(v) $C_6H_5OH + 3HNO_3 \xrightarrow{H_2SO_4}$  $+ 3H_2O$

2,4,6-Trinitrophenol

(vi) $C_6H_5CH_3 + \frac{3}{2}O_2 \xrightarrow{V_2O_5} C_6H_5COOH + H_2O$

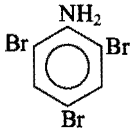
Benzoic acid

(vii) $C_6H_5NH_2 + CH_3COCl \xrightarrow{Base} C_6H_5NHCOCH_3 + HCl$

Acetanilide

(viii) $C_6H_5CONH_2 \xrightarrow{Br_2/4KOH} C_6H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O$

Aniline

(ix) $C_6H_5NH_2 + 3Br_2 \longrightarrow$  $+ 3HBr$

2,4,6-Tribromoaniline

(x) $C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O$

Aniline

(xi) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + HCl + H_3PO_3$

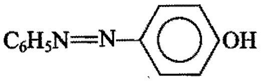
Benzene

(xii) $C_6H_5N_2Cl \xrightarrow[HCl]{Cu_2Cl_2} C_6H_5Cl + N_2$

Chlorobenzene

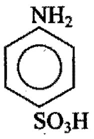
(xiii) $C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2 + H_2O$

Sodiumbenzoate

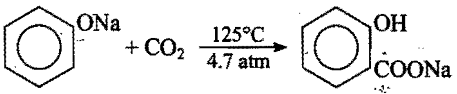
(xiv) $C_6H_5N_2Cl + C_6H_5OH \longrightarrow$  $+ HCl$

p-Hydroxy azobenzene

(xv) $C_6H_5NH_2 + H_2SO_4 \longrightarrow C_6H_5NH_3HSO_4$

$\xrightarrow{-H_2O} C_6H_5NHSO_3H \longrightarrow$ 

Sulphanilic acid

(xvi) 

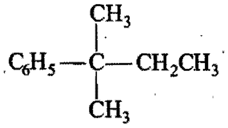
Sodium salicylate

(xvii) $C_6H_6 + CO + HCl \xrightarrow{AlCl_3} C_6H_5CHO + HCl$

Benzaldehyde

(xviii) $C_6H_5OH + NH_3 \xrightarrow[300°C]{ZnCl_2} C_6H_5NH_2 + H_2O$

Aniline

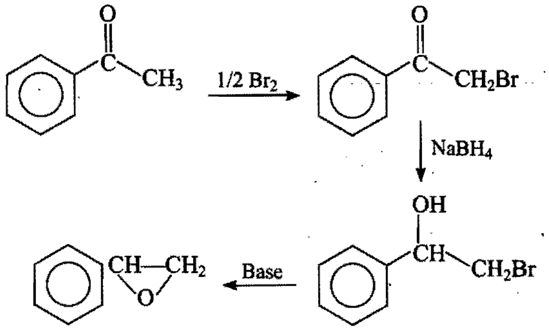
(xix) $C_6H_6 + (CH_3)_3C{-}CH_2Br \xrightarrow{AlCl_3}$ 

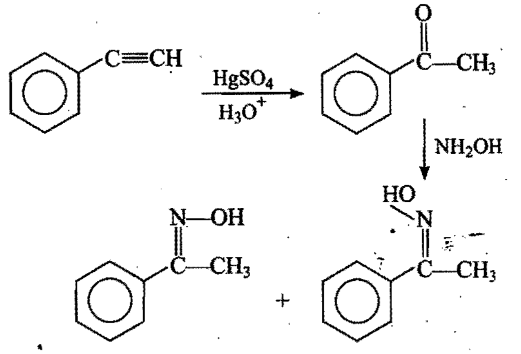
$C_6H_5{-}C(CH_3)_2{-}CH_2CH_3$

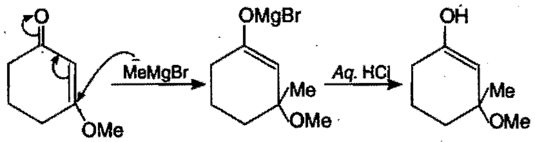
1,1-Dimethyl propyl benzene

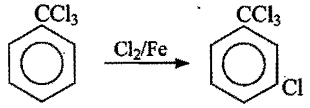
(xx) $6C_6H_5OH + FeCl_3 \longrightarrow (C_6H_5O)_6Fe + 3HCl + 3H^+$

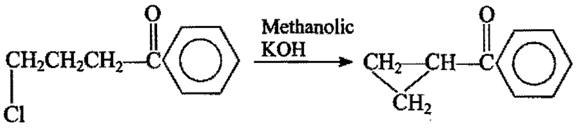
Complex

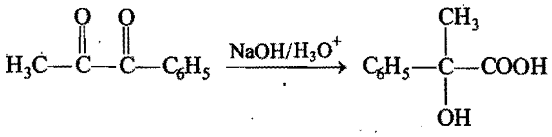
(xxi) 

(xxii) 

(xxiii) 

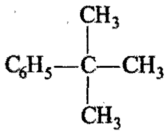
(xxiv) 

(xxv) 

(xxvi) 

$H_3C{-}CO{-}CO{-}C_6H_5 \xrightarrow{NaOH/H_3O^+} C_6H_5{-}C(CH_3)(OH){-}COOH$

(This rearrangement is known as benzilic acid rearrangement.)

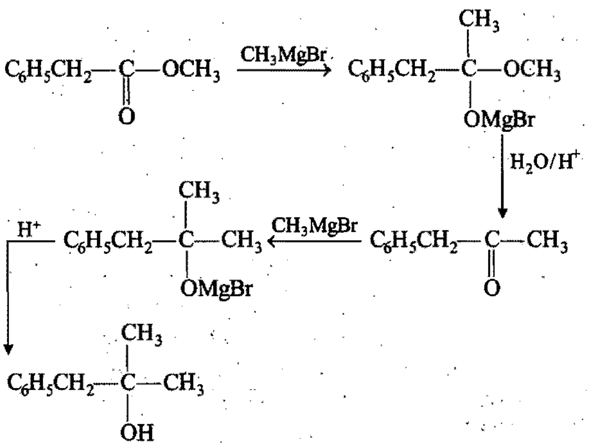
(xxvii) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$ 

$C_6H_5{-}C(CH_3)_2{-}CH_3$

Based on Friedel-Crafts reaction

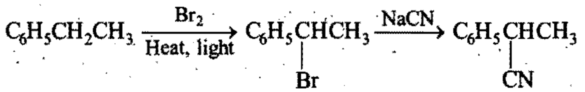
2-Methyl-2-phenyl propane

(xxviii)



2-Methyl-1-phenyl propan-2-ol

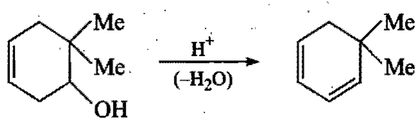
(xxix)



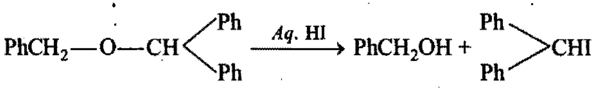
$C_6H_5CH_2CH_3 \xrightarrow[\text{Heat, light}]{Br_2} C_6H_5\underset{Br}{CH}CH_3 \xrightarrow{NaCN} C_6H_5\underset{CN}{CH}CH_3$

2-Phenyl propane nitrile

(xxx)

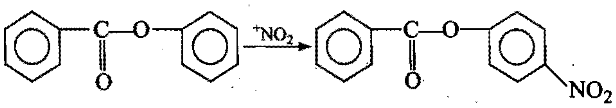


(xxxi)

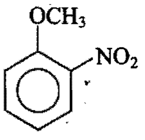


$PhCH_2—O—CH\langle^{Ph}_{Ph} \xrightarrow{Aq.\ HI} PhCH_2OH + {}^{Ph}_{Ph}\rangle CHI$

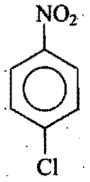
(xxxii)



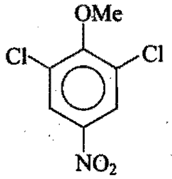
8. (A)



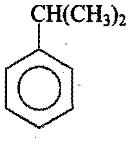
(B)



(C)

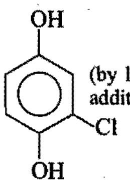


(D)



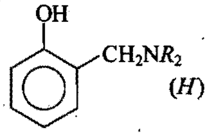
(E)

(F)

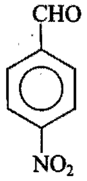


(by 1: 4 addition)

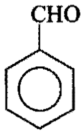
(G)



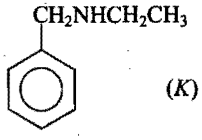
(H)



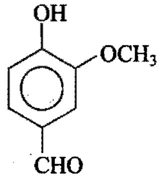
(I)



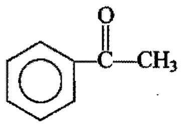
(J)



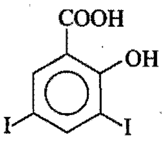
(K)



(L)

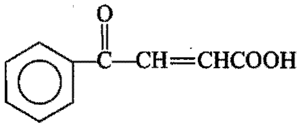


(M)

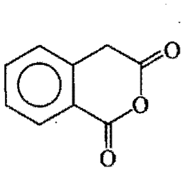


(N)

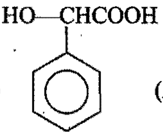
(O)



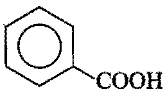
(P)



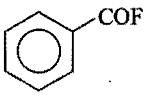
(Q)



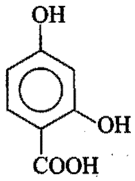
(R)



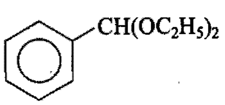
(S)



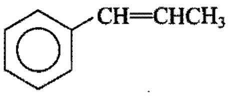
(T)



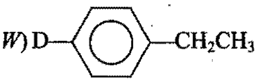
(U)



(V)

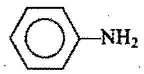


(W)

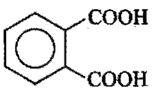


(X)

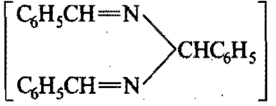
(Y)



(Z)



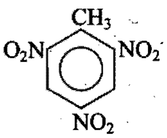
9. (i) Toluene, (ii) Acetophenone, (iii) Benzene, (iv) Benzene, (v) 1,3,5-Trinitrobenzene, (vi) Cyclohexane, (vii) Hydrobenzamide



, (viii) *o*-and *p*-nitrotoluenes, (ix) Benzyl chloride, (x) Benzoic acid, (xi) Benzaldehyde, (xii) Benzene diazonium chloride, (xiii) Picric acid, (xiv) 2,4,6-Tribromophenol, (xv) Benzamide, (xvi) Phenyl cyanide, (xvii) Glyoxal, (xviii) Benzaldoxime, (xix) Phenolphthalein, (xx) Benzaldehyde cyanohydrin.

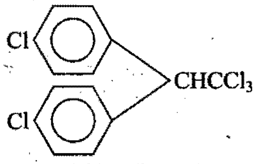
10. (a) 2-Nitrophenol (b) 1,3,5-Trimethylbenzene (c) 1-Ethyl-2-methyl benzene or 2-Ethyltoluene (d) 3-Phenyl-2-butanol. (e) 1-Bromo-3-chlorobenzene or *m*-Bromochlorobenzene.

11. (a)



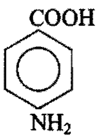
2,4,6-Trinitrotoluene

(b)



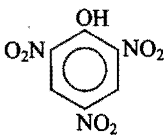
4,4′-Dichlorodiphenyl trichloroethane

(c)

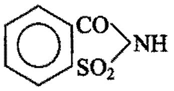


p-Aminobenzoic acid

(d)



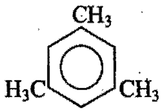
2,4,6-Trinitrophenol

(e) 

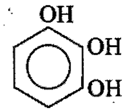
o-Sulphobenzoic imide

(f) 

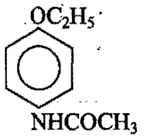
Acetyl salicylic acid

(g) 

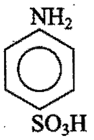
1,3,5-Trimethylbenzene

(h) 

1,2,3-Trihydroxy benzene

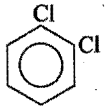
(i) 

p-Ethoxy acetanilide

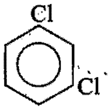
(j) 

Sulphanilic acid

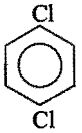
12. (a) There are three di-isomers:



1,2-Dichlorobenzene or *o*-Dichlorobenzene

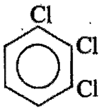


1,3-Dichlorobenzene or *m*-Dichlorobenzene

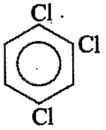


1,4-Dichlorobenzene or *p*-Dichlorobenzene

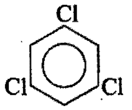
(b) There are three tri-isomers:



1,2,3-Trichlorobenzene

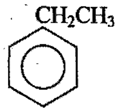


1,2,4-Trichlorobenzene

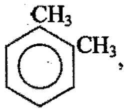


1,3,5-Trichlorobenzene

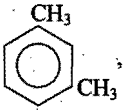
13. (a) 2-Bromo-2′-chlorobiphenyl, (b) 3,5,2′,6′-Tetramethylbiphenyl, (c) 2,4′-Dibromo-4-nitrobiphenyl.

14. (a) 

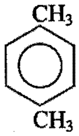
Ethylbenzene



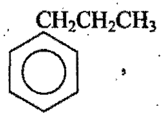
o-Xylene



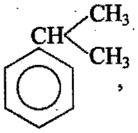
m-Xylene



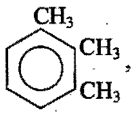
p-Xylene

(b) 

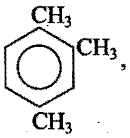
n-Propylbenzene



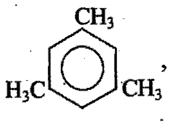
Isopropylbenzene



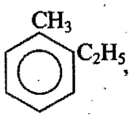
1,2,3-Trimethyl benzene



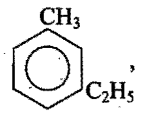
1,2,4-Trimethyl benzene



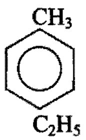
1,3,5-Trimethyl-benzene



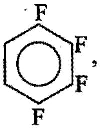
2-Ethyltoluene



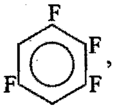
3-Ethyltoluene



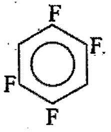
4-Ethyltoluene

(c) 

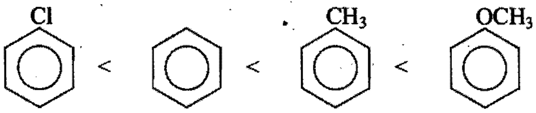
1,2,3,4-Tetrafluoro-benzene



1,2,3,5-Tetrafluoro-benzene



1,2,4,5-Tetrafluoro-benzene

15.(a) 

Chlorobenzene < Benzene < Toluene < Methoxy benzene

[—OCH_3 and —CH_3 are activating groups. In methoxy group, the oxygen atom has two lone pairs of electrons due to which mesomeric and electromeric effects operate while in —CH_3 group only inductive effect operate to activate the benzene ring, —Cl is a deactivating group.]

(b) —O^- > OH^- > —$OCOCH_3$

(c) $C_6H_5CHClCH_3 > C_6H_5CH_2CH_2Cl > C_6H_5CH{=}CHCl$

(d) $C_6H_5CH_2Br > CH_3CH_2Br > C_6H_5Br$

(e) *m*-ClC_6H_4OH > *p*-ClC_6H_4OH > C_6H_5OH

[Chlorine causes –*I* effect which decreases with increasing distance between —Cl and —OH. The *meta*-position being more closer than the *para*-position.]

(f) *p*-$NO_2C_6H_4OH$ > *m*-$NO_2C_6H_4OH$ > C_6H_5OH

[—NO_2 group is electron withdrawing and acid strengthening. Its resonance effect (which occurs from *o*- and *p*-positions) predominates over inductive effect.]

(g) *o*-bromophenol < *meta*-bromophenol < *p*-bromophenol.

[Acidity decreases as the distance of electron withdrawing substituent increases from —OH group.]

(h) *p*-nitrophenol ≈ *o*-nitrophenol < *m*-nitrophenol.

(i) phenol < *p*-nitrophenol < carbonic acid < benzoic acid.

(j) *m*-cresol < phenol < *m*-chlorophenol < *m*-nitrophenol.

(k) *p*-$NO_2C_6H_4COOH$ > *p*-ClC_6H_4COOH > *p*-BrC_6H_4COOH > C_6H_5COOH > *p*-$CH_3C_6H_4COOH$ > *p*-OHC_6H_4COOH

(l) *N,N*-dimethyl *p*-toluidine > *p*-toluidine > aniline > *p*-nitroaniline.

(m) Dimethylamine > methylamine > *N*-methyl aniline > aniline.

(n) $CH_3NH_2 > NH_3 > C_6H_5NH_2 > (C_6H_5)_2NH > (C_6H_5)_3N$

16. (a) (*A*) Nitrobenzene; (*B*) *m*-bromonitrobenzene; (*C*) *m*-bromoaniline.

(b) (*A*) Nitrobenzene; (*B*) *m*-dinitrobenzene; (*C*) *m*-nitroaniline.

(c) (*A*) Aniline; (*B*) benzene diazonium chloride; (*C*) phenol.

(d) (*A*) *m*-Nitroaniline; (*B*) *m*-nitrobenzene diazonium chloride; (*C*) *m*-chloronitrobenzene.

(e) (*A*) 1-Phenyl-1-ethanol; (*B*) acetophenone; (*C*) bromoform; (*D*) sodium benzoate.

(f) (*A*) Sodium phenolate; (*B*) salicylic acid; (*C*) phenol.

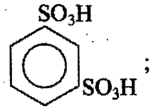
(g) (*A*) *m*-Bromonitrobenzene; (*B*) *m*-bromoaniline; (*C*) *m*-bromobenzene diazonium chloride; (*D*) *m*-bromochlorobenzene.

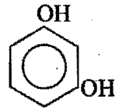
(h) (*A*) Benzene diazonium chloride; (*B*) phenol; (*C*) *o*-salicylaldehyde; (*D*) *p*-salicylaldehyde.

(i) (*A*) CH_3Cl; (*B*) $C_6H_5CH_2Cl$; (*C*) KCN; (*D*) $C_6H_5CH_2COOH$; (*E*) $C_6H_5CH_2COCl$; (*F*) $C_6H_5CH_2COC_6H_5$.

(j) (*A*) PCl_5; (*B*) $C_6H_5CONH_2$; (*C*) P_2O_5.

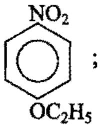
(k) (*A*) C_6H_5COCl; (*B*) $C_6H_5CONH_2$; (*C*) $C_6H_5CH_2NH_2$;

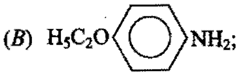
(l) (*A*) 

; (*B*) 

(m) (*A*) C_6H_5CN; (*B*) C_6H_5COOH.

(n) (*A*) Br_2, light; (*B*) $C_6H_5CH_3$; (*C*) Cl_2, light; (*D*) C_6H_5CHO; (*E*) $C_6H_5CH{=}CHCOOH$; (*F*) NH_2OH.

(o) (*A*) 

; (*B*) 

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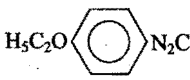
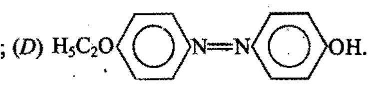
(*C*) 

; (*D*) 

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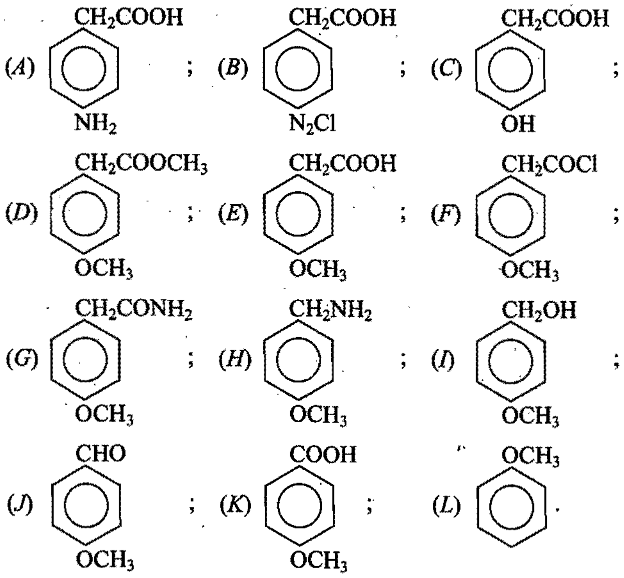
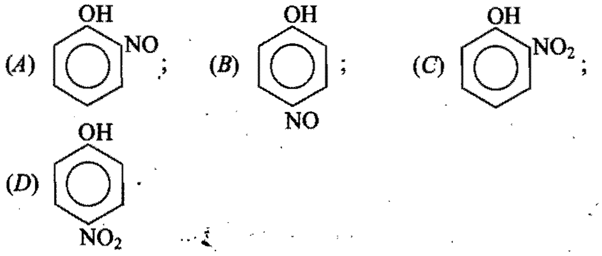
(p)

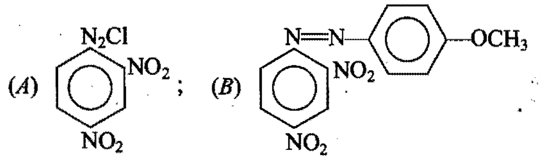


(q) (A) C_6H_5COOH; (B) $C_6H_5CONH_2$; (C) P_2O_5; (D) $C_6H_5CH_2NH_2$; (E) $C_6H_5CH_2NCO$.

(r)

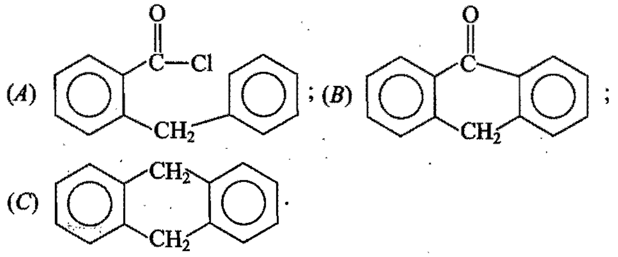


(s)

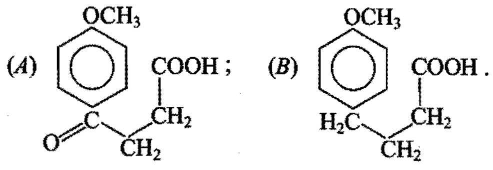


(t) (A) $C_6H_5CH{=}CHCOOC_2H_5$.

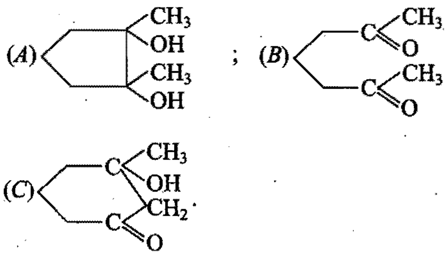
(u)



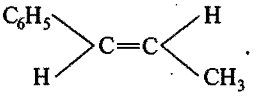
(v)



(w)

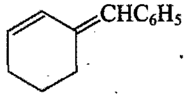


(x) (A) $C_6H_5C{\equiv}CCH_3$; (B)



(y) (A) $C_6H_5CHBrCH_2Br$; (B) $C_6H_5C{\equiv}C{-}CH_3$.

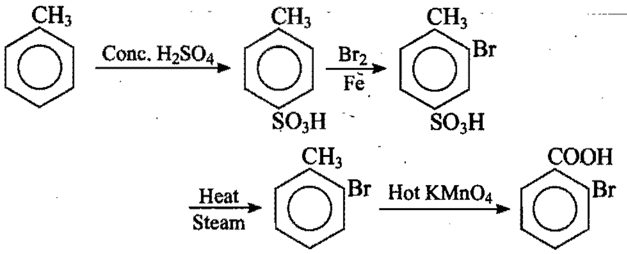
(z) (A) $C_6H_5CH{=}O$; (B)



29. (a) $C_6H_6 \xrightarrow{Br_2/Fe} C_6H_5Br \xrightarrow[Ether]{Mg} C_6H_5MgBr \xrightarrow[(ii)\ H^+/H_2O]{(i)\ HCHO}$

$C_6H_5CH_2OH \xrightarrow[Fe]{Cl_2} p\text{-}ClC_6H_4CH_2OH \xrightarrow{CrO_3/pyridine} p\text{-}ClC_6H_4CHO$

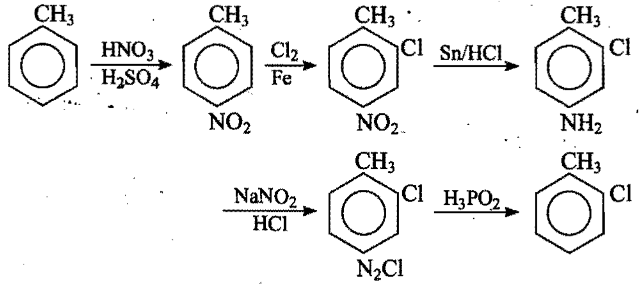
(b)



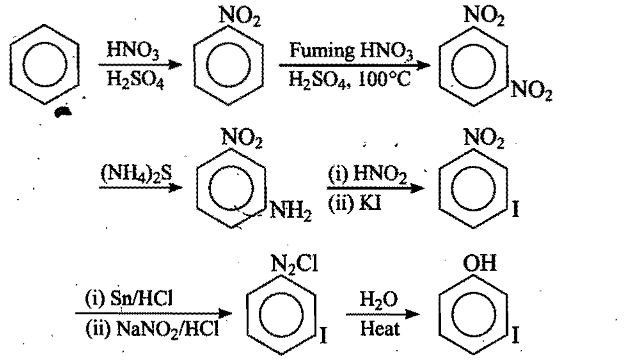
(c) $C_6H_6 \xrightarrow{H_2/Pd} \underset{\text{Cyclohexane}}{C_6H_{12}} \xrightarrow[h\nu]{Cl_2} \underset{\text{Chlorocyclohexane}}{C_6H_{11}Cl}$

$\xrightarrow{\text{Alc. KOH}} \underset{\text{Cyclohexene}}{C_6H_{10}} \xrightarrow[H^+]{KMnO_4} \underset{\text{Adipic Acid}}{HOOC(CH_2)_4COOH}$

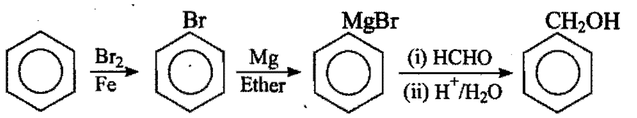
(d)



(e)



(f)



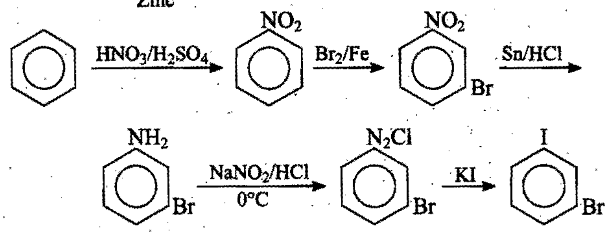
31. (i) $\underset{\text{Benzene}}{C_6H_6} \xrightarrow[Fe]{Cl_2} \underset{\text{Chlorobenzene}}{C_6H_5Cl} \xrightarrow[\text{200 atm. press.}]{NaOH/300°C} \underset{\text{Phenol}}{C_6H_5OH}$

(ii) $\underset{\text{Benzene}}{C_6H_6} \xrightarrow[\text{reaction}]{\text{Friedel-Crafts}} \underset{\text{Toluene}}{C_6H_5CH_3}$

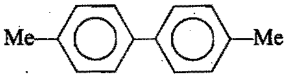
(iii) $\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[KMnO_4]{[O]} C_6H_5COOH \xrightarrow[\text{Heat}]{\text{Soda lime}} \underset{\text{Benzene}}{C_6H_6}$

(iv) $\text{Phenol} \xrightarrow[\text{Zinc}]{\text{Heat}} \text{Benzene}$

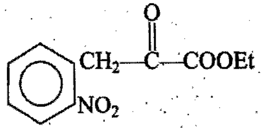
34.



35. (i) (a) Ph—C≡C—Ph; (b)

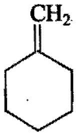


(c)

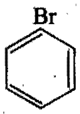


(d)

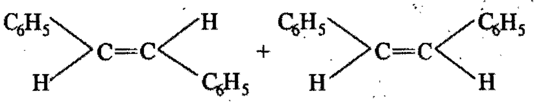
(e)



(f)

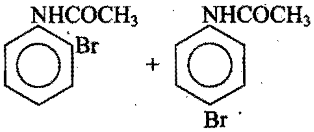


(ii) (g)

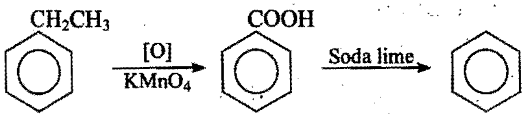


(Major product)

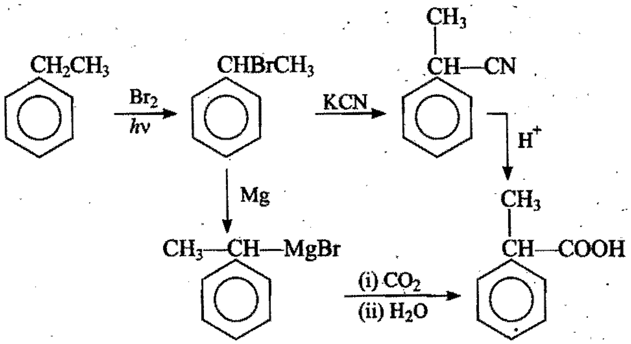
(h)



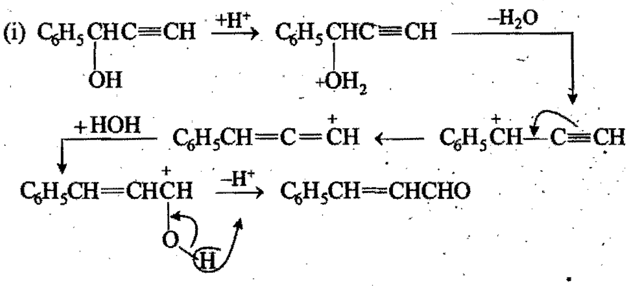
36. (i)



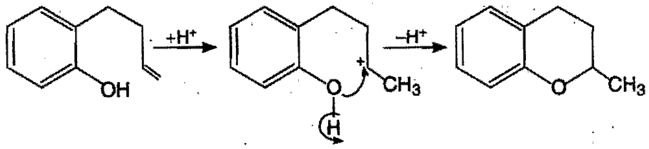
(ii)



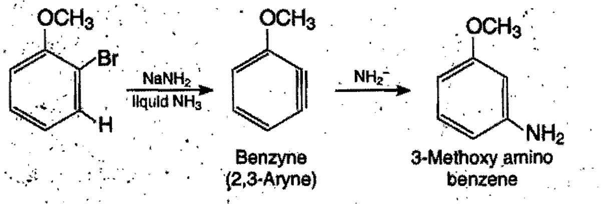
37. (i)



(ii)

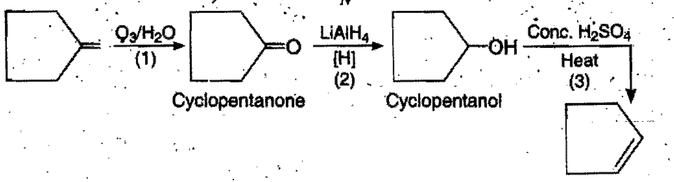


(iii)

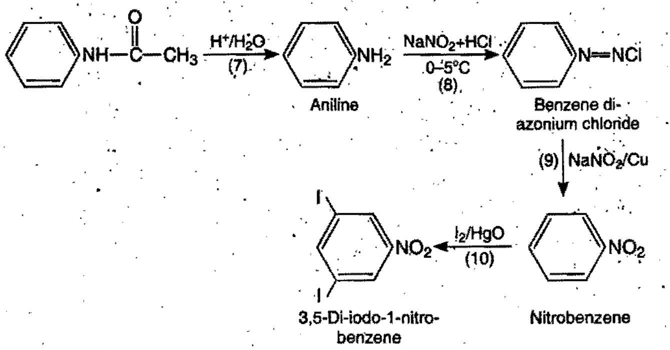


The reaction proceeds through benzyne mechanism (Elimination addition mechanism) instead of S_N2 mechanism.

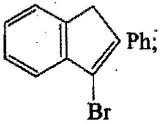
(a)



(b)

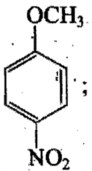


39. (i)

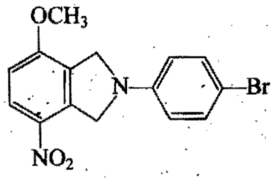


(ii)

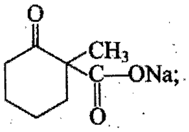
(iii)



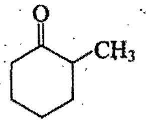
(iv)



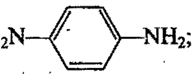
40. (i) (A)



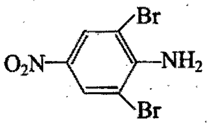
(B) $CHBr_3$; (C)



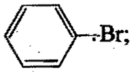
(ii) (A)



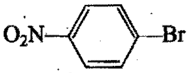
(B)



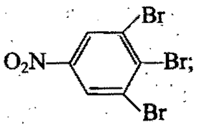
(X)



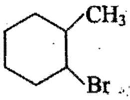
(Y)



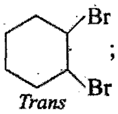
(Z)



(iii) (E)

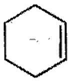


(iv) (F)

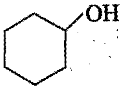


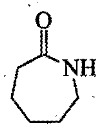
Trans

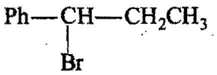
(G)



(H)

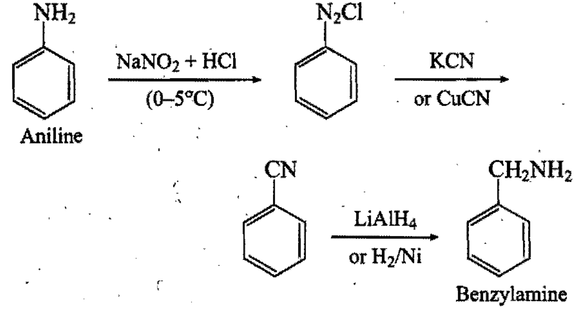


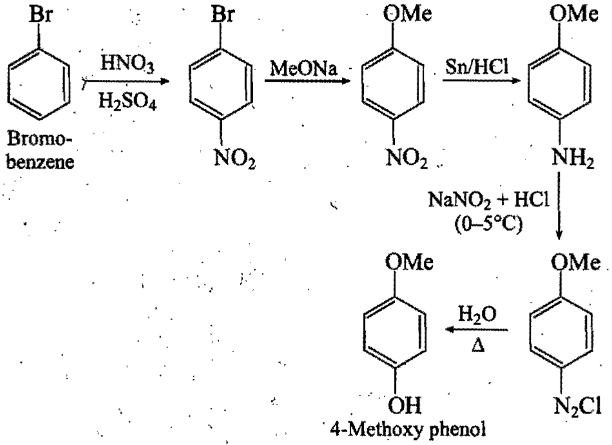
(v) (*I*)  (Caprolactum); (*J*) $\left[\!\!-CO(CH_2)_5NH-\!\!\right]_n$ Nylon

(vi) (*K*) 

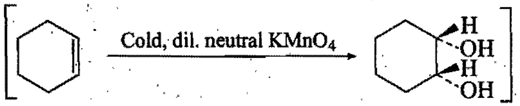
$Ph-\underset{Br}{\underset{|}{C}}H-CH_2CH_3$

1-Bromo-1-phenylpropane

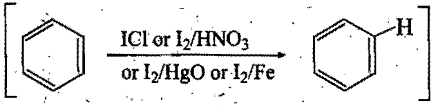
41. (i) 

(ii) 

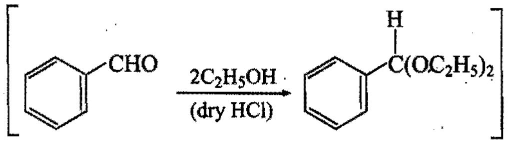
42. (i) (c), Cold, dil. neutral $KMnO_4$ or HCOOH or *aq*. $KMnO_4$ or OsO_4/*aq*. $NaHSO_3$



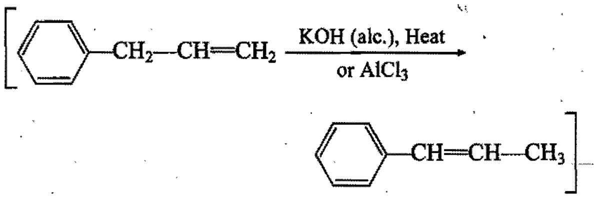
(ii) (a), Reagent —ICl or I_2/HNO_3 or HgO or I_2/Fe

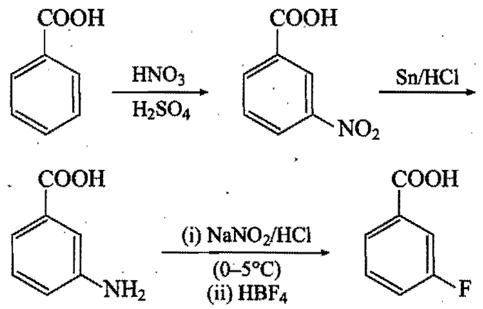


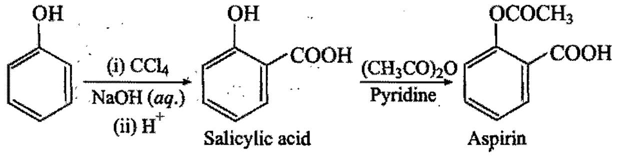
(iii) (d), Reagent —C_2H_5OH/dry HCl or HCl

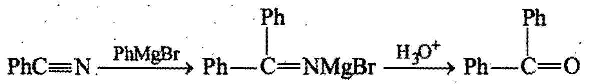


(iv) (b), Reagent —Alc. KOH, heat or $AlCl_3$ or H^+



43. (a) 

(b) 

(c) 

$PhC{\equiv}N \xrightarrow{PhMgBr} Ph-\overset{Ph}{\overset{|}{C}}{=}NMgBr \xrightarrow{H_3O^+} Ph-\overset{Ph}{\overset{|}{C}}{=}O$

44. The treatment of the solution with HCl causes *p*-amino benzoic acid to dissolve in it, while *p*-hydroxy benzoic acid remains undissolved. Treating the acid solution with alkali, it will cause the recovery of *p*-amino benzoic acid.

Both the compounds give effervescence with $NaHCO_3$ indicating the presence of —COOH group.

The group —NH_2 can be confirmed by carbylamine test or azodye test.

The phenolic —OH group can be confirmed by the $FeCl_3$ test which gives violet colour.

45. A—(p,q,t); B—(p,q,s,t); C—(r,s); D—(p)

46. A—(r,s); B—(t); C—(p,q); D—(r)

PROBLEMS BASED ON STRUCTURE AND PROPERTIES

Problem 1. *A hydrocarbon (A) with molecular formula* C_8H_8 *gave the following reactions :*

(*i*) *On shaking with bromine, a bromo derivative (B) with the composition* $C_8H_8Br_2$ *was formed.*

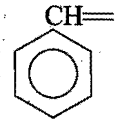
(*ii*) *The rapid oxidation of hydrocarbon with alkaline* $KMnO_4$ *gave a monobasic acid (C).*

(*iii*) *The acid (C) on distillation with soda lime gave benzene.*

Deduce the structures of (A), (B) and (C) and name the compound (A).

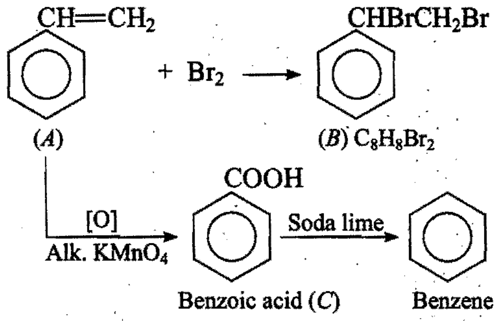
Solution : The compound (*A*) forms an addition compound with bromine, hence (*A*) should be an unsaturated hydrocarbon. Since, (*A*) on oxidation gives a monobasic acid which on distillation with soda lime forms benzene, (*A*) should be a benzene derivative having unsaturated side-chain.

The possible hydrocarbon (*A*) can be:



Vinyl benzene (styrene)

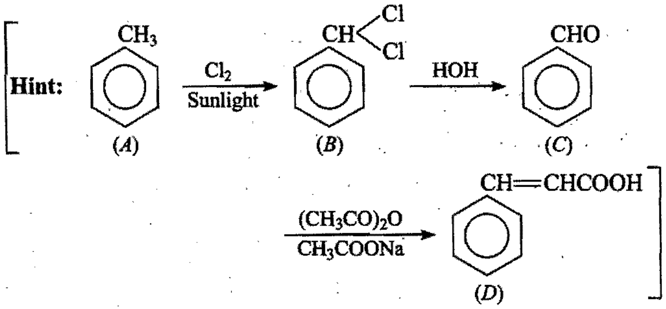
Reactions :



The name of hydrocarbon (A) is styrene.

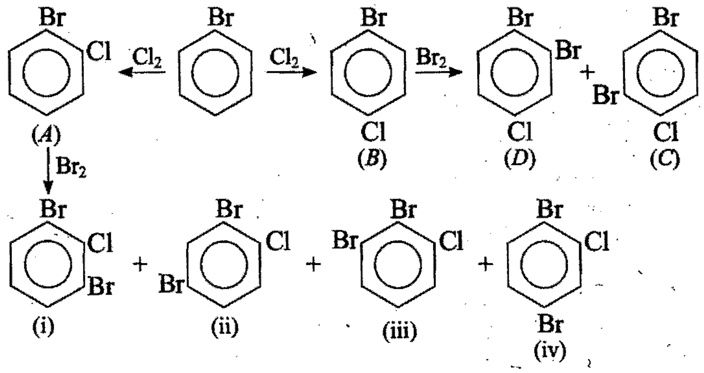
Problem 2. *Compound (A), having an empirical formula* C_7H_8, *is chlorinated in sunlight to give a product (B), which on hydrolysis gives a compound (C). (C) gives a positive test with Tollens' reagent, and with sodium acetate and acetic anhydride gives an acid (D), with equivalent weight* 148.15. *Identify (A), (B), (C) and (D) and explain the reactions involved.*

Hint:



Problem 3. *When bromobenzene is monochlorinated two isomeric compounds (A) and (B) are obtained. Monobromination of (A) gives several isomeric products of molecular formula* $C_6H_3ClBr_2$ *while monobromination of (B) yields only two isomers (C) and (D). Compound (C) is identical with one of the compounds obtained from the bromination of (A), however (D) is totally different from any of the isomeric compounds obtained from the bromination of (A). Give the structures of (A), (B), (C) and (D) and also structures of isomeric monobrominated products of (A). Support your answer with reasoning.*

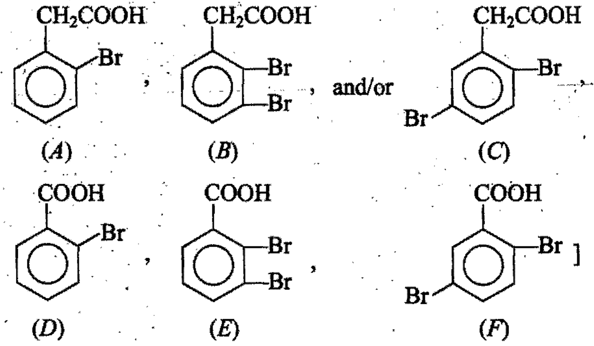
Solution : Bromine is *o*-, *p*-directing, hence *ortho* and *para* products are formed.



Products *ortho/para* to bromine and chlorine are formed. Compound (C) is identical with (ii) but (D) is different from (i), (ii), (iii) and (iv).

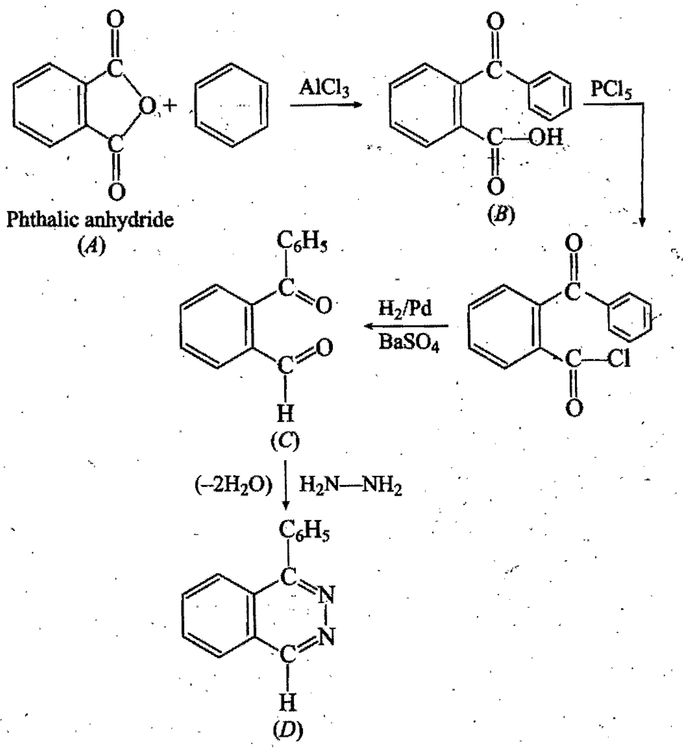
Problem 4. *An acid (A)* $C_8H_7O_2Br$ *on bromination in presence of* $FeBr_3$ *gives two isomers, (B) and (C) of formula* $C_8H_6O_2Br_2$. *Vigorous oxidation of (A), (B) and (C) gives acids (D), (E) and (F) respectively. (D)* $C_7H_5O_2Br$ *is the strongest acid among all of its isomers, whereas (E) and (F) each has a molecular formula of* $C_7H_4O_2Br_2$. *Give the structures of (A) to (F) with justification.* **[Roorkee 2000]**

Ans.

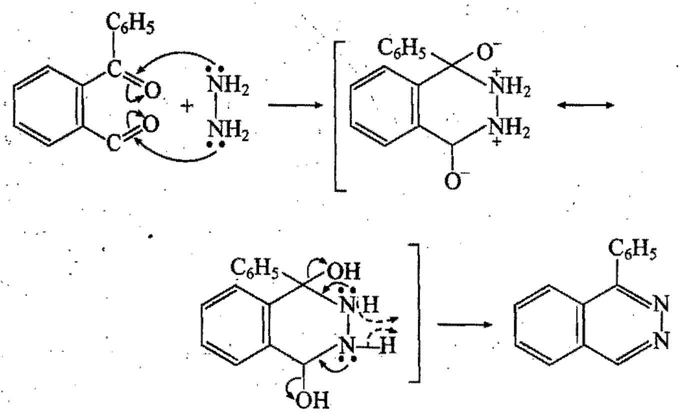


Problem 5. *An organic compound (A),* $C_8H_4O_3$, *in dry benzene in the presence of anhydrous* $AlCl_3$ *gives compound (B). The compound (B) on treatment with* PCl_5, *followed by reaction with* $H_2/Pd\text{-}BaSO_4$ *gives compound (C), which on reaction with hydrazine gives a cyclised compound (D) of formula* $C_{14}H_{10}N_2$. *Identify (A), (B), (C) and (D). Explain the formation of (D) from (C).* **[IIT 2000]**

Solution :

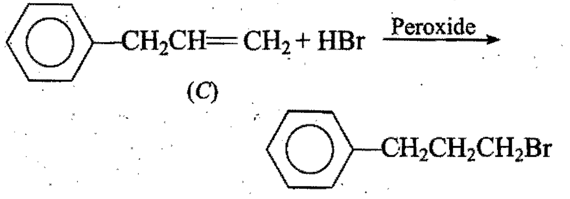


The formation of (D) from (C) may be explained as follows:



Problem 6. *A Grignard reagent (A) and a haloalkene (B) react together to give (C). Compound (C) on heating with* KOH *yields a mixture of two geometrical isomers, (D) and (E), of which (D) predominates. (C) and (E) have the same molecular formula and (C) gives 1-bromo-3-phenyl propane on reaction with* HBr *in the presence of a peroxide. Give structures of (A), (B) and (C) and configurations of (D) and (E) with reasons.* **[Roorkee 2001]**

Solution. Since, (C) gives 1-bromo-3-phenyl propane on reaction with HBr in the presence of a peroxide, therefore, (C) is 3-phenyl prop-1-ene.



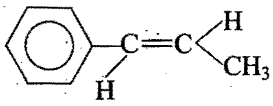
1-Bromo-3-phenyl propane

Because (C) and (E) have same molecular formula, therefore, they are isomers and the reaction is:

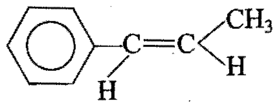
$$(C) \xrightarrow{\text{KOH}} (D) + (E)$$

it is a isomerization reaction.

So, (D) and (E) are 3-phenyl prop-2-ene.

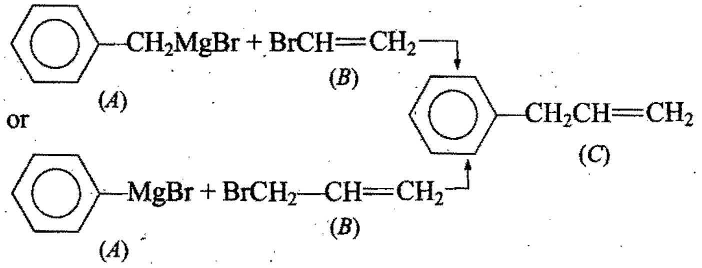


and

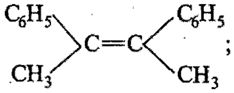
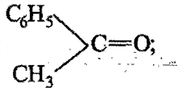


(D) (E)

Since, (C) is obtained by the reaction of a Grignard reagent (A) with haloalkene (B), therefore, (A) and (B) are:

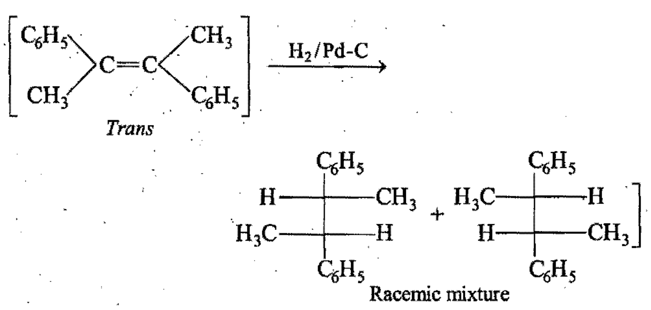


Problem 7. *An alkene (A),* $C_{16}H_{16}$ *on ozonolysis gives only one product (B),* C_8H_8O. *Compound (B) on reaction with* NaOH/I$_2$ *yields sodium benzoate. Compound (B) reacts with* KOH/NH$_2$NH$_2$ *yielding a hydrocarbon (C)* C_8H_{10}. *Write the structure of compounds (B) and (C). Based on this information two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation* (H_2/Pd-C) *gives a racemic mixture.* **[IIT 2001]**

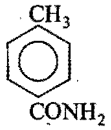
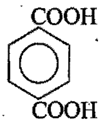
[**Ans.** (A):  ; (B): 

$(C_6H_5)(CH_3)C{=}C(C_6H_5)(CH_3)$; $(C_6H_5)(CH_3)C{=}O$

(C): $C_6H_5CH_2CH_3$



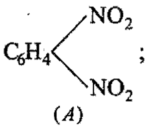
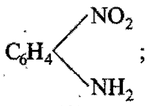
Problem 8. *Compound (A)* C_8H_9NO *is insoluble in dilute acid (A) when treated with* $KMnO_4$ *(acidic) gives nitrogen free compound (B). (B) is soluble in aq.* $NaHCO_3$ *solution and gives only one mononitro substitution product. What are (A) are (B)?*

[**Ans.** (A)  ; (B) ]

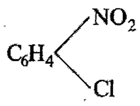
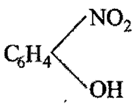
Problem 9. *Compound (A)* C_8H_9Cl *is hydrolysed by aqueous KOH to form (B),* $C_8H_{10}O$. *(B) on mild oxidation gives (C) which gives positive iodoform test. What are (A), (B) and (C)?*

[**Ans.** (A) $C_6H_5CHClCH_3$; (B) $C_6H_5CHOHCH_3$;
(C) $C_6H_5COCH_3$]

Problem 10. *An organic compound (A)* $C_6H_4N_2O_4$ *is reduced by* $(NH_4)_2S$ *and gives (B)* $C_6H_6N_2O_2$. *(B) on reaction with* $NaNO_2$ + HCl *at 0°C followed by the action of* Cu_2Cl_2/HCl *gives (C)* $C_6H_4O_2NCl$. *(C) on treating with* NaOH *at high pressure and temperature gives (D)* $C_6H_5O_3N$ *which is steam volatile. What are (A) to (D)?*

[**Ans.**  $C_6H_4(NO_2)_2$;  $C_6H_4(NO_2)(NH_2)$;

(A) Ortho (B) Ortho

 $C_6H_4(NO_2)(Cl)$;  $C_6H_4(NO_2)(OH)$]

(C) Ortho (D) Ortho

OBJECTIVE QUESTIONS

SET I : This set contains questions with single correct answer.

1. Aromatic compounds are:
(a) open-chain compounds ☐
(b) closed-chain compounds ☐
(c) both open and closed-chain compounds ☐
(d) closed-chain compounds which are structurally similar to benzene ☐

2. Coal-tar is a main source of:
(a) aromatic compounds ☐
(b) alicyclic compounds ☐
(c) aliphatic compounds ☐
(d) heterocyclic compounds ☐

3. The general formula of arenes is:
(a) C_nH_{2n} ☐ (b) C_nH_{2n-4} ☐
(c) C_nH_{2n+2} ☐ (d) C_nH_{2n-6} ☐

4. Benzene was discovered by:
(a) Cavendish ☐ (b) Faraday ☐
(c) Berzelius ☐ (d) Wöhler ☐

5. Mark the fraction of the coal-tar distillation in which benzene and toluene both are present:
(a) light-oil ☐ (b) middle-oil ☐
(c) heavy-oil ☐ (d) anthracene-oil ☐

6. Which one of the following statements is wrong?
(a) Aromatic compounds are richer in carbon content ☐
(b) Aromatic compounds burn with smoky flame ☐
(c) Aromatic compounds are generally unstable ☐
(d) Aromatic compounds show substitution reactions ☐

7. The ring structure of benzene was first proposed by:
(a) Wöhler ☐ (b) Faraday ☐
(c) Kekule ☐ (d) Baeyer ☐

8. The carbon-carbon bond order in benzene is: **[BCECE (Med.) 2008]**
(a) 1 ☐ (b) between 1 and 2 ☐
(c) 1.5 ☐ (d) 2 ☐

9. The carbon-carbon bond length in benzene molecule is:
(a) 1.54 Å ☐ (b) 1.39 Å ☐
(c) 1.33 Å ☐ (d) 1.20 Å ☐

10. The carbon atoms in benzene are:
(a) sp^2-hybridized ☐ (b) sp-hybridized ☐
(c) sp^3-hybridized ☐ (d) non-hybridized ☐

11. The benzene molecule is:
(a) trigonal ☐ (b) tetrahedral ☐
(c) planar ☐ (d) pyramidal ☐

12. The C—C—C bond angle in benzene is:
(a) 90° ☐ (b) 60° ☐
(c) 109° ☐ (d) 120° ☐

13. The centric formula of benzene was proposed by:
(a) Dewar ☐ (b) Baeyer and Armstrong ☐
(c) Ladenberg ☐ (d) Kekule ☐

14. The number of π-electrons in benzene molecule is:
(a) 6 ☐ (b) 3 ☐
(c) 5 ☐ (d) 4 ☐

15. Benzene gives mainly: **[DPMT 2007]**
(a) substitution reaction ☐ (b) addition reaction ☐
(c) elimination reaction ☐ (d) all of these ☐

16. Six carbon atoms of benzene are of:
(a) one type ☐ (b) two types ☐
(c) three types ☐ (d) six types ☐

17. The compound that is most reactive towards electrophilic substitution is: **[AMU (Engg.) 2009]**
(a) toluene ☐ (b) benzene ☐
(c) nitrobenzene ☐ (d) benzoic acid ☐

18. The decreasing order of reactivity towards electrophilic substitution reaction of the following compounds,
benzene, chlorobenzene, nitrobenzene, toluene is:
1 2 3 4
[PMT (Kerala) 2008]
(a) 1 > 3 > 4 > 2 ☐ (b) 4 > 1 > 3 > 2 ☐
(c) 4 > 1 > 2 > 3 ☐ (d) 4 > 2 > 1 > 3 ☐
(e) 2 > 4 > 1 > 3 ☐

19. The nitro group in nitrobenzene is:
(a) *ortho*-directing ☐
(b) *meta*-directing ☐
(c) *para*-directing ☐
(d) *ortho*- and *para*-directing ☐

20. Which of the following is *meta*-directing group?
(a) —COOH ☐ (b) —OH ☐
(c) —NH_2 ☐ (d) —Cl ☐

21. Disubstituted derivatives of benzene are of...... type/types.
(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) 6 ☐

22. Nitration of benzene is: **[BCECE (Med.) 2005]**
(a) nucleophilic substitution ☐
(b) nucleophilic addition ☐
(c) electrophilic substitution ☐
(d) electrophilic addition ☐

23. The function of anhydrous aluminium chloride in the Friedel-Crafts reaction is:
(a) to absorb water ☐
(b) to absorb hydrochloric acid ☐
(c) to produce an electrophile ☐
(d) to produce nucleophile ☐

24. Chlorination of benzene in the presence of halogen carrier is an example of : **[PET (Kerala) 2010]**
(a) aromatic nucleophilic substitution ☐
(b) aromatic electrophilic substitution ☐
(c) aromatic nucleophilic addition ☐

(d) aromatic electrophilic addition ☐
(e) free radical substitution ☐

25. In the nitration of benzene with a mixture of conc. HNO_3 and conc. H_2SO_4, the active species involved is: **[VMMC 2007; DCE (Engg.) 2007]**
(a) NO_3^- ☐ (b) NO_2 ☐
(c) NO_2^- ☐ (d) NO_2^+ ☐

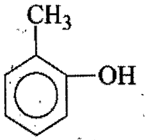
26. In the sulphonation of benzene, the electrophile involved is: **[CET (Karnataka) 2009]**
(a) HSO_4^- ☐ (b) SO_3 ☐
(c) SO_2 ☐ (d) SO_4^{2-} ☐

27. Among the following groups, the group that deactivates the benzene ring for further electrophilic substitution, is:
(a) methyl ☐ (b) amino ☐
(c) hydroxyl ☐ (d) chloro ☐

28. In the halogenation of aromatic nucleus, the halogen carrier, is used to generate the species:
(a) $Cl\bullet$ ☐ (b) Cl^+ ☐
(c) Cl^- ☐ (d) Cl ☐

29. When sodium benzoate is heated with soda lime, we get:
(a) toluene ☐ (b) ethylene ☐
(c) benzene ☐ (d) aniline ☐

30. Which is most reactive towards electrophilic reagent? **[CBSE (PMT) Prelims 2010]**

(a) 

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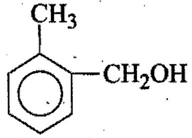
(b) 

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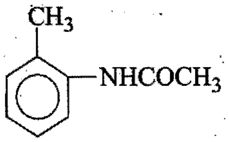
(c) 

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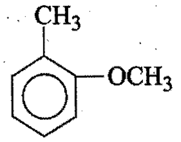
(d) 

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31. The reaction,

$$C_6H_5Br + 2Na + C_2H_5Br \longrightarrow C_6H_5C_2H_5 + 2NaBr$$

is known as:
(a) Friedel-Crafts reaction ☐
(b) Wurtz reaction ☐
(c) Sandmeyer's reaction ☐
(d) Wurtz-Fittig reaction ☐

32. In Friedel-Crafts reaction for preparation of toluene, the reactants in addition to anhydrous $AlCl_3$ are:
(a) $C_6H_5Cl + CH_4$ ☐ (b) $C_6H_5Cl + CH_3Cl$ ☐
(c) $C_6H_6 + CH_4$ ☐ (d) $C_6H_6 + CH_3Cl$ ☐

33. When phenol is distilled with zinc dust, the main product is:
(a) biphenyl ☐ (b) benzene ☐
(c) benzaldehyde ☐ (d) phenolphthalein ☐

34. Benzene reacts with acetyl chloride in presence of anhydrous aluminium chloride to form:
(a) acetophenone ☐ (b) phenyl acetate ☐
(c) chlorobenzene ☐ (d) benzoic acid ☐

35. When benzene is treated with conc. HNO_3 at room temperature, it will give:
(a) CO_2 and H_2O ☐ (b) nitrobenzene ☐
(c) *m*-dinitrobenzene ☐ (d) none of these ☐

36. Nitration of benzene is carried out with:
(a) HNO_3 (dil.) ☐
(b) HNO_3 (conc.) ☐
(c) HNO_3 (fuming) ☐
(d) HNO_3 (conc.) + H_2SO_4 (conc.) ☐

37. In the presence of iron catalyst, benzene reacts with chlorine to form:
(a) chlorobenzene ☐ (b) benzene hexachloride ☐
(c) hexachlorobenzene ☐ (d) none of these ☐

38. The reaction of chlorine with toluene in presence of ferric chloride gives predominantly: **[AIEEE 2007]**
(a) benzoyl chloride ☐ (b) *m*-chlorotoluene ☐
(c) benzyl chloride ☐ (d) *o*- and *p*-chlorotoluene ☐

39. Nitration of benzene in presence of conc. H_2SO_4 at 100°C gives:
(a) nitrobenzene ☐ (b) *m*-dinitrobenzene ☐
(c) *o*-dinitrobenzene ☐ (d) *p*-dinitrobenzene ☐

40. Toluene may be oxidised to benzaldehyde by the use of:
(a) $KMnO_4 + H_2SO_4$ ☐ (b) $K_2Cr_2O_7 + H_2SO_4$ ☐
(c) CrO_2Cl_2 ☐ (d) all of these ☐

41. Given are cyclohexanol (I), acetic acid (II), 2,4,6-trinitrophenol (III) and phenol (IV). In these the order of decreasing acidic character will be : **[CBSE (PMT) Prelims 2010]**
(a) III > II > IV > I ☐ (b) II > III > I > IV ☐
(c) II > III > IV > I ☐ (d) III > IV > II > I ☐

42. The oxidation of toluene to benzaldehyde with chromyl chloride in carbon tetrachloride is called:
(a) Sandmeyer's reaction ☐ (b) Perkin's reaction ☐
(c) Fittig reaction ☐ (d) Etard's reaction ☐

43. In Raschig's process for the preparation of chlorobenzene, the reactants are:
(a) C_6H_6 and Cl_2 ☐ (b) C_6H_5OH and PCl_5 ☐
(c) $C_6H_6 + HCl + O_2$ ☐ (d) C_6H_5OH and HCl ☐

44. Chlorobenzene when condensed with chloral in the presence of conc. H_2SO_4 yields:
(a) Gammexane ☐ (b) DDT ☐
(c) TNB ☐ (d) C_6Cl_6 ☐

45. The chemical name of DDT is:
(a) dichloro dinitrotoluene ☐
(b) dichloro dimethyl toluene ☐
(c) *p*, *p*'-dichloro diphenyl trichloroethane ☐
(d) none of the above ☐

46. Gammexane is:
(a) hexachlorobenzene ☐ (b) benzene hexachloride ☐
(c) *p*-dichlorobenzene ☐ (d) chlorobenzene ☐

47. Chlorobenzene is commercially prepared by:
(a) Dow's process ☐ (b) Deacon's process ☐
(c) Raschig's process ☐ (d) Etard's process ☐

48. Chlorobenzene can be prepared by reacting aniline with: **[AMU (Engg.) 2009]**

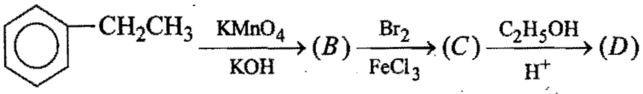
(a) HCl and Cu_2Cl_2 ☐

(b) chlorine in presence of U.V. light ☐

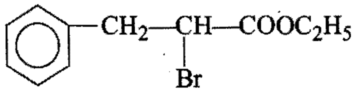
(c) chlorine in presence of anhydrous $AlCl_3$ ☐

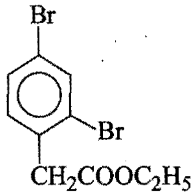
(d) nitrous acid followed by heating with Cu_2Cl_2 ☐

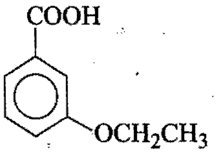
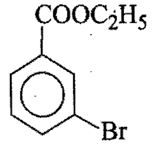
49. In a set of reactions, ethylbenzene yielded a product(D).



(D) would be : **[CBSE (PMT) Prelims 2010]**

(a)  ☐

(b)  ☐

(c)  ☐ (d)  ☐

50. When sodium benzene sulphonate is fused with sodium hydroxide (solid), the product formed is:

(a) benzene ☐ (b) phenol ☐

(c) benzene triphenol ☐ (d) none of these ☐

51. Which of the following acids is strongest?

(a) $C_6H_5SO_3H$ ☐ (b) CH_3COOH ☐

(c) C_6H_5COOH ☐ (d) $(COOH)_2$ ☐

52. Artificial oil of bitter almonds or oil of Mirabane is the name given to:

(a) chlorobenzene ☐ (b) benzaldehyde ☐

(c) aniline ☐ (d) nitrobenzene ☐

53. Nitrobenzene when reduced with tin and hydrochloric acid, *i.e.*, in acidic medium, the product formed is:

(a) aniline ☐ (b) benzene ☐

(c) phenylhydrazine ☐ (d) nitrobenzene ☐

54. Nitrobenzene on reduction with Zn dust and aqueous NH_4Cl forms: **[AIIMS 2006; EAMCET (Engg.) 2007]**

(a) $C_6H_5NH_2$ ☐ (b) C_6H_5NO ☐

(c) $C_6H_5N{=}NC_6H_5$ ☐ (d) C_6H_5NHOH ☐

55. Nitrobenzene on electrolytic reduction in strong sulphuric acid solution gives:

(a) aniline ☐ (b) phenyl hydroxylamine ☐

(c) p-aminophenol ☐ (d) hydrazobenzene ☐

56. Aniline on treatment with nitrous acid ($NaNO_2$ + HCl) at 0°C, forms:

(a) phenol ☐

(b) nitrobenzene ☐

(c) nitrosobenzene ☐

(d) benzene diazonium chloride ☐

57. The substituent which is predominantly *ortho-para* directing but deactivating in aromatic electrophilic substitution : **[PMT (Kerala) 2010]**

(a) —NO_2 ☐ (b) —OH ☐

(c) —OCH_3 ☐ (d) —CH_3 ☐

(e) —Cl ☐

58. Which one of the following is most reactive towards aqueous NaOH?

(a) C_6H_5Cl ☐ (b) $C_6H_5CH_2Cl$ ☐

(c) C_6H_5Br ☐ (d) BrC_6H_4Br ☐

59. Benzene diazonium chloride when reacted with hypophosphorus acid, produces:

(a) phenol ☐ (b) phenyl phosphate ☐

(c) benzene ☐ (d) phenyl phosphite ☐

60. Aniline on treatment with aqueous bromine gives:

(a) 2,4,6-tribromoaniline ☐ (b) o-bromoaniline ☐

(c) 2,4-dibromoaniline ☐ (d) p-bromoaniline ☐

61. Aniline on heating with fuming sulphuric acid gives:

(a) aniline sulphate ☐

(b) sulphanilic acid ☐

(c) aniline 2,4-disulphonic acid ☐

(d) nitrobenzene ☐

62. The products of the reaction between $C_6H_5NH_2$, $CHCl_3$ and KOH are: **[BCECE (Med.) 2007]**

(a) $C_6H_5Cl + NH_4Cl + KCl$ ☐

(b) $C_6H_5CN + KCl + H_2O$ ☐

(c) $C_6H_5NC + KCl + H_2O$ ☐

(d) $C_6H_5OH + NH_4Cl + H_2O$ ☐

63. The above reaction is called:

(a) Carbylamine reaction ☐ (b) Sandmeyer's reaction ☐

(c) Wurtz reaction ☐ (d) Perkin's reaction ☐

64. Aniline is separated from a mixture by:

(a) fractional crystallisation ☐

(b) fractional distillation ☐

(c) steam distillation ☐

(d) vacuum distillation ☐

65. Aniline when treated with acetyl chloride in presence of alkali, the product formed is: **[BCECE (Med.) 2007]**

(a) acetanilide ☐ (b) benzoyl chloride ☐

(c) acetophenone ☐ (d) aniline hydrochloride ☐

66. When aniline is heated with benzaldehyde, the product is:

(a) benzoin ☐ (b) Schiff base ☐

(c) unsaturated acid ☐ (d) azoxy benzene ☐

67. In the reaction,

$$C_6H_5NH_2 \xrightarrow[0\text{–}5°C]{NaNO_2 + HCl} (A) \xrightarrow[KCN]{CuCN} (B) \xrightarrow{H^+/H_2O} (C)$$

the product (C) is:

(a) $C_6H_5CH_2NH_2$ ☐ (b) C_6H_5COOH ☐

(c) C_6H_5OH ☐ (d) none of these ☐

68. Benzene diazonium chloride on hydrolysis gives:
(a) benzene ☐ (b) benzyl alcohol ☐
(c) phenol ☐ (d) chlorobenzene ☐

69. When benzene diazonium chloride is treated with cuprous chloride in HCl, chlorobenzene is formed. This reaction is called:
(a) Perkin's reaction ☐ (b) Etard's reaction ☐
(c) Gattermann reaction ☐ (d) Sandmeyer's reaction ☐

70. When phenol is treated with excess of bromine water, it gives:
(a) *m*-bromophenol ☐ (b) *o*- and *p*-bromophenol ☐
(c) 2,4-dibromophenol ☐ (d) 2,4,6-tribromophenol ☐

71. Which of the following is an insecticide? **[PET (MP) 2007]**
(a) DDT ☐ (b) $CHCl_3$ ☐
(c) CHI_3 ☐ (d) $CF_3—CF_3$ ☐

72. Picric acid is a yellow coloured compound. Its chemical name is: **[VMMC 2003]**
(a) trinitrobenzene ☐ (b) 2,4,6-trinitrophenol ☐
(c) trinitrotoluene ☐ (d) trinitroaniline ☐

73. Sodium phenoxide when heated with CO_2 under pressure at 125°C gives:
(a) sodium benzoate ☐ (b) salol ☐
(c) sodium salicylate ☐ (d) salicylaldehyde ☐

74. Phenol when condensed with phthalic anhydride in presence of conc. H_2SO_4, yields:
(a) methyl orange ☐ (b) phenolphthalein ☐
(c) phenol red ☐ (d) salicylic acid ☐

75. Phenol is heated with CCl_4 and alk. KOH to form salicylic acid. The reaction is known as:
(a) Friedel-Crafts reaction ☐
(b) Rosenmund reaction ☐
(c) Reimer-Tiemann reaction ☐
(d) Perkin's reaction ☐

76. Phenol reacts with bromine in carbon disulphide at low temperature to give:
(a) *m*-bromophenol ☐ (b) *o*- and *p*-bromophenol ☐
(c) *p*-bromophenol ☐ (d) 2,4,6-tribromophenol ☐

77. Phenol is also called:
(a) salicylic acid ☐ (b) benzyl alcohol ☐
(c) carbolic acid ☐ (d) salol ☐

78. Phenols do not react with:
(a) sodium bicarbonate ☐ (b) sodium hydroxide ☐
(c) potassium hydroxide ☐ (d) ferric chloride ☐

79. Phenols react with ferric chloride solution to give:
(a) blue colouration ☐ (b) purple colouration ☐
(c) green colouration ☐ (d) all of these ☐

80. Phenol is less acidic than:
(a) *p*-nitrophenol ☐ (b) ethanol ☐
(c) cresol ☐ (d) benzyl alcohol ☐

81. In the reaction,

$$C_6H_5CH_2Cl \xrightarrow{\text{Aq. NaOH}} (A) \xrightarrow[\text{Cu(NO}_3)_2]{\text{Oxidation}} (B),$$

(*B*) is:
(a) benzoic acid ☐ (b) phenol ☐
(c) toluene ☐ (d) benzaldehyde ☐

82. The Cannizzaro's reaction would be given by:
(a) CH_3COCH_3 ☐ (b) C_6H_5CHO ☐
(c) $C_6H_5COCH_3$ ☐ (d) $C_2H_5COCH_3$ ☐

83. The reaction involving condensation of acetic anhydride with an aromatic aldehyde by a carboxylate ion is an example of:
(a) aldol condensation ☐ (b) benzoin condensation ☐
(c) Perkin's reaction ☐ (d) Wurtz reaction ☐

84. Benzaldehyde when refluxed with aqueous alcoholic KCN forms:
(a) benzoin ☐ (b) benzene ☐
(c) phenyl cyanide ☐ (d) phenyl isocyanide ☐

85. Benzaldehyde reacts with PCl_5 to give:
(a) benzyl chloride ☐ (b) benzo trichloride ☐
(c) benzal chloride ☐ (d) chlorobenzene ☐

86. When benzaldehyde is heated with acetic anhydride in the presence of sodium acetate, the product obtained is:
(a) cinnamic acid ☐ (b) phenyl acetic acid ☐
(c) benzoic acid ☐ (d) benzoic anhydride ☐

87. Benzaldehyde reacts with conc. NaOH to give:
(a) sodium benzoate ☐
(b) benzyl alcohol ☐
(c) phenol ☐
(d) benzyl alcohol and sodium benzoate ☐

88. Which of the following does not react with Fehling's solution?
(a) Acetaldehyde ☐ (b) Glucose ☐
(c) Benzaldehyde ☐ (d) Formaldehyde ☐

89. Chlorine reacts with benzaldehyde to give:
(a) benzyl chloride ☐ (b) benzal chloride ☐
(c) benzoyl chloride ☐ (d) chlorobenzene ☐

90. Which of the following gives silver mirror with ammoniacal silver nitrate?
(a) Benzyl alcohol ☐ (b) Benzaldehyde ☐
(c) Benzoic acid ☐ (d) Benzene ☐

91. Aspirin is obtained by action of CH_3COCl with:
(a) salicylic acid ☐ (b) phenol ☐
(c) benzaldehyde ☐ (d) aniline ☐

92. The reaction,

$$C_6H_5CHO + CH_3CHO \longrightarrow C_6H_5CH{=}CHCHO$$

is called:
(a) benzoin condensation ☐ (b) Claisen condensation ☐
(c) Perkin's reaction ☐ (d) Cannizzaro's reaction ☐

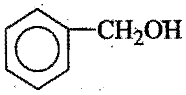
93. Salicylic acid when treated with zinc dust, gives:
(a) phenol ☐ (b) salicylaldehyde ☐
(c) benzene ☐ (d) benzoic acid ☐

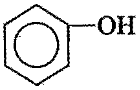
94. Aspirin is:
(a) antibiotic ☐ (b) sedative ☐
(c) antipyretic ☐ (d) antiseptic ☐

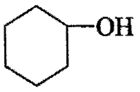
95. The formation of salicylic acid from phenol using NaOH and CO_2 is known as:
(a) Friedel-Crafts reaction ☐
(b) Kolbe's reaction ☐
(c) Reimer-Tiemann reaction ☐
(d) Fittig reaction ☐

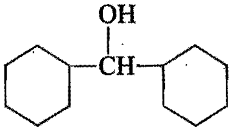
96. When calcium benzoate and calcium formate are heated, they form:
(a) benzaldehyde ☐ (b) acetophenone ☐
(c) benzophenone ☐ (d) acetaldehyde ☐

97. Which of the following compounds has the most acidic nature? **[CBSE (PMT) Prelims 2010]**

(a)  ☐

(b)  ☐

(c)  ☐

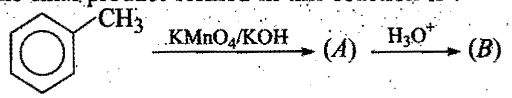
(d)  ☐

98. Which one of the following compounds forms benzoic acid on oxidation?
(a) Chlorophenol ☐ (b) Benzyl chloride ☐
(c) Chlorobenzene ☐ (d) Chlorotoluene ☐

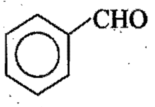
99. Benzoic acid when treated with PCl_5, the product is:
(a) chlorobenzene ☐ (b) benzyl chloride ☐
(c) benzoyl chloride ☐ (d) benzene ☐

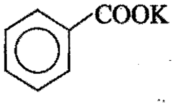
100. When benzamide is heated with phosphorus pentoxide, the product formed is:
(a) phenyl cyanide ☐ (b) phenyl isocyanide ☐
(c) aniline ☐ (d) benzyl alcohol ☐

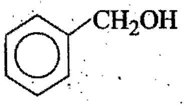
101. The final product formed in this reaction is :

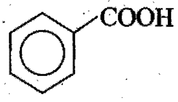


[JEE (Orissa) 2010]

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

102. Pure aniline is a:
(a) brown coloured liquid ☐ (b) colourless solid ☐
(c) colourless liquid ☐ (d) brown coloured solid ☐

103. Cumene $\xrightarrow[\text{(ii) } H_2O,\ H^+]{\text{(i) } O_2}$ (X) and (Y);
(X) and (Y) respectively are:
(a) toluene, propene ☐
(b) toluene, propylchloride ☐
(c) phenol, acetone ☐
(d) phenol, acetaldehyde ☐

104. Phenol (1 mole) reacts with bromine to give *s*-tribromophenol. The amount of bromine required is:
(a) 3.0 moles ☐ (b) 1.5 moles ☐
(c) 4.5 moles ☐ (d) 6.0 moles ☐

105. Phenol $\xrightarrow[\text{distillation}]{\text{Zinc}} (A) \xrightarrow[\text{Conc. } H_2SO_4 \text{ at } 60^\circ C]{\text{Conc. } HNO_3} (B) \xrightarrow[\text{NaOH}]{\text{Zn}} (C)$

In the above reaction, compounds (A), (B) and (C) are:
(a) benzene, nitrobenzene and aniline ☐
(b) benzene, dinitrobenzene and *m*-nitroaniline ☐
(c) toluene, *m*-nitrobenzene and *m*-toluidine ☐
(d) benzene, nitrobenzene and hydrazobenzene ☐

106. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to:
(a) the formation of less stable carbocation ☐
(b) resonance stabilization ☐
(c) longer carbon-halogen bond ☐
(d) inductive effect ☐

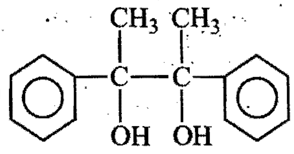
107. Chlorination of toluene in presence of light and heat followed by treatment with aqueous NaOH gives:
(a) *o*-cresol ☐
(b) *p*-cresol ☐
(c) 2 : 4 dihydroxy toluene ☐
(d) benzoic acid ☐

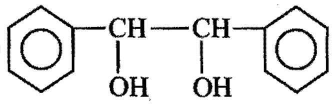
108. *m*-Chlorobenzaldehyde on reaction with conc. KOH at room temperature gives:
(a) potassium *m*-chlorobenzoate and *m*-hydroxy benzaldehyde ☐
(b) *m*-hydroxy benzaldehyde and *m*-hydroxy alcohol ☐
(c) *m*-chlorobenzyl alcohol and *m*-hydroxy benzyl alcohol ☐
(d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol ☐

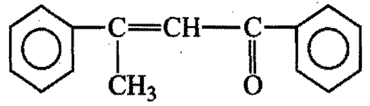
109. Hydrogenation of benzoyl chloride in presence of Pd on $BaSO_4$ gives:
(a) benzyl alcohol ☐ (b) benzaldehyde ☐
(c) benzoic acid ☐ (d) phenol ☐

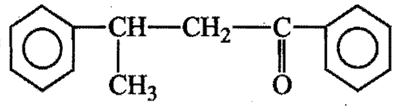
110. Phenol is:
(a) a base weaker than ammonia ☐
(b) an acid stronger than carbonic acid ☐
(c) an acid weaker than carbonic acid ☐
(d) a neutral compound ☐

111. Acetophenone when reacted with a base, C_2H_5ONa, yields a stable compound which has the structure: **[CBSE (Med.) 2008]**

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

112. Amongst the following, the compound that can be most readily, sulphonated is:
(a) benzene ☐ (b) nitrobenzene ☐
(c) toluene ☐ (d) chlorobenzene ☐

113. Which one of the following compounds would undergo nitration with greatest ease?
(a) Benzene ☐ (b) Phenol ☐
(c) Nitrobenzene ☐ (d) Benzoic acid ☐

114. Aspirin is:
(a) acetyl salicylic acid ☐ (b) methyl salicylic acid ☐
(c) salicylic acid ☐ (d) salicylaldehyde ☐

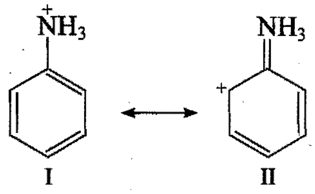
115. Nitrobenzene is generally used for:
(a) preparing shoe polish ☐
(b) preparing cheap scented soap ☐
(c) preparing of aniline ☐
(d) all of the above ☐

116. The ratio of σ- and π-bonds in benzene is:
(a) 2 ☐ (b) 4 ☐
(c) 6 ☐ (d) 8 ☐

117. Benzyl alcohol is obtained from benzaldehyde by:
(a) Wurtz reaction ☐ (b) Cannizzaro's reaction ☐
(c) Perkin's reaction ☐ (d) Claisen reaction ☐

118. Which of the following statements is not correct regarding aniline?
(a) It is less basic than ethylamine ☐
(b) It can be steam distilled ☐
(c) It reacts with sodium to give hydrogen ☐
(d) It is soluble in water ☐

119. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below:



(a) II is not an acceptable canonical structure because carbocation ions are less stable than ammonium ions ☐
(b) II is not an accepted canonical structure because it is non-aromatic ☐
(c) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons ☐
(d) II is an acceptable canonical structure ☐

120. The direct iodination of benzene is not possible because:
(a) I_2 is an oxidising agent ☐
(b) resulting C_6H_5I is reduced to C_6H_6 by HI ☐
(c) HI is unstable ☐
(d) the ring gets deactivated ☐

121. $C_6H_6 + CO + HCl \xrightarrow{\text{Anhyd. AlCl}_3} (X) + HCl$;
The compound (X) is:
(a) C_6H_5CHO ☐ (b) C_6H_5COOH ☐
(c) $C_6H_5CH_2Cl$ ☐ (d) $C_6H_5CH_3$ ☐

122. Benzyl alcohol and phenol can be distinguished by the use of:
(a) $FeCl_3$ ☐ (b) Na ☐
(c) Lucas reagent ☐ (d) none of these ☐

123. The product of the following reaction

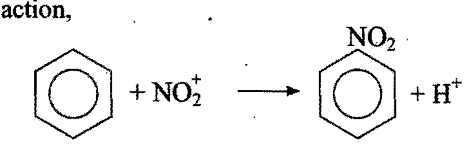
$$C_6H_6 + Cl_2 \xrightarrow{\text{Sunlight}} ?\ ;\ \text{is:}$$

(a) C_6H_5Cl ☐ (b) *Ortho* $C_6H_4Cl_2$ ☐
(c) $C_6H_6Cl_6$ ☐ (d) *Para* $C_6H_4Cl_2$ ☐

124. Carbolic acid is: **[AFMC 2005; EAMCET (Med.) 2007]**
(a) C_6H_5OH ☐ (b) C_6H_5COOH ☐
(c) C_6H_6 ☐ (d) C_6H_5CHO ☐

125. Which one of the following is an explosive?
(a) Nitrobenzene ☐ (b) Nitrophenol ☐
(c) Nitromethane ☐ (d) Trinitrobenzene ☐

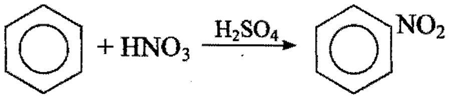
126. The reaction,

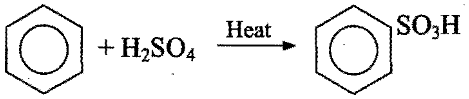


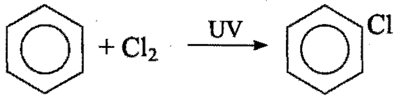
is a (an):
(a) addition reaction ☐
(b) electrophilic substitution reaction ☐
(c) nucleophilic substitution reaction ☐
(d) elimination reaction ☐

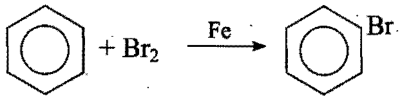
127. The compound with molecular formula C_8H_{10} which will give only two isomers on electrophilic substitution with $Cl_2/FeCl_3$ or with HNO_3/H_2SO_4 is: **[DUMET 2010]**
(a) *p*-dimethylbenzene ☐ (b) *m*-dimethylbenzene ☐
(c) *o*-dimethylbenzene ☐ (d) ethylbenzene ☐

128. The reaction least likely to occur is:

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

129. Carbon-carbon bond distance in benzene is:
(a) longer than a C=C double bond ☐
(b) shorter than a C=C double bond ☐
(c) shorter than a C≡C triple bond ☐
(d) longer than a C—C single bond ☐

130. Which of the following is the most reactive towards ring nitration?
(a) Benzene ☐ (b) Toluene ☐
(c) *m*-Xylene ☐ (d) Mesitylene ☐

131. Toluene on treatment with CH_3Cl and $AlCl_3$ at 80°C gives the major product as:
(a) *o*-xylene ☐ (b) *p*-xylene ☐
(c) *m*-xylene ☐ (d) ethylbenzene ☐

132. The position least nitrated, when *m*-bromochlorobenzene is nitrated, is:
(a) position *ortho* to bromine ☐
(b) position *ortho* to chlorine ☐
(c) position *ortho* to bromine and chlorine ☐
(d) position *meta* to chlorine ☐

133. Which of the following would not react with benzene sulphonyl chloride in aqueous NaOH?
(a) Aniline ☐ (b) Methylamine ☐
(c) *N,N*-Dimethylaniline ☐ (d) *N*-Methylaniline ☐

134. Which of the following would not react with HNO_2?
(a) *N,N*-Dimethylaniline ☐ (b) *p*-Toluidine ☐
(c) Sulphanilic acid ☐ (d) Ethylamine ☐

135. When ethylbenzene is treated with bromine in presence of light and heat, the only product is:
(a) 1-bromo-1-phenylethane ☐
(b) 2-bromo-1-phenylethane ☐
(c) *o*-bromoethylbenzene ☐
(d) *p*-bromoethylbenzene ☐

136. Which of the following is least basic?
(a) Aniline ☐ (b) *p*-Methylaniline ☐
(c) Diphenylamine ☐ (d) Triphenylamine ☐

137. Which of the following is strongly acidic?
(a) Phenol ☐ (b) *m*-Nitrophenol ☐
(c) *m*-Bromophenol ☐ (d) *m*-Cresol ☐

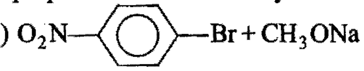
138. Which of the following is the weakest acid?
(a) Benzene sulphonic acid ☐
(b) Benzoic acid ☐
(c) Benzyl alcohol ☐
(d) Phenol ☐

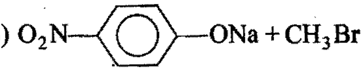
139. An organic compound '*X*' having molecular formula $C_6H_7O_2N$ has 6 carbon atoms in a ring system, two double bonds and also a nitro group as substituent, '*X*' is:
(a) homocyclic but not aromatic ☐
(b) aromatic but not homocyclic ☐
(c) homocyclic and aromatic ☐
(d) heterocyclic ☐

140. The weakest acid among the following is:
(a) benzoic acid ☐
(b) *o*-nitrobenzoic acid ☐
(c) cyclohexane carboxylic acid ☐
(d) *p*-nitrobenzoic acid ☐

141. According to Huckel rule, an aromatic compound must possess: **[CET (J&K) 2007]**
(a) $(4n+1)\pi$ electrons ☐ (b) $(4n+2)\pi$ electrons ☐
(c) $(2n+2)\pi$ electrons ☐ (d) $4n\pi$ electrons ☐

142. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene ?

(A) 

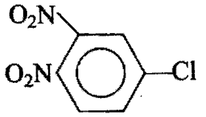
(B) 

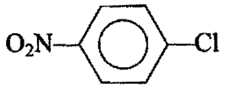
[AMU (Med.) 2010]
(a) both A and B ☐ (b) only A ☐
(c) only B ☐ (d) none of these ☐

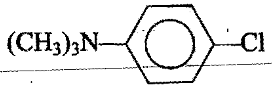
143. How many 120° angles does benzene molecule has?
(a) 9 ☐ (b) 12 ☐
(c) 15 ☐ (d) 18 ☐

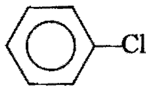
144. Which of the following is most volatile?
(a) *p*-Nitrophenol ☐ (b) *m*-Nitrophenol ☐
(c) *o*-Nitrophenol ☐ (d) All of these ☐

145. Which chloroderivative of benzene among the following would undergo hydrolysis most readily with aqueous NaOH to furnish the corresponding hydroxy compound?

(a)  ☐

(b)  ☐

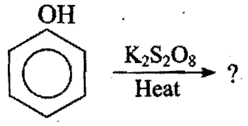
(c)  ☐

(d)  ☐

146. Salol is prepared from:
(a) salicylic acid and methyl alcohol ☐
(b) salicylic acid and phenol ☐
(c) both (a) and (b) ☐
(d) none of the above ☐

147. $C_6H_5OH \xrightarrow[\text{NaOH (aq.)}]{\text{ClOCCH}_3} C_6H_5OOCCH_3$;

The above reaction is an example of:
(a) acetylation ☐
(b) benzoylation ☐
(c) Schotten-Baumann reaction ☐
(d) Reimer-Tiemann reaction ☐

148. 

The product formed in the reaction is:

(a) benzoquinone ☐ (b) diphenyl ether ☐
(c) benzene sulphuric acid ☐ (d) hydroquinone ☐

149. Phenol on standing in air develops a red colour due to formation of:
(a) cyclohexane ☐ (b) resorcinol ☐
(c) phenoquinone ☐ (d) quinol ☐

150. Benzoic acid gives benzene on being heated with '*X*' and phenol gives benzene on being heated with '*Y*'. Therefore '*X*' and '*Y*' are respectively:
(a) soda lime and copper ☐
(b) zinc dust and sodium hydroxide ☐
(c) zinc dust and soda lime ☐
(d) soda lime and zinc dust ☐

151. The number of sigma and pi bonds in benzene molecule is:
(a) 6σ and 6π ☐ (b) 12σ and 3π ☐
(c) 6σ and 9π ☐ (d) 9σ and 3π ☐

152. Select the correct statement about benzene.
(a) There is a cyclic delocalisation of pi electrons in benzene ☐
(b) There are two types of C—C bonds in benzene molecule ☐
(c) Because of unsaturation benzene undergoes addition reactions ☐
(d) Mono substitution of benzene gives three isomeric substances ☐

153. Which is not an aromatic compound?
(a) Pyridine ☐ (b) Xylene ☐
(c) Naphthalene ☐ (d) Cyclohexane ☐

154. According to Huckel rule, the number of pi electrons in naphthalene is:
(a) 6 ☐ (b) 10 ☐
(c) 14 ☐ (d) 16 ☐

155. Anhydrous $AlCl_3$ is used in Friedel-Crafts reaction because it is:
(a) soluble in ether ☐
(b) ionisable to Al and Cl ions ☐
(c) electron rich ☐
(d) electron deficient molecule ☐

156. The carbon-carbon bond length in benzene is: **[CET (Karnataka) 2009]**
(a) same as in C_2H_4 ☐
(b) in between C_2H_6 and C_2H_2 ☐
(c) in between C_2H_6 and C_2H_4 ☐
(d) in between C_2H_4 and C_2H_2 ☐

157. Benzene reacts with *n*-propyl chloride in the presence of anhydrous $AlCl_3$ to give predominantly:
(a) *n*-propylbenzene ☐
(b) isopropylbenzene ☐
(c) 3-propyl-1-chlorobenzene ☐
(d) no reaction ☐

158. Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form: **[CBSE (Med.) 2009]**
(a) toluene ☐ (b) xylene ☐
(c) chlorobenzene ☐ (d) benzyl chloride ☐

159. Benzene on reaction with conc. HNO_3 in presence of conc. H_2SO_4 followed by the treatment of Cl_2 in presence of $FeCl_3$, it gives:
(a) 2-chloro-1-nitrobenzene ☐
(b) 3-chloro-1-nitrobenzene ☐
(c) 4-chloro-1-nitrobenzene ☐
(d) a mixture of 2-chloro and 4-chloro-1-nitrobenzene ☐

160. Which does not show substitution in benzene ring?
(a) $ClSO_3H$ ☐
(b) Conc. H_2SO_4 on heating ☐
(c) Conc. HCl ☐
(d) $CH_3Cl/AlCl_3$ ☐

161. Oxidation of naphthalene by acidic $KMnO_4$ gives:
(a) toluene ☐ (b) benzoic acid ☐
(c) benzaldehyde ☐ (d) phthalic acid ☐

162. Which of the following is the most abundant individual substance obtained from coal-tar?
(a) Benzene ☐ (b) Naphthalene ☐
(c) Diphenyl ☐ (d) Kerosene oil ☐

163. Toluene reacts with chlorine in the presence of light to give:
(a) benzyl chloride ☐ (b) benzoyl chloride ☐
(c) *o*-chlorotoluene ☐ (d) *p*-chlorotoluene ☐

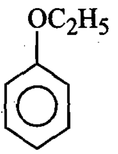
164. Benzene vapour mixed with air when passed over V_2O_5 catalyst at 500°C gives:
(a) oxalic acid ☐ (b) glyoxal ☐
(c) fumaric acid ☐ (d) maleic anhydride ☐

165. Which one of the following will undergo *meta* substitution on mono chlorination?
(a) Chlorobenzene ☐ (b) Phenol ☐
(c) Ethylbenzoate ☐ (d) Ethoxy ethane ☐

166. Which of the following group increases the maximum electron density in benzene ring?
(a) OH ☐ (b) NH_2 ☐
(c) CH_3 ☐ (d) *X* ☐

167. Ozonolysis of toluene gives:
(a) two molecules of glyoxal ☐
(b) three molecules of glyoxal ☐
(c) two molecules of glyoxal and one molecule of methyl glyoxal ☐
(d) two molecules of methyl glyoxal and one molecule of glyoxal ☐

168. Most reactive compound towards electrophilic substitution is: **[DPMT 2008]**

(a) 

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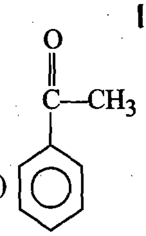
(b) 

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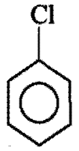
(c) 

☐ (d) none of these ☐

169. Which is difficult to be nitrated directly?
(a) Benzene ☐ (b) Toluene ☐
(c) Phenol ☐ (d) Nitrobenzene ☐

170. $X \xrightarrow{Cl_2}$ Benzotrichloride $\xrightarrow{\text{Hydrolysis}} Y$;
X and Y respectively are:
(a) benzene and benzoic acid ☐
(b) benzene and benzaldehyde ☐
(c) toluene and benzoic acid ☐
(d) toluene and benzaldehyde ☐

171. Most stable carbocation ion is:
(a) $p\text{-}NO_2—C_6H_4—\overset{+}{C}H_2$ ☐
(b) $C_6H_5\overset{+}{C}H_2$ ☐
(c) $p\text{-}Cl—C_6H_4—\overset{+}{C}H_2$ ☐
(d) $p\text{-}CH_3O—C_6H_4—\overset{+}{C}H_2$ ☐

172. Ulmann reaction is used for the preparation of:
(a) diphenyl ☐ (b) toluene ☐
(c) iodobenzene ☐ (d) naphthalene ☐

173. Phenol $\xrightarrow[\text{(ii) H}^+]{\text{(i) CHCl}_3\text{/NaOH}}$ Salicylaldehyde
This reaction is known as:
(a) Gattermann aldehyde synthesis ☐
(b) Duff reaction ☐
(c) Perkin's reaction ☐
(d) Reimer-Tiemann reaction ☐

174. Neutral $FeCl_3$ gives purple colour with:
(a) only phenol ☐
(b) only salicylic acid ☐
(c) both phenol and salicylic acid ☐
(d) only benzoic acid ☐

175. Kolbe-Schmidt reaction is used for:
(a) Salicylaldehyde ☐ (b) Salicylic acid ☐
(c) Phenol ☐ (d) Hydrocarbon ☐

176. Which of the following does not give effervescence with $NaHCO_3$?
(a) Benzoic acid ☐ (b) 2,4-Dinitrophenol ☐
(c) Phenol ☐ (d) 2,4,6-Trinitrophenol ☐

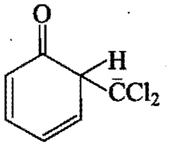
177. Phenol on treatment with conc. HNO_3 gives:
(a) picric acid ☐ (b) *o*- and *p*-nitrophenols ☐
(c) *m*-nitrophenol ☐ (d) none of these ☐

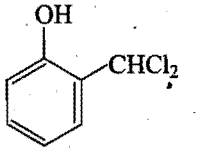
178. Phenol on treatment with dil. HNO_3 gives:
(a) picric acid ☐
(b) *o*- and *p*-nitrophenols ☐
(c) *o*- and *m*-nitrophenols ☐
(d) *p*- and *m*-nitrophenols ☐

179. When phenol reacts with benzene diazonium chloride, the product obtained is:
(a) phenylhydrazine ☐
(b) *p*-amino azobenzene ☐
(c) phenol hydroxylamine ☐
(d) *p*-hydroxy azobenzene ☐

180. When phenol reacts with chloroform and an alkali, the compound formed is salicylaldehyde. If pyrene is used in place of chloroform, the product obtained is:
(a) salicylaldehyde ☐ (b) salicylic acid ☐
(c) cyclohexanol ☐ (d) phenolphthalein ☐

181. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates?

(a) 

☐ (b) 

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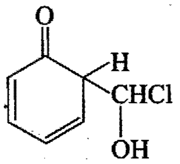
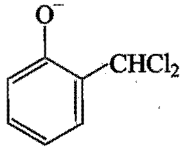
(c) 

☐ (d) 

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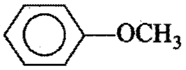
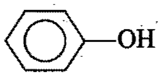
182. The most suitable method of separation of a equal (1 : 1) mixture of *o*- and *p*-nitrophenols is:
(a) sublimation ☐ (b) crystallisation ☐
(c) chromatography ☐ (d) distillation ☐

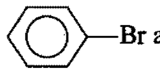
183. The reagent(s) which can be used to distinguish acetophenone from benzophenone is (are):
(a) 2,4-dinitrophenyl hydrazine ☐
(b) Benedict's reagent ☐
(c) I_2 and Na_2CO_3 ☐
(d) aqueous solution of $NaHSO_3$ ☐

184. In the reaction 

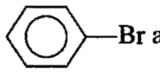
$\xrightarrow{HBr}$? the products are : **[IIT 2010]**

(a) 

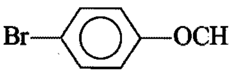
and CH_3Br ☐

(b) 

and CH_3Br ☐

(c) 

and CH_3OH ☐

(d) 

and H_2 ☐

185. Reimer-Tiemann reaction involves an intermediate:
(a) carbocation ☐ (b) carbanion ☐
(c) free radical ☐ (d) carbene ☐

186. *m*-chloro benzaldehyde on reaction with conc. KOH at room temperature gives:

(a) potassium *m*-chlorobenzoate and *m*-hydroxy benzaldehyde ☐
(b) *m*-chlorobenzyl alcohol and *m*-hydroxy benzaldehyde ☐
(c) *m*-chlorobenzyl alcohol and *m*-hydroxy benzyl alcohol ☐
(d) *m*-chlorobenzyl alcohol and potassium-*m*-chloro-benzoate ☐

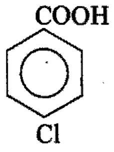
187. Benzaldehyde in Clemmensen reduction forms:
(a) toluene ☐ (b) phenyl methane ☐
(c) methylbenzene ☐ (d) all of these ☐

188. When phenyl cyanide is reduced with $SnCl_2$ and HCl in ethereal solution and the product is hydrolysed, it gives:
(a) benzaldehyde ☐ (b) benzoic acid ☐
(c) benzamide ☐ (d) aniline ☐

189. Salicylic acid on heating with soda lime forms:
(a) benzene ☐ (b) phenol ☐
(c) benzyl alcohol ☐ (d) benzoic acid ☐

190. Salicylic acid on bromination gives:
(a) 2,4,6-tribromosalicylic acid ☐
(b) 2,4,6-tribromophenol ☐
(c) 2,4,6-tribromobenzoic acid ☐
(d) *p*-bromosalicylic acid ☐

191. Which aromatic acid among the following is weaker than simple benzoic acid?

(a) 

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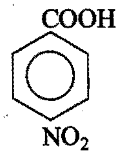
(b) 

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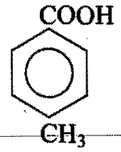
(c) 

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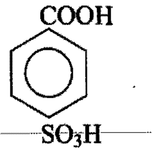
(d) 

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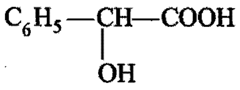
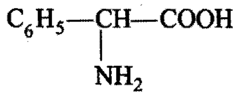
192. The organic products formed in the reaction,

$$C_6H_5COOCH_3 \xrightarrow{LiAlH_4,\ H^+} \text{are:}$$

(a) $C_6H_5CH_2OH$ and CH_3OH ☐
(b) C_6H_5COOH and CH_4 ☐
(c) $C_6H_5CH_3$ and CH_3OH ☐
(d) $C_6H_5CH_3$ and CH_4 ☐

193. Which of the following carboxylic acids undergoes decarboxylation easily?
(a) $C_6H_5-CO-CH_2-COOH$ ☐
(b) $C_6H_5-CO-COOH$ ☐
(c) 
$C_6H_5-\underset{OH}{\underset{|}{CH}}-COOH$ ☐
(d) 
$C_6H_5-\underset{NH_2}{\underset{|}{CH}}-COOH$ ☐

194. Decarboxylation of cinnamic acid gives:
(a) benzene ☐ (b) toluene ☐
(c) ethylbenzene ☐ (d) styrene ☐

195. By the action of malonic acid in ethanolic ammonia on benzaldehyde in the presence of pyridine, it forms:
(a) benzoic acid ☐ (b) phenyl acetic acid ☐
(c) cinnamic acid ☐ (d) phthalic acid ☐

196. Which has a smell of oil of winter green? **[VMMC 2007]**
(a) Ethyl salicylate ☐ (b) Methyl salicylate ☐
(c) Benzaldehyde ☐ (d) Phenyl salicylate ☐

197. Salicylic acid is used:
(a) as an antiseptic ☐
(b) as a medicine for rheumatic pain ☐
(c) in the preparation of azo dyes ☐
(d) all of the above ☐

198. Which of the following may be used as a food preservative?
(a) Benzene ☐
(b) Sodium benzoate ☐
(c) Toluene ☐
(d) Sodium *meta*-aluminate ☐

199. Among the following four compounds
(I) Phenol (II) Methyl phenol
(III) *m*-Nitrophenol (IV) *p*-Nitrophenol
The acidity order is : **[CBSE (PMT) 2010]**
(a) IV > III > I > II ☐ (b) III > IV > I > II ☐
(c) I > IV > III > II ☐ (d) II > I > III > IV ☐

200. Intramolecular rearrangement of phenyl acetate to give *o*- and *p*-hydroxy acetophenone in presence of anhydrous $AlCl_3$ is known as:
(a) Reimer-Tiemann reaction ☐
(b) Kolbe-Schmidt reaction ☐
(c) Fries rearrangement ☐
(d) Friedel-Crafts reaction ☐

201. Phthalic anhydride on heating with resorcinol in the presence of conc. H_2SO_4 gives:
(a) phenol ☐ (b) fluorescein ☐
(c) phenolphthalein ☐ (d) alizarin ☐

202. Dyes are formed when benzene diazonium salts are coupled with:
(a) phenol ☐ (b) aniline ☐
(c) *N,N*-dimethyl aniline ☐ (d) all of these ☐

203. Towards electrophilic substitution, the most reactive will be:
(a) nitrobenzene ☐ (b) aniline ☐
(c) *N*-acetyl aniline ☐ (d) aniline hydrochloride ☐

204. Arrange in order of decreasing reactivity towards electrophilic reagent in;
chlorobenzene (I), benzene (II), toluene (III), phenol (IV) would be: **[CBSE (Med.) 2007]**
(a) IV > III > II > I ☐ (b) IV > I > II > III ☐
(c) II > I > IV > III ☐ (d) I > II > IV > III ☐

205. In Friedel-Crafts reaction, the electrophilic reagent is:
(a) $AlCl_3$ ☐ (b) RCO^+ ☐
(c) $R\overset{+}{C}OCl$ ☐ (d) none of these ☐

206. An aromatic amine (X) was treated with alcoholic potash and another compound (Y) when foul smelling gas was formed as C_6H_5NC. The compound (Y) was formed by reacting a compound (Z) with Cl_2 in the presence of slaked lime. The compound (Z) is:
(a) $CHCl_3$ ☐ (b) CH_3COCH_3 ☐
(c) CH_3OH ☐ (d) $C_6H_5NH_2$ ☐

207. The increasing order of acid strength among *p*-methoxy phenol (I), *p*-methyl phenol (II) and *p*-nitrophenol (III) is:
(a) II < I < III ☐ (b) III < I < II ☐
(c) III < II < I ☐ (d) I < II < III ☐

208. When ethylbenzoate is hydrolysed with aqueous alkali, the products present in the medium are:
(a) C_6H_5COOH and C_2H_5OH ☐
(b) C_6H_5COOH and $C_2H_5O^-$ ☐
(c) $C_6H_5COO^-$ and C_2H_5OH ☐
(d) $C_6H_5COO^-$ and $C_2H_5O^-$ ☐

209. Which of the following is strongly acidic?
(a) *o*-Nitrobenzoic acid ☐ (b) *p*-Nitrobenzoic acid ☐
(c) *m*-Nitrobenzoic acid ☐ (d) *p*-Nitrophenol ☐

210. By the action of bromine and alkali on benzamide, it gives:
(a) benzene ☐ (b) aniline ☐
(c) bromobenzene ☐ (d) acetanilide ☐

211. Which order is correct about acidity?
(a) $C_6H_5OH > C_6H_5COOH > CH_3COOH$ ☐
(b) $C_6H_5OH > CH_3COOH > C_6H_5COOH$ ☐
(c) $CH_3COOH > C_6H_5COOH > C_6H_5OH$ ☐
(d) $C_6H_5COOH > CH_3COOH > C_6H_5OH$ ☐

212. Aniline when acetylated, the product on nitration followed by alkaline hydrolysis gives:
(a) acetanilide ☐ (b) *o*-nitroacetanilide ☐
(c) *p*-nitroaniline ☐ (d) *m*-nitroaniline ☐

213. Amongst the following, the most basic compound is: **[CET (J&K) 2007]**
(a) benzyl amine ☐ (b) aniline ☐
(c) *p*-nitroaniline ☐ (d) acetanilide ☐

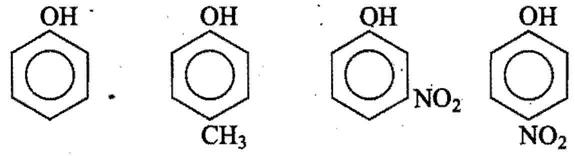
214. 1,2,3-Trihydroxy benzene is called as:
(a) phloroglucinol ☐ (b) pyrogallol ☐
(c) hydroxy quinol ☐ (d) resorcinol ☐

215. Which of the following compounds reacts slower than benzene in electrophilic bromination?
(a) $C_6H_5CH_3$ ☐ (b) C_6H_5OH ☐
(c) $C_6H_5NO_2$ ☐ (d) $C_6H_5NH_2$ ☐

216. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product formed is *m*-bromonitrobenzene. Statement which is related to obtain the *m*-isomer is:
(a) the electron density on *meta* carbon is more than that on *ortho* and *para* positions ☐
(b) loss of aromaticity when Br^+ attacks at the *ortho* and *para* positions and not at *meta* position ☐
(c) easier loss of H^+ to regain aromaticity from the *meta* position than from *ortho* and *para* positions ☐
(d) none of the above ☐

217. Which would decolourise cold aqueous potassium permanganate solution?
(a) Benzoic acid ☐ (b) Cinnamic acid ☐
(c) *m*-Toluic acid ☐ (d) *p*-Toluic acid ☐

218. In the following compounds,



(I) (II) (III) (IV)

the order of acidity is:
(a) III > IV > I > II ☐ (b) I > IV > III > II ☐
(c) II > I > III > IV ☐ (d) IV > III > I > II ☐

219. In the Cannizzaro's reaction given below,

$$2\text{Ph—CHO} \xrightarrow{\text{OH}^-} \text{Ph—CH}_2\text{OH} + \text{PhCO}_2^-$$

the slowest step is: **[AIEEE 2009]**
(a) attack of OH^- at the carbonyl group ☐
(b) the transfer of hydride to the carbonyl group ☐
(c) the abstraction of proton from the carboxylic acid ☐
(d) the deprotonation of $\text{Ph—CH}_2\text{OH}$ ☐

220. In the following compounds,
anisole (I), benzene (II), and nitrobenzene (III)
the ease of reaction with electrophiles is:
(a) I > II > III ☐ (b) II > III > I ☐
(c) II > I > III ☐ (d) III > II > I ☐

221. The replacement of chlorine from chlorobenzene to give phenol requires a drastic condition, but the chlorine of 2,4-dichloronitro-benzene is readily replaced since:
(a) nitro groups make the aromatic ring electron rich at *ortho*/*para*-positions ☐
(b) nitro groups withdraw electrons from the *meta*-position of the aromatic ring ☐
(c) nitro groups donate electrons at *meta*-position ☐
(d) nitro groups withdraw electrons from *ortho*/*para*-positions of the aromatic ring ☐

222. 1-Phenylethanol can be prepared by the reaction of benzaldehyde with:
(a) ethyl iodide and magnesium ☐
(b) methyl iodide and magnesium ☐
(c) methyl bromide and aluminium bromide ☐
(d) methyl bromide ☐

223. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture, HNO_3 acts as a: **[CBSE (Med.) 2009]**
(a) base ☐ (b) acid ☐
(c) reducing agent ☐ (d) catalyst ☐

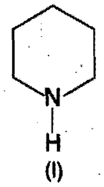
224. In the following groups,

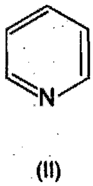
$$\underset{(I)}{\text{—OAc}},\ \underset{(II)}{\text{—OMe}},\ \underset{(III)}{\text{—OSO}_2\text{Me}},\ \underset{(IV)}{\text{—SO}_2\text{CF}_3}$$

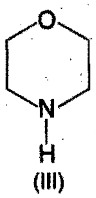
the order of leaving group ability is:

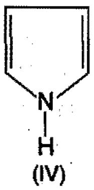
(a) I > II > III > IV ☐ (b) IV > III > I > II ☐
(c) III > II > I > IV ☐ (d) II > III > IV > I ☐

225. In the following compounds,


(I)


(II)


(III)


(IV)

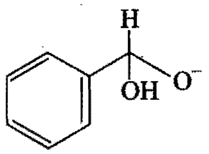
the order of basicity is:

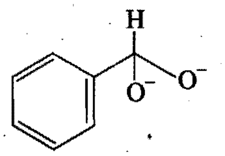
(a) IV > I > III > II ☐ (b) III > I > IV > II ☐
(c) II > I > III > IV ☐ (d) I > III > II > IV ☐

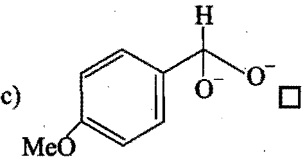
226. Among the following statements on the nitration of aromatic compounds, the false one is:

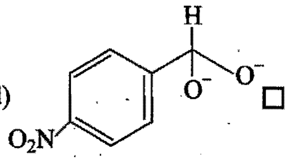
(a) The rate of nitration of benzene is almost the same as that of hexa deuterobenzene ☐
(b) The rate of nitration of toluene is greater than that of benzene ☐
(c) The rate of nitration of benzene is greater than that of hexa deuterobenzene ☐
(d) Nitration is an electrophilic substitution reaction ☐

227. In a Cannizzaro's reaction, the intermediate that will be the best hydride donor is:

(a)  ☐

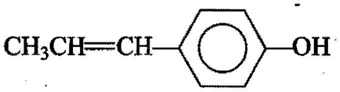
(b)  ☐

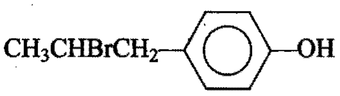
(c)  ☐

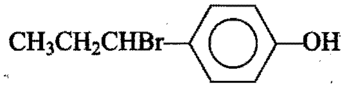
(d)  ☐

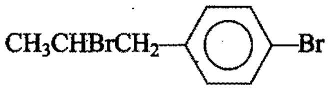
228. In the reaction *p*-chlorotoluene with KNH_2 in liquid NH_3, the major product is:

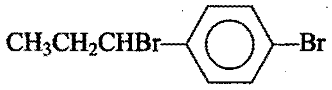
(a) *o*-toluidine ☐ (b) *m*-toluidine ☐
(c) *p*-toluidine ☐ (d) *p*-chloroaniline ☐

229. The reaction of  with HBr gives:

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

230. *p*-Chloroaniline and anilinium hydrochloride can be distinguished by:

(a) Sandmeyer's reaction ☐ (b) $NaHCO_3$ ☐
(c) $AgNO_3$ ☐ (d) Carbylamine test ☐

231. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with:

(a) SO_2Cl_2 ☐ (b) $SOCl_2$ ☐
(c) Cl_2 ☐ (d) NaOCl ☐

232. A new carbon-carbon bond formation is possible in: **[DPMT 2009]**

(a) Cannizzaro's reaction ☐
(b) Friedel-Crafts alkylation ☐
(c) Clemmensen reduction ☐
(d) Reimer-Tiemann reaction ☐

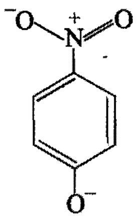
233. Among the following compounds, which will react with acetone to give a product $>C=N-$?

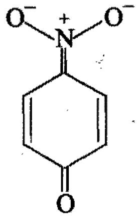
(a) $C_6H_5NH_2$ ☐ (b) $(CH_3)_3N$ ☐
(c) $C_6H_5NHC_6H_5$ ☐ (d) $C_6H_5NHNH_2$ ☐

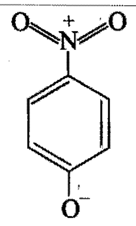
234. A positive carbylamine test is given by:

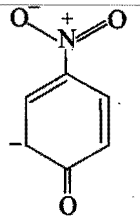
(a) *N,N*-dimethyl aniline ☐
(b) 2,4-dimethyl aniline ☐
(c) *N*-methyl-*o*-methyl aniline ☐
(d) *p*-methylbenzyl amine ☐

235. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is:

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

236. Benzoyl chloride is prepared from benzoic acid by: **[IIT 2000]**

(a) $Cl_2, h\nu$ ☐ (b) SO_2Cl_2 ☐
(c) $SOCl_2$ ☐ (d) Cl_2, H_2O ☐

237. In the reaction,

$$C_6H_5CHO + C_6H_5NH_2 \longrightarrow \underset{(A)}{C_6H_5N{=}CHC_6H_5} + H_2O$$

the compound (A) is known as: **[AIIMS 2002]**

(a) Aldol ☐ (b) Schiff base ☐
(c) Schiff reagent ☐ (d) Benedict's reagent ☐

238. In the reaction,

$$C_6H_5NH_2 \xrightarrow[273\ K]{NaNO_2/HBF_4} (A) \xrightarrow{\Delta H} C_6H_5F$$

the compound (A) is known as: **[CPMT 2002]**

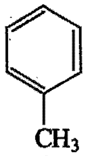
(a) *m*-nitro fluorobenzene ☐

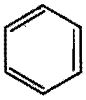
(b) a mixture of fluoroanilines ☐

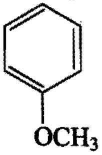
(c) benzene diazonium fluoride ☐

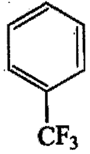
(d) benzene diazonium tetrafluoroborate ☐

239. Among the following compounds, the decreasing order of reactivity towards electrophilic substitution is: **[CBSE (Med.) 2000]**


I


II

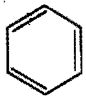

III


IV

(a) III > I > II > IV ☐ (b) IV > I > II > III ☐

(c) I > II > III > IV ☐ (d) II > I > III > IV ☐

240. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds: **[IIT (S) 2002]**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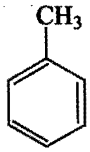
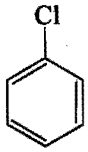
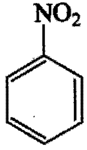

II


III


IV

(a) I > II > III > IV ☐ (b) IV > III > II > I ☐

(c) II > I > III > IV ☐ (d) II > III > I > IV ☐

241. A set of compounds in which the reactivity of halogen atom is in the ascending order, is: **[KCET 2002]**

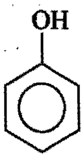
(a) chlorobenzene, vinylchloride, chloroethane ☐

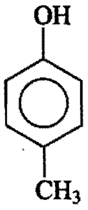
~~(b) chloroethane, chlorobenzene, vinylchloride~~ ☐

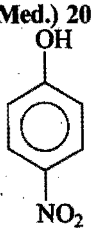
(c) vinylchloride, chlorobenzene, chloroethane ☐

(d) vinylchloride, chloroethane, chlorobenzene ☐

242. The correct acidic order of the following is: **[CBSE (Med.) 2001]**


I


II


III

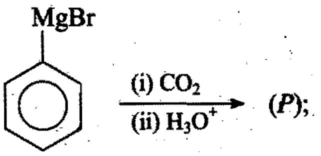
(a) I > II > III ☐ (b) III > I > II ☐

(c) II > III > I ☐ (d) I > III > II ☐

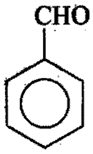
243. When phenol is treated with $CHCl_3$ and NaOH, the product formed is: **[CBSE (Med.) 2002]**

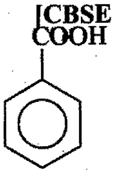
(a) benzaldehyde ☐ (b) salicylaldehyde ☐

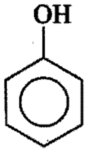
(c) salicyclic acid ☐ (d) benzoic acid ☐

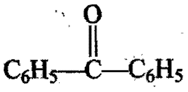
244. 

In the above reaction, product, (P) is: **[CBSE (Med.) 2002]**

(a)  ☐

(b)  ☐

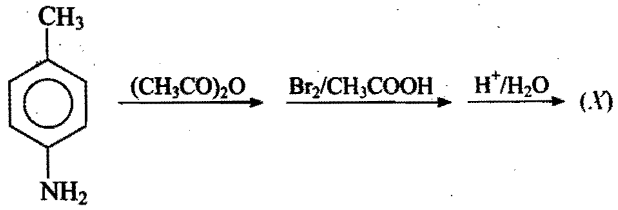
(c)  ☐

(d)  $C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-C_6H_5$ ☐

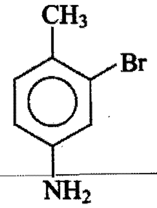
245. Among the following, the strongest base is: **[IIT (S) 2000; AFMC 2009]**

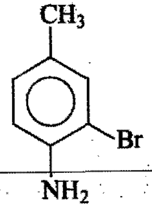
(a) $C_6H_5NH_2$ ☐ (b) p-$NO_2-C_6H_4NH_2$ ☐

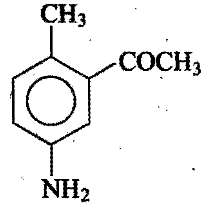
(c) p-$CH_3-C_6H_4NH_2$ ☐ (d) $C_6H_5CH_2NH_2$ ☐

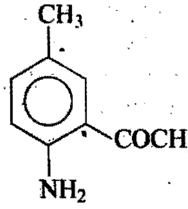
246. 

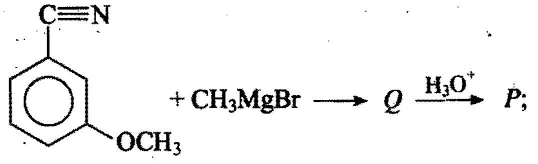
What is X ? **[DPMT 2000]**

(a)  ☐

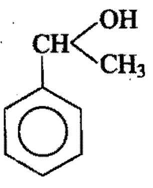
(b)  ☐

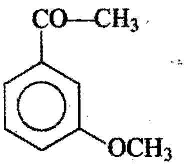
(c)  ☐

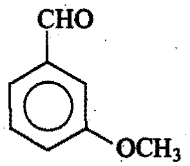
(d)  ☐

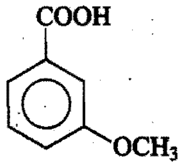
247. 

The product 'P' in the above reaction is: **[CBSE (Med.) 2002]**

(a)  ☐

(b)  ☐

(c) 

☐ (d) 

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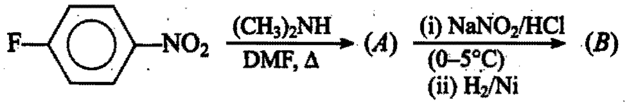
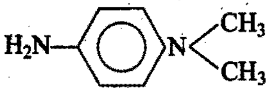
248. 

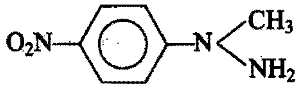
(*B*) is: [IIT (S) 2003]

(a) 

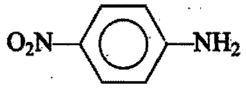
☐

(b) 

☐

(c) 

☐

(d) 

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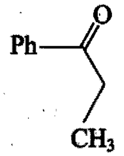
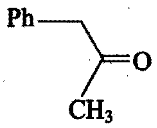
249. $Ph—C\equiv C—CH_3 \xrightarrow{Hg^{2+}/H^+} (A)$; (*A*) is: [IIT (S) 2003]

(a) 

☐ (b) 

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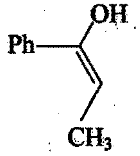
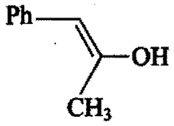
(c) 

☐ (d) 

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250. Benzamide on reaction with $POCl_3$ gives:

(a) aniline ☐ (b) chlorobenzene ☐

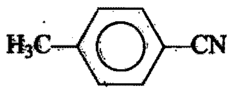
(c) benzylamine ☐ (d) benzonitrile ☐

251. Which of the following reagents will produce salicylaldehyde on reaction with phenol? [DPMT 2004]

(a) $CHCl_3/NaOH$ ☐ (b) $CCl_4/NaOH$ ☐

(c) $CH_2Cl_2/NaOH$ ☐ (d) $CH_3Cl/NaOH$ ☐

252. The reaction of chloroform with alcoholic KOH and *p*-toluidine forms: [AIEEE 2003]

(a) 

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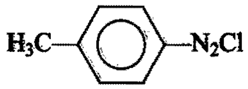
(b) 

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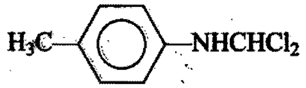
(c) 

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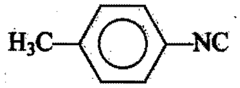
(d) 

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253. The conversion of acetophenone to acetanilide is best accompanied by using: [UPSEAT 2004]

(a) Beckmann rearrangement ☐

(b) Curtius rearrangement ☐

(c) Lossen rearrangement ☐

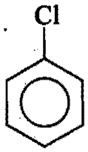
(d) Hofmann rearrangement ☐

254. Which of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid? [AIEEE 2004]

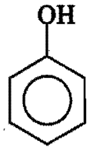
(a) Phenol ☐ (b) Benzaldehyde ☐

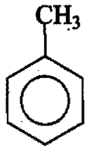
(c) Butanol ☐ (d) Benzoic acid ☐

255. Which of the following will be most easily attacked by an electrophile? [PMT (MP) 2004]

(a) 

☐ (b) 
☐

(c) 

☐ (d) 

☐

256. Using anhydrous $AlCl_3$ as catalyst, which of the following reactions produces ethylbenzene (PhEt)? [CBSE (Med.) 2004]

(a) $CH_3CH_2OH + C_6H_6$ ☐

(b) $CH_3CH{=}CH_2 + C_6H_6$ ☐

(c) $H_2C{=}CH_2 + C_6H_6$ ☐

(d) $H_3C—CH_3 + C_6H_6$ ☐

257. Nitrobenzene is used as a solvent for Friedel-Crafts alkylation of bromobenzene because: [AIIMS 2004]

(a) nitrobenzene cannot be used in alkylation ☐

(b) nitrobenzene is less reactive than bromobenzene ☐

(c) nitrobenzene is more reactive than bromobenzene ☐

(d) none of the above ☐

258. Aromatic nitriles (ArCN) are not prepared by: [AIIMS 2004]

(a) $ArX + KCN$ ☐ (b) $ArN_2 + CuCN$ ☐

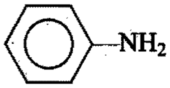
(c) $ArCONH_2 + P_2O_5$ ☐ (d) $ArCONH_2 + SOCl_2$ ☐

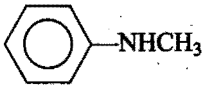
259. Aniline reacts with which of these to form Schiff base? [AFMC 2004]

(a) Acetic acid ☐ (b) Benzaldehyde ☐

(c) Acetone ☐ (d) NH_3 ☐

260. Which of the following is the strongest base? [AIEEE 2004]

(a) 

☐ (b) 

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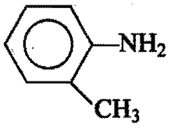
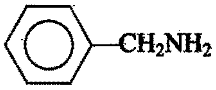
(c) 

☐ (d) 

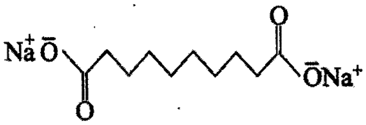
☐

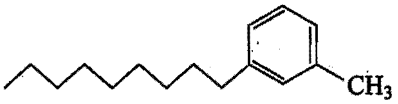
261. DDT is prepared by reacting chlorobenzene with: **[BHU 2005]**

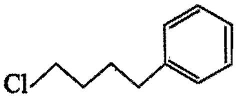
(a) $CHCl_3$ ☐ (b) CCl_3—CHO ☐
(c) CCl_4 ☐ (d) C_2H_6 ☐

262. Which of the following molecules is most suitable to disperse benzene in water? **[AIIMS 2005]**

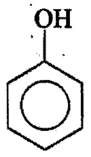
(a)  ☐

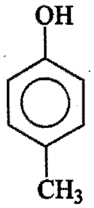
(b)  ☐

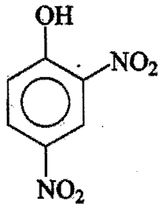
(c)  ☐

(d)  ☐

263. Strength of acidity is in order:


(I)


(II)

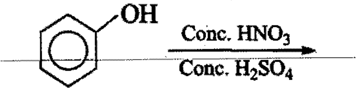

(III)


(IV)

[DCE 2005]

(a) II > I > III > IV ☐ (b) III > IV > I > II ☐
(c) I > IV > III > II ☐ (d) IV > III > I > II ☐

264. The product of the following reaction is:



[JEE (Orissa) 2010]

(a) *o*-Nitrophenol ☐ (b) *m*-Nitrophenol ☐
(c) 2,4-Dinitrophenol ☐ (d) 2,4,6-Trinitrophenol ☐

265. The bad smelling substance formed by the action of alcoholic potash on chloroform and aniline is: **[AMU (Engg.) 2007]**

(a) nitrobenzene ☐ (b) phenyl cyanide ☐
(c) phenyl isocyanide ☐ (d) phenyl isocyanate ☐

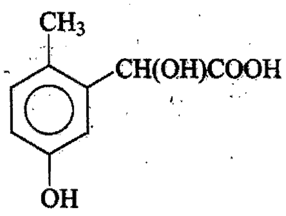
266. The compound prepared by a substitution reaction of benzene is: **[EAMCET (Engg.) 2005]**

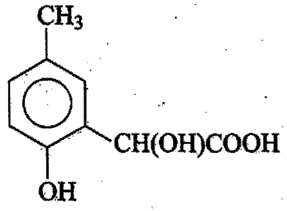
(a) acetophenone ☐
(b) glyoxal ☐
(c) cyclohexane ☐
(d) hexabromocyclohexane ☐

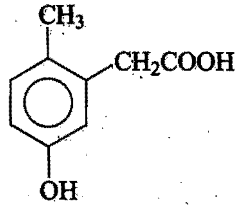
267. The reaction in which phenol differs from alcohol is: **[KCET 2005]**

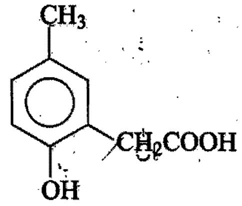
(a) it undergoes esterification with carboxylic acid ☐
(b) it reacts with NH_3 ☐
(c) it forms yellow crystals of iodoform ☐
(d) it liberates H_2 with Na metal ☐

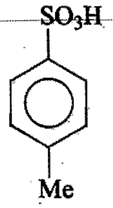
268. *p*-Cresol reacts with chloroform in alkaline medium to give the compound (*A*) which adds hydrogen cyanide to form, the compound (*B*). The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of carboxylic acid is: **[AIEEE 2005]**

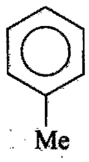
(a)  ☐

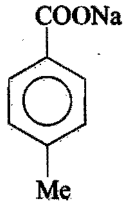
(b)  ☐

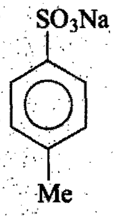
(c)  ☐

(d)  ☐

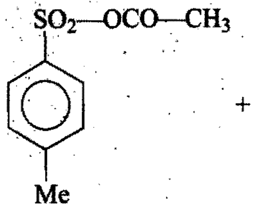
269. When  reacts with $CH_3CO\bar{O}\overset{+}{Na}$ (excess), product formed is: **[IIT (S) 2005]**

(a)  ☐

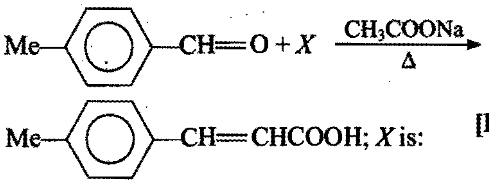
(b)  + SO_3 ☐

(c) 

+ CH_3COOH ☐

(d) 

+ NaOH ☐

270. 

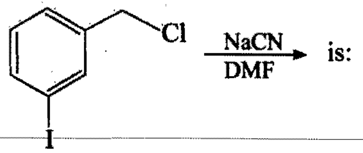
[IIT (S) 2005]

(a) $BrCH_2COOH$ ☐ (b) OHC—COOH ☐
(c) CH_3COOH ☐ (d) $(CH_3CO)_2O$ ☐

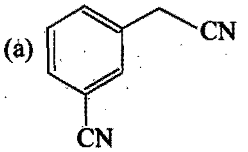
271. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory: **[AIEEE 2006]**

(a) by heating phenol with HF and KF ☐
(b) from aniline by diazotisation followed by heating the diazonium salt with HBF_4 ☐
(c) by direct fluorination of benzene with F_2 gas ☐
(d) by reacting bromobenzene with NaF solution ☐

272. The structure of the major product formed in the following reaction;



[AIEEE 2006]

(a) 

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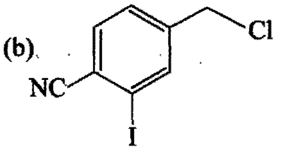
(b) 

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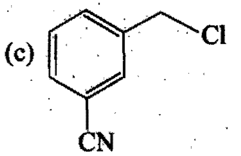
(c) 

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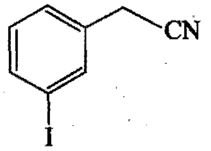
(d) 

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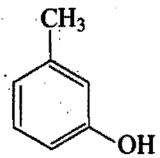
273. Phenyl magnesium bromide reacts with methanol to give: **[AIEEE 2006; DPMT 2009]**

(a) a mixture of anisole and Mg(OH)Br ☐
(b) a mixture of benzene and Mg(OMe)Br ☐
(c) a mixture of toluene and Mg(OH)Br ☐
(d) a mixture of phenol and Mg(Me)Br ☐

274. The structure of the compound that gives a tribromo derivative on treatment with bromine water is: **[AIEEE 2006]**

(a) 

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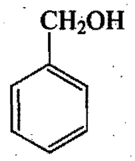
(b) 

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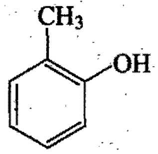
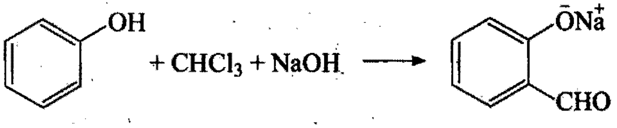
(c) 

☐
(d) 

☐

275. 

The electrophile involved in the above reaction is: **[AIEEE 2006]**

(a) dichloromethyl cation ($\overset{\oplus}{C}HCl_2$) ☐
(b) dichlorocarbene ($:CCl_2$) ☐
(c) trichloromethyl anion ($\overset{\ominus}{C}Cl_3$) ☐
(d) formyl cation ($\overset{\oplus}{C}HO$) ☐

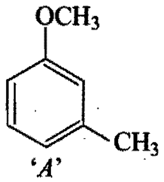
276. Which of the following sequence of reactions (reagents) can be used for the conversion of $C_6H_5CH_2CH_3$ into $C_6H_5CH{=}CH_2$? **[AIIMS 2006]**

(a) $SOCl_2$; H_2O ☐ (b) SO_2Cl_2; alc. KOH ☐
(c) $Cl_2/h\nu$; H_2O ☐ (d) $SOCl_2$; alc. KOH ☐

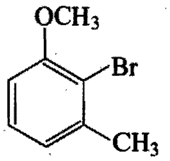
277. Isopropyl benzene on air oxidation in the presence of dilute acid gives: **[AIIMS 2006]**

(a) C_6H_5COOH ☐ (b) $C_6H_5COCH_3$ ☐
(c) C_6H_5CHO ☐ (d) C_6H_5OH ☐

278. The major product obtained on the monobromination (with $Br_2/FeBr_3$) of the following compound 'A' is: **[AIIMS 2006]**



'A'

(a) 

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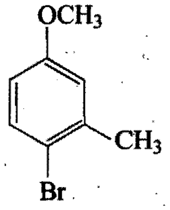
(b) 

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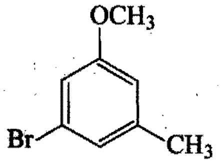
(c) 

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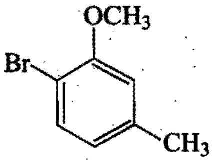
(d) 

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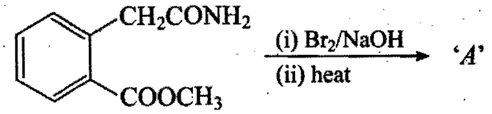
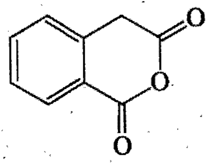
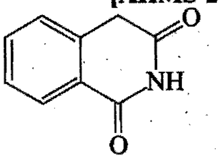
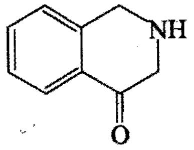
279. The following sequence of reactions on '*A*' gives:

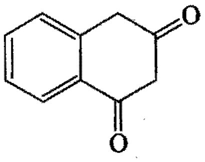


[AIIMS 2006]

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

280. Which of the following compounds would not evolve CO_2 when treated with $NaHCO_3$ solution? **[CET (Karnataka) 2006]**

(a) Salicylic acid ☐ (b) Phenol ☐

(c) Benzoic acid ☐ (d) 4-Nitrobenzoic acid ☐

281. Which of the following does not give benzoic acid on hydrolysis? **[KCET 2006; AFMC 2008]**

(a) Phenyl cyanide ☐ (b) Benzoyl chloride ☐

(c) Benzyl chloride ☐ (d) Methyl benzoate ☐

282. Phenol can be distinguished from ethanol by the following reagents except: **[PET (Kerala) 2006]**

(a) sodium ☐ (b) $NaOH/I_2$ ☐

(c) neutral $FeCl_3$ ☐ (d) Br_2/H_2O ☐

(e) phthalic anhydride/conc. H_2SO_4 and NaOH ☐

283. Which of the following is more basic than aniline? **[CBSE (Med.) 2006]**

(a) Benzylamine ☐ (b) Diphenylamine ☐

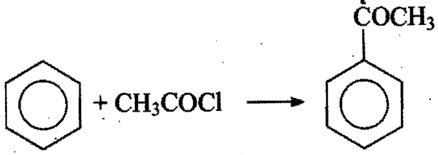
(c) Triphenylamine ☐ (d) *p*-Nitroaniline ☐

284. Hydrolysis of phenyl isocyanide forms: **[AFMC 2006]**

(a) benzoic acid ☐ (b) formic acid ☐

(c) acetic acid ☐ (d) none of these ☐

285. In which reaction, polysubstitution takes place? **[AMU (Med.) 2006]**

(a) 

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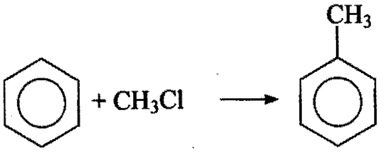
(b) 

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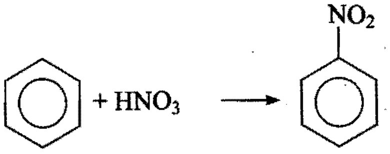
(c) 

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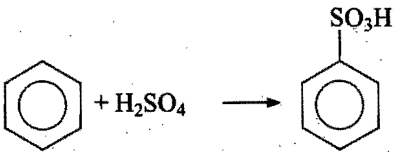
(d) 

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286. Which gives only monosubstituted product? **[DPMT 2005; MGIMS (Wardha) 2006]**

(a) *o*-Dinitrobenzene ☐ (b) *m*-Dinitrobenzene ☐

(c) *p*-Dinitrobenzene ☐ (d) Nitrobenzene ☐

287. The reagent(s) used in the preparation of aspirin from salicylic acid is/are: **[CET (J & K) 2006]**

(a) $SOCl_2$, pyridine ☐ (b) $CH_3Cl, AlCl_3$ ☐

(c) CH_3CO_2H, HCl ☐ (d) $(CH_3CO)_2O, H^+$ ☐

288. Which of the following reacts with benzene in presence of anhydrous $AlCl_3$ to form acetophenone? **[EAMCET (Engg.) 2006]**

(a) CH_3Cl ☐ (b) CH_3COOH ☐

(c) CH_3CHO ☐ (d) CH_3COCl ☐

289. The reagents and the reaction conditions used in the formation of benzene diazonium chloride from aniline are: **[EAMCET (Med.) 2006]**

(a) aq. $NaNO_2$, HCl, 25°C ☐

(b) dil. HCl, 0–5°C ☐

(c) aq. NaCl, HCl, 20°C ☐

(d) aq. $NaNO_2$, HCl, 0–5°C ☐

290. Which reaction is used for the preparation of acetophenone? **[WB JEE (Engg.) 2006]**

(a) Reimer-Tiemann reaction ☐

(b) Wurtz-Fittig reaction ☐

(c) Friedel-Crafts reaction ☐

(d) Cannizzaro's reaction ☐

291. The strongest *ortho-para* and strongest *meta*-directing groups respectively are: **[PMT (Kerala) 2006]**

(a) $—NO_2$ and $—NH_2$ ☐

(b) $—CONH_2$ and $—NH_2$ ☐

(c) $—NH_2$ and $—CONH_2$ ☐

(d) $—X$ and $—CONH_2$ ☐

(e) $—NH_2$ and $—NO_2$ ☐

292. Which of the following is not aromatic? **[PMT (Kerala) 2006, 08]**

(a) Benzene ☐

(b) Cyclopropenyl cation ☐

(c) Tropylium cation ☐

(d) Cyclopentadienyl cation ☐

(e) Cyclopentadienyl anion ☐

293. Acylation of phenols with aromatic acyl chloride in presence of NaOH is known as: **[PMT (HP) 2006]**

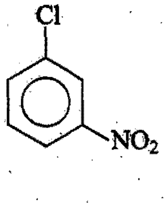
(a) Schotten-Baumann reaction ☐

(b) Hell-Volhard-Zelinsky reaction ☐

(c) Haloform reaction ☐

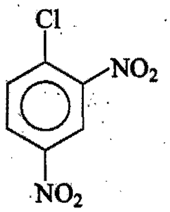
(d) Cannizzaro's reaction ☐

294. Reactivity order of following towards NaOEt, EtOH: **[DPMT 2006]**



(I)

(II)



(III)

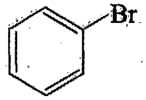
(a) III > II > I ☐ (b) II > I > III ☐
(c) I > II > III ☐ (d) III > I > II ☐

295. Toluene by Etard's reaction gives: [DPMT 2006]
(a) *ortho*-cresol ☐ (b) benzoic acid ☐
(c) benzyl alcohol ☐ (d) benzaldehyde ☐

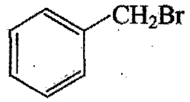
296. Phenol on reaction with $CHCl_3$ and NaOH gives benzaldehyde. Intermediate of this reaction is: [DCE 2006]
(a) carbocation ☐ (b) carbanion ☐
(c) free radical ☐ (d) carbene ☐

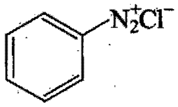
297. $X \xrightarrow[HNO_3]{AgNO_3}$ Yellow or white ppt.

Which of the following cannot be X? [DCE 2006]

(a) 

☐ (b) $(CH_3)_3CCl$ ☐

(c) 

☐ (d) 

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298. Which of the following species is less reactive than benzene towards electrophilic substitution reactions? [BV (Pune) 2006]
(a) Aniline ☐ (b) Nitrobenzene ☐
(c) Bromobenzene ☐ (d) Phenol ☐

299. Which of these does not contain —COOH group? [CET (Punjab) Engg. 2006]
(a) Aspirin ☐ (b) Benzoic acid ☐
(c) Picric acid ☐ (d) Salicylic acid ☐

300. In the following reaction,

$$X \xrightarrow{\text{Bromination}} Y \xrightarrow[\text{HCl}]{\text{NaNO}_2}$$

$$Z \xrightarrow[C_2H_5OH]{\text{Boiling}} \text{Tribromobenzene, } X \text{ is:}$$

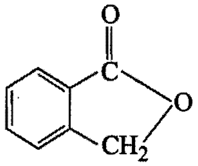
[PMT (Uttarakhand) 2006]
(a) benzoic acid ☐ (b) salicylic acid ☐
(c) phenol ☐ (d) aniline ☐

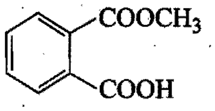
301. When benzene sulphonic acid and *p*-nitrophenol are treated with $NaHCO_3$, the gases released respectively are: [IIT 2006]
(a) SO_2, NO_2 ☐ (b) SO_2, NO ☐
(c) SO_2, CO_2 ☐ (d) CO_2, CO_2 ☐

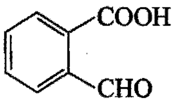
302. (I) 1,2-Dihydroxy benzene (II) 1,3-Dihydroxy benzene
(III) 1,4-Dihydroxy benzene (IV) Hydroxy benzene
The increasing order of boiling points of the above mentioned alcohols is: [IIT 2006]
(a) I < II < III < IV ☐ (b) I < II < IV < III ☐
(c) IV < I < II < III ☐ (d) IV < II < I < III ☐

303. The IUPAC name of C_6H_5COCl is: [IIT 2006]
(a) benzoyl chloride ☐
(b) benzene chloroketone ☐
(c) benzene carbonyl chloride ☐
(d) chlorophenyl ketone ☐

304. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product? [IIT 2006]



(a) 

☐ (b) 

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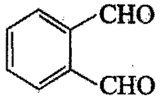
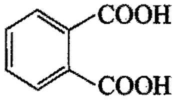
(c) 

☐ (d) 

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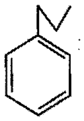
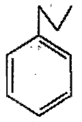
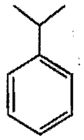
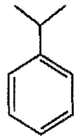
305.  $+ \text{Cl—CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{AlCl_3} P \xrightarrow[\text{(ii) } H_2O]{\text{(i) } O_2/\Delta} Q + \text{Phenol}$

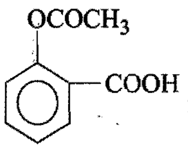
The major products P and Q are: [IIT 2006]

(a)  and CH_3CH_2CHO ☐

(b)  and CH_3COCH_3 ☐

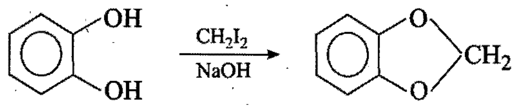
(c)  and CH_3CH_2CHO ☐

(d)  and CH_3COCH_3 ☐

306. The compound 

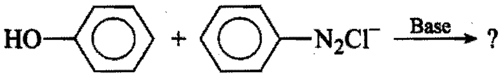
is used as: [AIIMS 2007]
(a) antiseptic ☐ (b) antibiotic ☐
(c) analgesic ☐ (d) pesticide ☐

307. The reaction

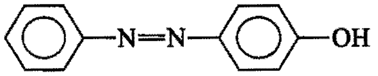


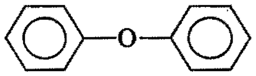
is an example of: **[PMT (Kerala) 2007]**

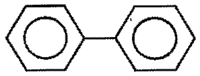
(a) Wurtz reaction ☐ (b) Williamson reaction ☐
(c) Ulmann reaction ☐ (d) Wittig reaction ☐
(e) Wurtz-Fittig reaction ☐

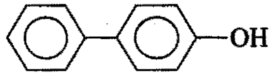
308. 

[AFMC 2007]

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

309. What amount of bromine will be required to convert 2g of phenol into 2,4,6-tribromophenol? **[UPSEE (Engg.) 2007]**

(a) 20.44 g ☐ (b) 6.00 g ☐
(c) 4.00 g ☐ (d) 10.22 g ☐

310. In order to distinguish between $C_2H_5NH_2$ and $C_6H_5NH_2$, which of the following reagent(s) is useful? **[BHU (Mains) 2007]**

(a) Hinsberg reagent ☐ (b) β-naphthol ☐
(c) $CHCl_3/KOH$ ☐ (d) NaOH ☐

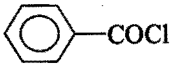
311. Aniline is prepared in presence of Fe/HCl from: **[CPMT 2007]**

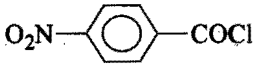
(a) benzene ☐ (b) nitrobenzene ☐
(c) dinitrobenzene ☐ (d) none of these ☐

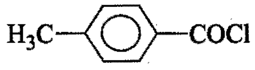
312. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound known as: **[UPSEE (Engg.) 2007]**

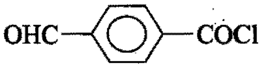
(a) an amine ☐ (b) an imine ☐
(c) an enamine ☐ (d) a Schiff's base ☐

313. Consider the following compounds:

(i) 

(ii) 

(iii) 

(iv) 

The correct decreasing order of their reactivity towards hydrolysis is: **[CBSE (Med.) 2007]**

(a) (iv) > (ii) > (i) > (iii) ☐ (b) (ii) > (iv) > (i) > (iii) ☐
(c) (ii) > (iv) > (iii) > (i) ☐ (d) (i) > (ii) > (iii) > (iv) ☐

314. The compound formed as a result of oxidation of ethylbenzene by $KMnO_4$ is: **[AIEEE 2007]**

(a) benzylalcohol ☐ (b) benzophenone ☐
(c) acetophenone ☐ (d) benzoic acid ☐

315. Presence of a nitro group in a benzene ring: **[AIEEE 2007]**

(a) deactivates the ring towards electrophilic substitution ☐
(b) activates the ring towards electrophilic substitution ☐
(c) renders the ring basic ☐
(d) deactivates the ring towards nucleophilic substitution ☐

316. The functional groups present in 'salol' are: **[EAMCET (Engg.) 2007]**

(a) $—NH_2$ and $—OR$ ☐ (b) —OH and $—COR$ ☐
(c) $—NH_2$ and —COOH ☐ (d) —OH and $—COOR$ ☐

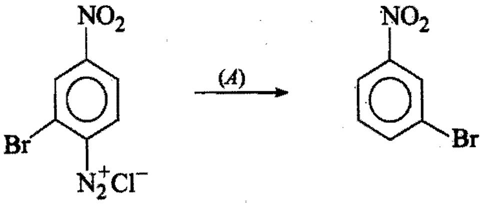
317. Nitrobenzene is reduced with Zn and alcoholic potash mixture to get: **[EAMCET (Med.) 2007]**

(a) $C_6H_5NH_2$ ☐
(b) $C_6H_5NH—NH—C_6H_5$ ☐
(c) $C_6H_5N{=}NC_6H_5$ ☐
(d) $C_6H_5—NH—CO—C_6H_5$ ☐

318. Phenol is more acidic than alcohol because: **[BCECE (Med.) 2007]**

(a) phenol is more soluble in polar solvents ☐
(b) alcohol does not lose hydrogen atom ☐
(c) phenoxide ion is stabilised by resonance ☐
(d) phenoxide ion does not exhibit resonance ☐

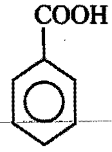
319. In the reaction,

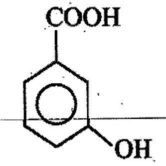


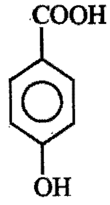
(*A*) is: **[DPMT (Med.) 2007]**

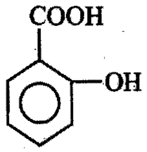
(a) H_3PO_2 ☐ (b) Cu_2Cl_2 ☐
(c) $HgSO_4/H_2SO_4$ ☐ (d) H^+/H_2O ☐

320. Which of the following aromatic acid is most acidic? **[AMU (Engg.) 2009]**

(a)  ☐

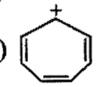
(b)  ☐

(c)  ☐

(d)  ☐

321. Pick out the wrong statement. **[PET (Kerala) 2007]**

(a) Toluene shows resonance. ☐

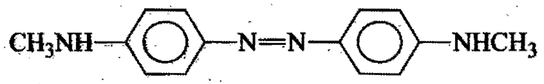
(b)  is non-aromatic. ☐

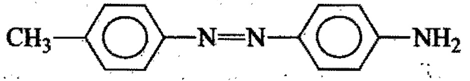
(c) The hybrid state of carbon in carbonyl group is sp^2. ☐

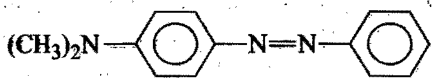
(d) Dipole moment of vinyl chloride is less than that of methyl chloride. ☐

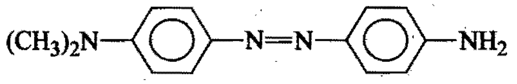
(e) The hyperconjugative effect is known as no bond resonance. ☐

322. Aniline when diazotised in cold and then treated with dimethylaniline gives a coloured product. Its structure would be: **[CBSE (Med.) 2004; UGET (Med.) 2007]**

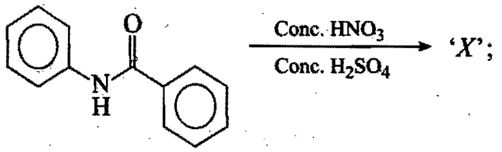
(a)  ☐

(b)  ☐

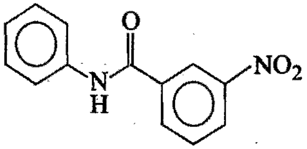
(c)  ☐

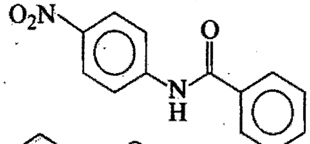
(d)  ☐

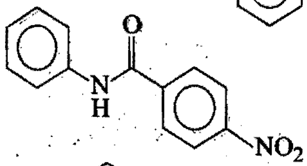
323. In the following reaction,

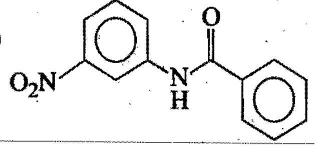


The structure of major product 'X' is: **[IIT 2007]**

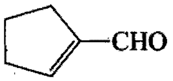
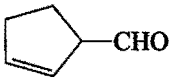
(a)  ☐

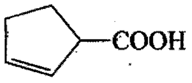
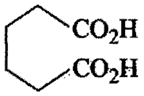
(b)  ☐

(c)  ☐

(d)  ☐

324. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on treatment with aqueous KOH yields compound F. Compound F is: **[IIT 2007]**

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

325. Bakelite is obtained from phenol by reaction with: **[AIEEE 2008]**

(a) HCHO ☐ (b) $(CH_2OH)_2$ ☐

(c) CH_3CHO ☐ (d) CH_3COCH_3 ☐

326. Phenol when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives: **[AIEEE 2008]**

(a) nitrobenzene ☐ (b) 2,4,6-trinitrobenzene ☐

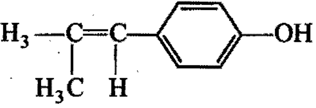
(c) *o*-nitrophenol ☐ (d) *p*-nitrophenol ☐

(e) none of these ☐

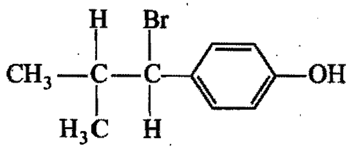
327. Among the following, which is least acidic? **[CET (Karnataka) 2008]**

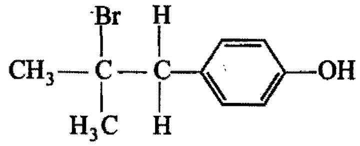
(a) *p*-Nitrophenol ☐ (b) *p*-Chlorophenol ☐

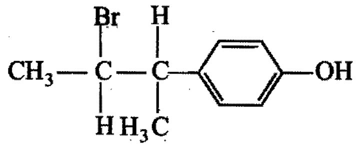
(c) Phenol ☐ (d) *o*-Cresol ☐

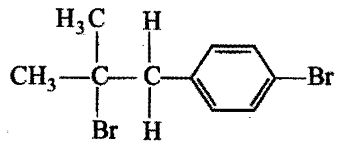
328. The reaction of  with HBr

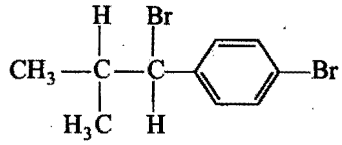
gives predominantly: **[PET (Kerala) 2008]**

(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

(e)  ☐

329. An organic compound (X) with molecular formula C_7H_8O is insoluble in aqueous $NaHCO_3$ but dissolves in NaOH. When treated with bromine water (X) rapidly gives (Y), $C_7H_5OBr_3$. The compounds (X) and (Y) respectively are: **[PET (Kerala) 2008]**

(a) benzyl alcohol and 2,4,6-tribromo-3-methoxy benzene ☐

(b) benzyl alcohol and 2,4,6-tribromo-3-methyl phenol ☐

(c) *o*-cresol and 3,4,5-tribromo-2-methyl phenol ☐

(d) methoxy benzene and 2,4,6-tribromo-3-methoxy benzene ☐

(e) *m*-cresol and 2,4,6-tribromo-3-methyl phenol ☐

330. Benzoylation of phenol in alkaline medium is known as: **[JEE (WB) 2008]**

(a) Friedel-Crafts reaction ☐

(b) Wurtz-Fittig reaction ☐

(c) Schotten-Baumann reaction ☐

(d) Sabatier-Sendern's reaction ☐

331. Anisole is the product obtained from phenol by the reaction known as: **[VITEEE 2008]**

(a) coupling ☐ (b) etherification ☐

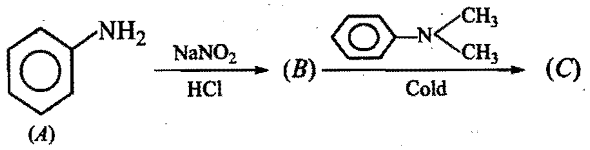
(c) oxidation ☐ (d) esterification ☐

332. Which of the following species does not exert a resonance effect? [CET (Karnataka) 2008]

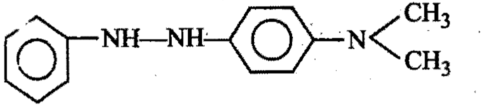
(a) C_6H_5OH ☐ (b) C_6H_5Cl ☐

(c) $C_6H_5NH_2$ ☐ (d) $C_6H_5\overset{+}{N}H_3$ ☐

333. In a reaction of aniline, a coloured product '*C*' was obtained.



The structure of '*C*' would be: [CBSE (Med.) 2008]

(a)


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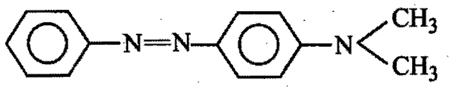
(b)


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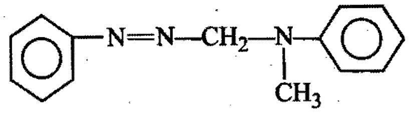
(c)


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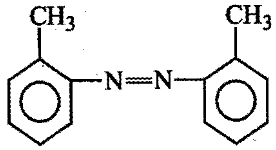
(d)


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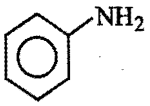
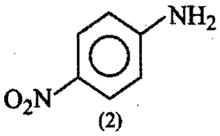
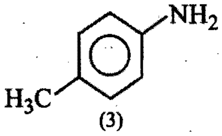
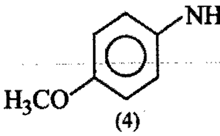
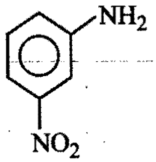
334. The correct order of increasing basic nature of the following bases is:


(1)


(2)


(3)


(4)


(5)

[PET (Kerala) 2008]

(a) 2 < 5 < 1 < 3 < 4 ☐ (b) 5 < 2 < 1 < 3 < 4 ☐

(c) 2 < 5 < 1 < 4 < 3 ☐ (d) 5 < 2 < 1 < 4 < 3 ☐

(e) 2 < 5 < 4 < 3 < 1 ☐

335. When nitrobenzene is reduced with zinc and methanolic NaOH, the product obtained is: [PMT (Kerala) 2008]

(a) aniline ☐ (b) phenyl hydroxylamine ☐

(c) *p*-aminophenol ☐ (d) azobenzene ☐

(e) hydrazobenzene ☐

336. Aniline reacts with ...... to yield ...... as the final product. [DCE 2008]

(a) bromine, 2-bromoaniline ☐

(b) bromine, 2,4,6-tribromoaniline ☐

(c) chloroform/KOH, phenyl cyanide ☐

(d) acetyl chloride, benzanilide ☐

337. Which of the following reactions can produce aniline as main product? [AFMC 2008]

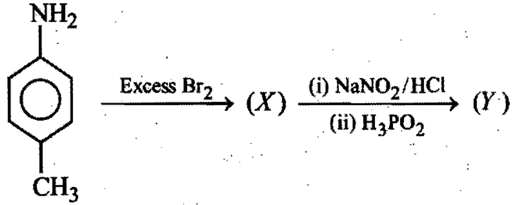
(a) $C_6H_5NO_2 + Zn/KOH$ ☐

(b) $C_6H_5NO_2 + Zn/NH_4Cl$ ☐

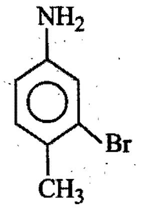
(c) $C_6H_5NO_2 + LiAlH_4$ ☐

(d) $C_6H_5NO_2 + Zn/HCl$ ☐

338. In the following reaction sequence,



The compounds (*X*) and (*Y*) respectively are: [CET (Punjab) Engg. 2008]

(a)

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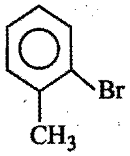
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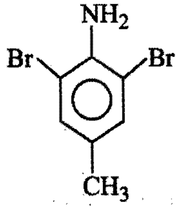
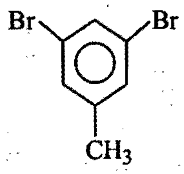
(b)

and

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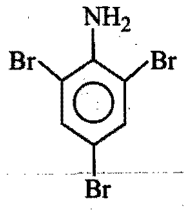
(c)

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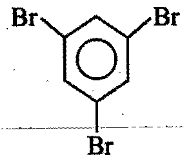
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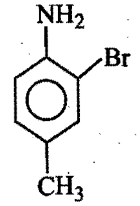
(d)

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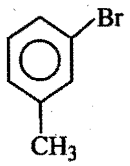
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339. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains a: [AIEEE 2008]

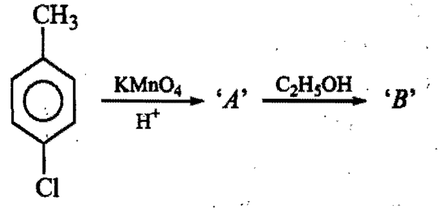
(a) mixture of *o*- and *m*-bromotoluenes ☐

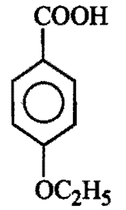
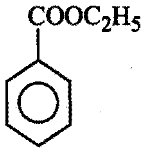
(b) mixture of *o*- and *p*-bromotoluenes ☐

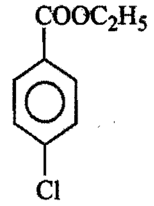
(c) mixture of *o*- and *p*-dibromobenzenes ☐

(d) mixture of *o*- and *p*-bromoanilines ☐

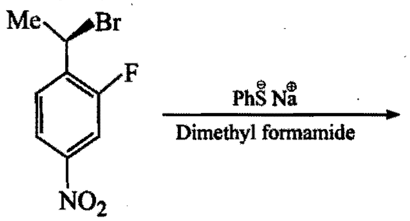
340. Identify '*B*' in the following reaction: [DPMT 2008]



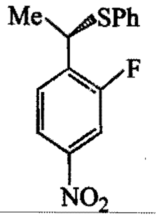
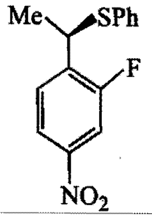
(a)  ☐ (b)  ☐

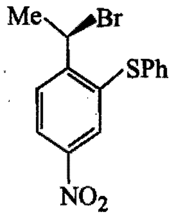
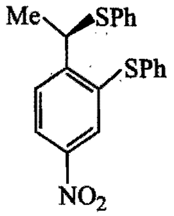
(c)  ☐ (d) none of these ☐

341. The major product of the following reaction,

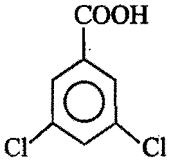
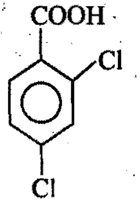


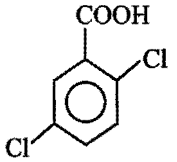
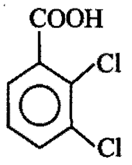
? ; is: [IIT 2008]

(a)  ☐ (b)  ☐

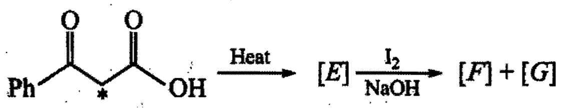
(c)  ☐ (d)  ☐

342. Dichlorobenzoic acid $\xrightarrow{\text{Mononitration}}$ Product (only one). The structure of reactant can be: [DPMT 2008]

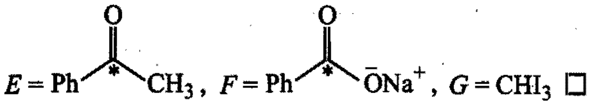
(a)  ☐ (b)  ☐

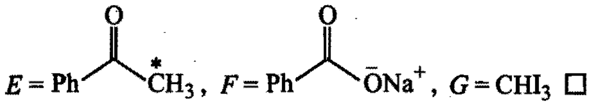
(c)  ☐ (d)  ☐

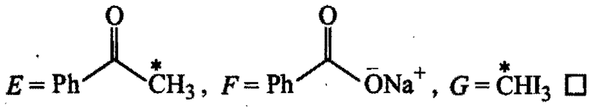
343. In the following reaction sequence, the correct structures of *E*, *F* and *G* are:

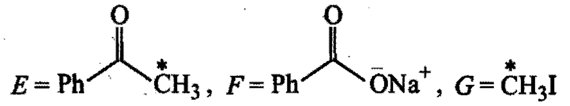


(* implies ^{13}C labelled carbon) [IIT 2008]

(a)  ☐

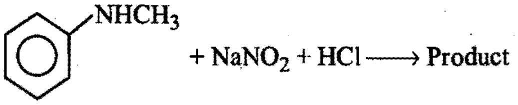
(b)  ☐

(c)  ☐

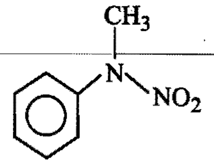
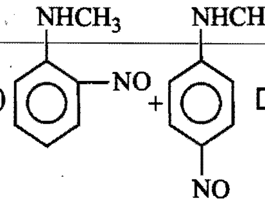
(d)  ☐

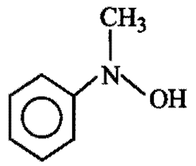
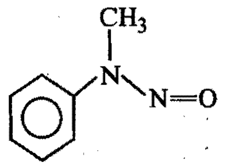
344. Consider the acidity of the following carboxylic acids:
(i) PhCOOH (ii) *o*-$NO_2C_6H_4COOH$
(iii) *p*-$NO_2C_6H_4COOH$ (iv) *m*-$NO_2C_6H_4COOH$
Which of the following orders is correct? [JCECE (Med.) 2008]
(a) (i) > (ii) > (iii) > (iv) ☐ (b) (ii) > (iv) > (iii) > (i) ☐
(c) (ii) > (iv) > (i) > (iii) ☐ (d) (ii) > (iii) > (iv) > (i) ☐

345. Predict the product:



[CBSE (Med.) 2009]

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

346. Amino group is *ortho*, *para*-directing for aromatic electrophilic substitution. On nitration of aniline, a good amount of *m*-nitroaniline is obtained. This is due to: [DCE 2009]
(a) in nitration mixture, *ortho*-, *para*-activity of —NH_2 group is completely lost ☐
(b) —NH_2 becomes —NH_3^+, which is *m*-directing ☐
(c) —NH_2 becomes —$NH^+SO_4^-$, which is *m*-directing ☐
(d) —NH_2 becomes —$NH^-NO_2^+$, which is *m*-directing ☐

347. Which one of the following is not the correct reaction of aryl diazonium salts? [DCE 2009]

(a) $C_6H_5N_2^+Cl^- + Cu_2Cl_2 \longrightarrow C_6H_5Cl$ ☐

(b) $C_6H_5N_2^+Cl^- + HBF_4 \xrightarrow{\text{Heat}} C_6H_5F$ ☐

(c) $C_6H_5N_2^+Cl^- + H_3PO_2 \longrightarrow C_6H_5PO_4$ ☐

(d) $C_6H_5N_2^+Cl^- + SnCl_2/HCl \longrightarrow C_6H_5NHNH_2$ ☐

348. In Gattermann reaction, a diazonium group is replaced by *X* using *Y*. What are *X* and *Y* ? [EAMCET 2009]

	X	*Y*	
(a)	Cl^-	Cu/HCl	☐
(b)	Cl^+	$CuCl_2$/HCl	☐
(c)	Cl^-	$CuCl_2$/HCl	☐
(d)	Cl_2	Cu_2O/HCl	☐

349. In electrophilic aromatic substitution reaction, the nitro group is *meta*-directing because it: [CET (Karnataka) 2009]

(a) decreases electron density at *meta*-position ☐

(b) increases electron density at *meta*-position ☐

(c) increases electron density at *ortho*- and *para*-positions ☐

(d) decreases electron density at *ortho*- and *para*-positions ☐

350. Which statement is incorrect? [JEE (WB) 2009]

(a) Phenol is a weak acid ☐

(b) Phenol is an aromatic compound ☐

(c) Phenol liberates CO_2 from Na_2CO_3 solution ☐

(d) Phenol is soluble in NaOH ☐

351. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is: [AIEEE 2009]

(a) benzoic acid ☐ (b) salicylic acid ☐

(c) salicylaldehyde ☐ (d) phthalic acid ☐

352. Consider the following reaction:

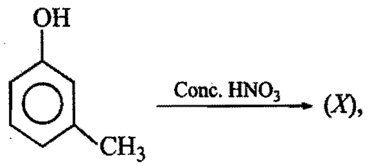
$$\text{Phenol} \xrightarrow{\text{Zn dust}} (X) \xrightarrow[\text{anhyd. AlCl}_3]{CH_3Cl} (Y) \xrightarrow{\text{Alkaline KMnO}_4} (Z);$$

the product (*Z*) is: [CBSE (Med.) 2009]

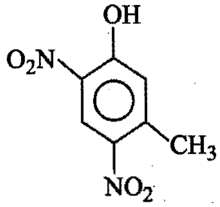
(a) benzaldehyde ☐ (b) benzoic acid ☐

(c) benzene ☐ (d) toluene ☐

353. In the reaction for dinitration, [DCE 2009]



the major dinitrated product (*X*) is:

(a) 

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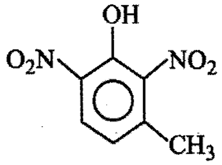
(b) 

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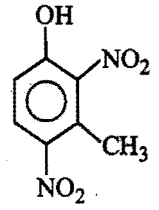
(c) 

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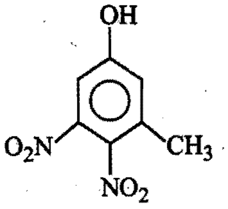
(d) 

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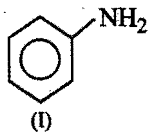
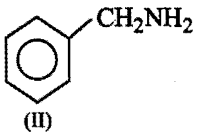
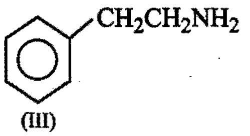
354. Consider the following compounds,



(I)



(II)



(III)

What is the correct order of basicity of the above compounds? [SCRA 2009]

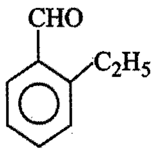
(a) I > II > III ☐ (b) III > I > II ☐

(c) III > II > I ☐ (d) I > III > II ☐

355. An aromatic compound *X* with molecular formula, $C_9H_{10}O$ gives the following chemical tests:

(i) Forms 2,4-DNP derivative (ii) Reduces Tollens' reagent (iii) Undergoes Cannizzaro reaction and (iv) On vigorous oxidation 1,2-benzenedicarboxylic acid is obtained.

'*X*' is: [DCE 2009]

(a) 

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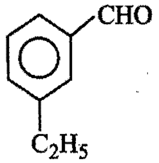
(b) 

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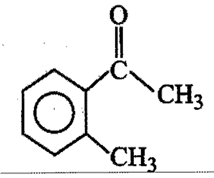
(c) 

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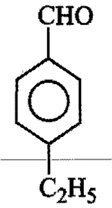
(d) 

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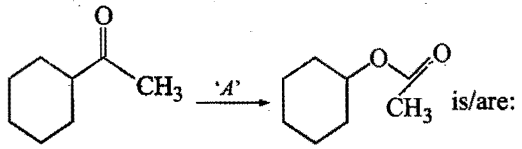
356. The most suitable reagent '*A*' for the reaction



is/are: [AMU (Engg.) 2009]

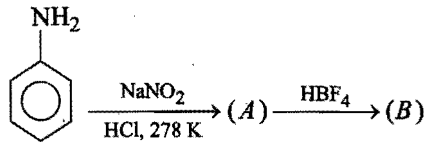
(a) O_3 ☐

(b) H_2O_2 ☐

(c) NaOH-H_2O_2 ☐

(d) *m*-chloroperbenzoic acid ☐

357. In the chemical reaction,



The compounds *A* and *B* respectively are: [AIEEE 2010]

(a) nitrobenzene and chlorobenzene ☐
(b) nitrobenzene and fluorobenzene ☐
(c) benzene diazonium chloride and fluorobenzene ☐
(d) phenol and benzene ☐

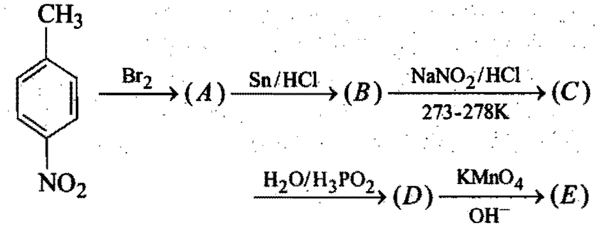
358. An orange dye *p*-hydroxy azobenzene can be synthesized from benzene diazonium chloride by: **[PMT (Kerala) 2010]**

(a) Sandmeyer reaction ☐ (b) Gomberg reaction ☐
(c) Coupling reaction ☐ (d) Gattermann reaction ☐
(e) Etard reaction ☐

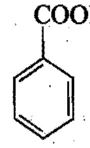
359. What is obtained when nitrobenzene is treated sequentially with (i) NH_4Cl/Zn dust and (ii) $H_2SO_4/Na_2Cr_2O_7$? **[JEE (WB) 2010]**

(a) Benzene ☐ (b) Nitrosobenzene ☐
(c) *m*-chlorobenzene ☐ (d) *p*-chloronitrobenzene ☐

360. Identify the product (*E*) in the following sequence of reactions :



[AMU (Med.) 2010]

(a) 

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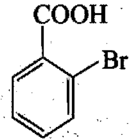
(b) 

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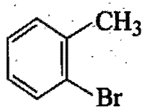
(c) 

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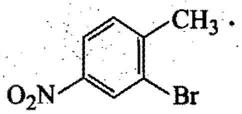
(d) 

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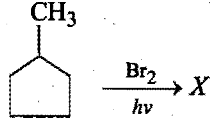
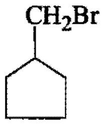
361. The most basic amine among the following is: **[PMT (Kerala) 2010]**

(a) *p*-toluidine ☐ (b) *o*-nitroaniline ☐
(c) *p*-nitroaniline ☐ (d) 2,4-dinitroaniline ☐
(e) *p*-fluoroaniline ☐

362. In the following reaction,



the major product '*X*' is: **[AMU (Med.) 2010]**

(a) 

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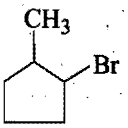
(b) 

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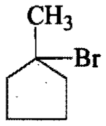
(c) 

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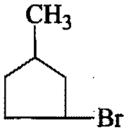
(d) 

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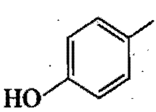
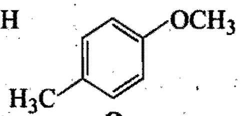
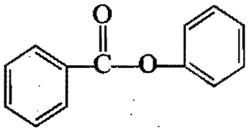
363. The compounds P, Q and S



P

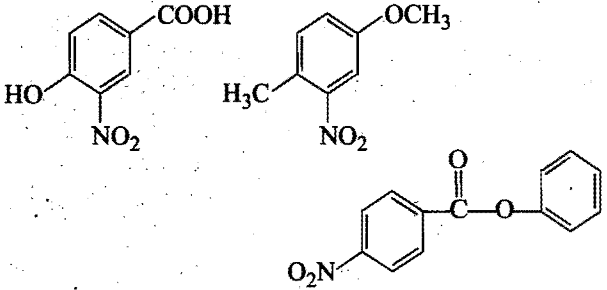


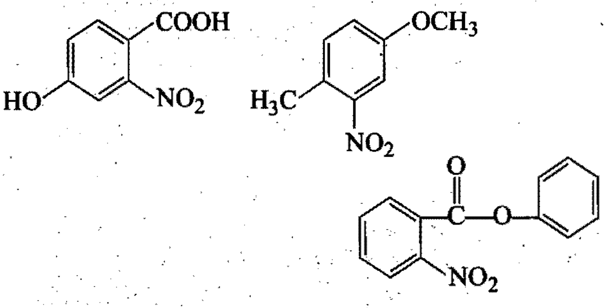
Q

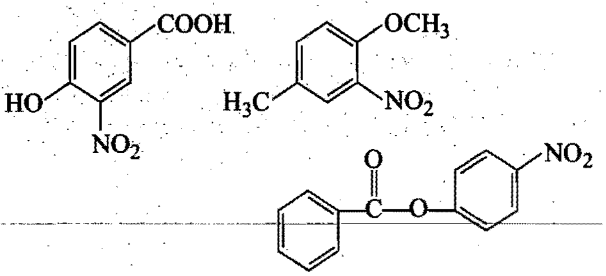


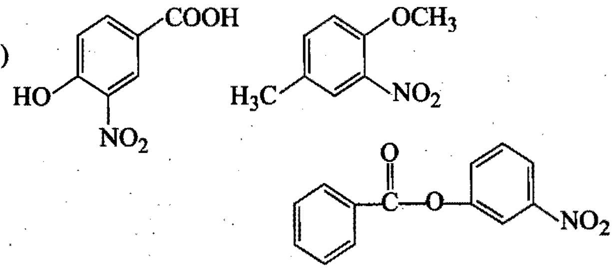
S

were separately subjected to nitration using HNO_3/H_2SO_4 mixture. The major product formed in each case respectively is: **[IIT 2010]**

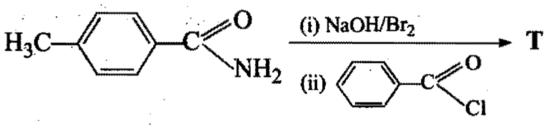
(a) 

(b) 

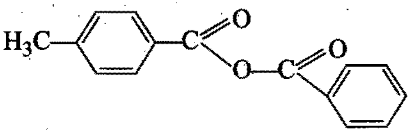
(c) 

(d) 

364. In the reaction



the structure of the product **T** is: **[IIT 2010]**

(a) 

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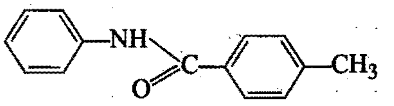
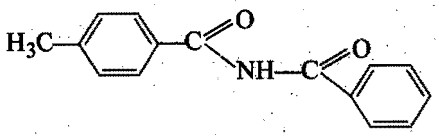
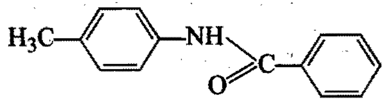
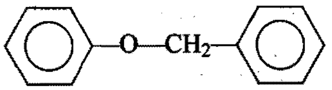
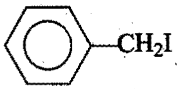
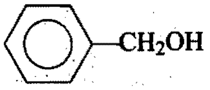
(b)  ☐

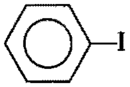
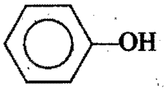
(c)  ☐

(d)  ☐

SET II : This set contains questions with two or more correct answers.

365. The ether  when treated with HI produces:

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

366. Toluene when treated with Br_2/Fe gives *p*-bromotoluene as the major product because the —CH_3 group:
(a) is *para*-directing ☐
(b) is *meta*-directing ☐
(c) activates the ring by hyperconjugation ☐
(d) deactivates the ring ☐

367. An aromatic molecule will:
(a) have $4n\pi$ electrons ☐
(b) have $(4n + 2)\pi$ electrons ☐
(c) be planar ☐
(d) be cyclic ☐

368. Which of the following are less reactive than benzene?
(a) Toluene ☐ (b) Chlorobenzene ☐
(c) Nitrobenzene ☐ (d) Benzoic acid ☐

369. Salicylic acid is prepared from phenol by: **[AFMC 2005]**
(a) Reimer-Tiemann reaction ☐
(b) Kolbe's electrolytic reaction ☐
(c) Kolbe's reaction ☐
(d) none of the above ☐

370. Which of the following are *meta*-directing?
(a) SO_2Cl ☐ (b) $COCH_3$ ☐
(c) CN ☐ (d) NH*R* ☐

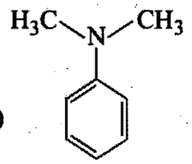
371. The type of substitution reactions of benzenoid hydrocarbons are:
(a) elimination ☐ (b) electrophilic ☐
(c) nucleophilic ☐ (d) free radical ☐

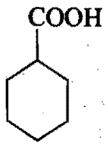
372. Which of the following compounds will reduce Fehling's solution?
(a) Formaldehyde ☐ (b) Acetaldehyde ☐
(c) Benzaldehyde ☐ (d) Chloral ☐

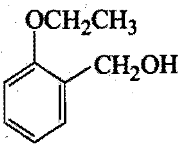
373. Benzene molecule has:
(a) 9 sigma and 3 pi-bonds ☐
(b) 30 electrons ☐
(c) 12 sigma and 3 pi-bonds ☐
(d) 21 electrons ☐

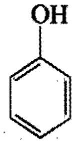
374. Benzene is obtained from benzene diazonium chloride by the:
(a) reduction with alkaline stannous chloride ☐
(b) reduction with acidic stannous chloride ☐
(c) action of hypophosphorus acid ☐
(d) action of ethyl alcohol ☐

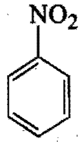
375. Amongst the following the total number of compounds soluble in aqueous NaOH is: **[IIT 2010]**

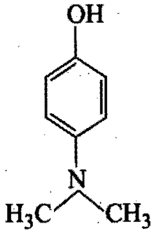
(a) 

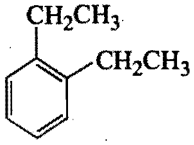
(b) 

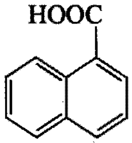
(c) 

(d) 

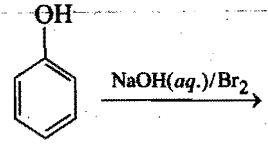
(e) 

(f) 

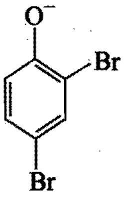
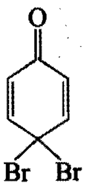
(g) 

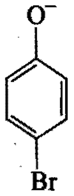
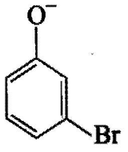
(h) 

376. In the reaction



the intermediate(s) is (are): **[IIT 2010]**

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

ASSERTION-REASON TYPE QUESTIONS

Following questions consists of an Assertion (A) and Reason (R). Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct and (R) is correct explanation of (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.
(e) If both (A) and (R) are incorrect.

1. (A) Acetaldehyde reduces Fehling's solution but benzaldehyde does not.
(R) Acetaldehyde is stronger reducing agent than benzaldehyde.

2. (A) *p*-methoxy benzaldehyde is less reactive than benzaldehyde towards cyanohydrin formation.
(R) The + *R* effect of methoxy group increases the electron deficiency of the carbonyl carbon.

3. (A) Phenol is more reactive than benzene towards electrophilic substitution.
(R) In the case of phenol, the intermediate carbocation is more resonance stabilized. [IIT 2000]

4. (A) *p*-Nitrophenol is stronger acid than *o*-nitrophenol.
(R) Intramolecular hydrogen bonding makes *ortho*-isomer weaker acid than *para*-isomer.

5. (A) Friedel-Crafts reaction between benzene and acetic anhydride in presence of anhydrous $AlCl_3$ yields acetophenone and not polysubstitution product.
(R) Acetophenone formed poisons the catalyst, preventing further reaction.

6. (A) *o*-Phenol sulphonic acid on heating at 100°C changes to *p*-phenol sulphonic acid.
(R) Sulphonation of phenol is a reversible process.

7. (A) Phenol and benzoic acid can be distinguished by NaOH.
(R) Benzoic acid is stronger acid than phenol.

8. (A) Nitrobenzene undergoes Friedel-Crafts reaction.
(R) Friedel-Crafts reaction is an electrophilic substitution reaction.

9. (A) Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.
(R) Cyanide ion (CN^-) is a strong nucleophile.

10. (A) In strongly acidic solution, aniline becomes more reactive towards electrophilic reagents.
(R) The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. [IIT 2001]

11. (A) Rates of nitration of benzene and hexadeuterobenzene are different.
(R) C—H bond is stronger than C—D bond. [AIIMS 2005]

12. (A) The presence of nitro group facilitates nucleophilic substitution reactions in aryl halides.
(R) The intermediate carbanion is stabilized due to the presence of nitro group. [AIIMS 2006]

13. (A) Aryl halides undergo nucleophilic substitution reactions with ease.
(R) The C—H bond in aryl halides has partial double bond character.

14. (A) Benzyl bromide when kept in acetone-water, it produces benzyl alcohol.
(R) The reaction follows S_N2 mechanism. [AIIMS 2003]

15. (A) Styrene on reaction with HBr gives 2-bromo-2-phenylethane.
(R) Benzyl radical is more stable than alkyl radical. [AIIMS 2004]

16. (A) *p*-Hydroxy benzoic acid has a lower boiling point than *o*-hydroxy benzoic acid.
(R) *o*-Hydroxy benzoic acid has intramolecular hydrogen bonding. [IIT 2007]

17. (A) Friedel-Crafts reaction is used to introduce an alkyl or acyl group in benzene nucleus.
(R) Benzene is a solvent for the Friedel-Crafts alkylation of bromobenzene. [AIIMS 2008]

18. (A) Nitration of aniline can be conveniently done by protecting the amino group by acetylation.
(R) Acetylation increases the electron density in the benzene ring. [AIIMS 2010]

19. (A) Reimer-Tiemann reaction of phenol with CCl_4 in NaOH at 340 K gives salicylic acid as the major product.
(R) The reaction occurs through intermediate formation of dichlorocarbene. [AIIMS 2010]

20. (A) 4-Nitro chlorobenzene undergoes nucleophilic substitution more readily than chlorobenzene.
(R) Chlorobenzene undergoes nucleophilic substitution by elimination addition mechanism while 4-nitrochlorobenzene undergoes nucleophilic substitution by addition elimination mechanism. [AIIMS 2010]

ANSWERS

OBJECTIVE QUESTIONS

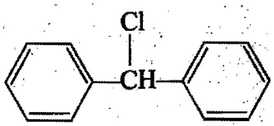
1. (d)	2. (a)	3. (d)	4. (b)	5. (a)	6. (c)	7. (c)	8. (b)	9. (b)	10. (a)
11. (c)	12. (d)	13. (b)	14. (a)	15. (a)	16. (a)	17. (a)	18. (c)	19. (b)	20. (a)
21. (c)	22. (c)	23. (c)	24. (b)	25. (d)	26. (b)	27. (d)	28. (b)	29. (c)	30. (a)
31. (d)	32. (d)	33. (b)	34. (a)	35. (d)	36. (d)	37. (a)	38. (d)	39. (b)	40. (c)
41. (a)	42. (d)	43. (c)	44. (b)	45. (c)	46. (b)	47. (c)	48. (d)	49. (d)	50. (b)
51. (a)	52. (d)	53. (a)	54. (d)	55. (c)	56. (d)	57. (e)	58. (b)	59. (c)	60. (a)
61. (b)	62. (c)	63. (a)	64. (c)	65. (a)	66. (b)	67. (b)	68. (c)	69. (d)	70. (d)
71. (a)	72. (b)	73. (c)	74. (b)	75. (c)	76. (b)	77. (c)	78. (a)	79. (d)	80. (a)
81. (d)	82. (b)	83. (c)	84. (a)	85. (c)	86. (a)	87. (d)	88. (c)	89. (c)	90. (b)
91. (a)	92. (b)	93. (d)	94. (c)	95. (b)	96. (a)	97. (b)	98. (b)	99. (c)	100. (a)
101. (d)	102. (c)	103. (c)	104. (b)	105. (d)	106. (b)	107. (d)	108. (d)	109. (b)	110. (c)
111. (c)	112. (c)	113. (b)	114. (a)	115. (d)	116. (b)	117. (b)	118. (d)	119. (c)	120. (b)
121. (a)	122. (a)	123. (c)	124. (a)	125. (d)	126. (b)	127. (c)	128. (c)	129. (a)	130. (d)
131. (b)	132. (d)	133. (c)	134. (a)	135. (a)	136. (d)	137. (b)	138. (c)	139. (a)	140. (c)
141. (b)	142. (a)	143. (d)	144. (c)	145. (a)	146. (b)	147. (a)	148. (d)	149. (c)	150. (d)
151. (b)	152. (a)	153. (d)	154. (b)	155. (d)	156. (c)	157. (b)	158. (a)	159. (b)	160. (c)
161. (d)	162. (b)	163. (a)	164. (d)	165. (c)	166. (b)	167. (c)	168. (a)	169. (c)	170. (c)
171. (b)	172. (a)	173. (d)	174. (c)	175. (b)	176. (c)	177. (a)	178. (b)	179. (d)	180. (b)
181. (a,d)	182. (d)	183. (c)	184. (a)	185. (d)	186. (d)	187. (d)	188. (a)	189. (b)	190. (b)
191. (c)	192. (a)	193. (a)	194. (d)	195. (c)	196. (b)	197. (d)	198. (b)	199. (a)	200. (c)
201. (c)	202. (b)	203. (b)	204. (a)	205. (b)	206. (b)	207. (a)	208. (c)	209. (a)	210. (b)
211. (d)	212. (c)	213. (a)	214. (b)	215. (c)	216. (a)	217. (b)	218. (d)	219. (b)	220. (a)
221. (d)	222. (b)	223. (a)	224. (b)	225. (d)	226. (a)	227. (c)	228. (b)	229. (b)	230. (c)
231. (c)	232. (b,d)	233. (a,d)	234. (b)	235. (c)	236. (c)	237. (b)	238. (d)	239. (a)	240. (c)
241. (a)	242. (b)	243. (b)	244. (b)	245. (d)	246. (b)	247. (b)	248. (a)	249. (a)	250. (d)
251. (a)	252. (d)	253. (a)	254. (b)	255. (c)	256. (c)	257. (b)	258. (a)	259. (b)	260. (d)
261. (b)	262. (c)	263. (b)	264. (d)	265. (c)	266. (a)	267. (c)	268. (b)	269. (c)	270. (d)
271. (b)	272. (d)	273. (b)	274. (a)	275. (b)	276. (b)	277. (d)	278. (b)	279. (c)	280. (b)
281. (c)	282. (a)	283. (a)	284. (b)	285. (b)	286. (b)	287. (d)	288. (d)	289. (d)	290. (c)
291. (e)	292. (d)	293. (a)	294. (a)	295. (d)	296. (d)	297. (a)	298. (b)	299. (c)	300. (d)
301. (d)	302. (c)	303. (c)	304. (c)	305. (d)	306. (c)	307. (b)	308. (a)	309. (d)	310. (b)
311. (b)	312. (c)	313. (b)	314. (d)	315. (a)	316. (d)	317. (b)	318. (c)	319. (a)	320. (d)
321. (b)	322. (c)	323. (b)	324. (a)	325. (a)	326. (e)	327. (d)	328. (a)	329. (e)	330. (c)
331. (b)	332. (d)	333. (b)	334. (a)	335. (d)	336. (b)	337. (d)	338. (b)	339. (b)	340. (c)
341. (a)	342. (b)	343. (c)	344. (d)	345. (d)	346. (b)	347. (c)	348. (a)	349. (d)	350. (c)
351. (b)	352. (b)	353. (a)	354. (c)	355. (a)	356. (d)	357. (c)	358. (c)	359. (b)	360. (b)
361. (a)	362. (c)	363. (c)	364. (d)	365. (a,d)	366. (a,c)	367. (b,c,d)	368. (b,c,d)	369. (a,c)	370. (a,b,c)
371. (b,c,d)	372. (a,b,d)	373. (b,c)	374. (a,c,d)	375. (b,d,f,h)	376. (a,c)				

ASSERTION-REASON TYPE QUESTIONS

1. (a)	2. (c)	3. (a)	4. (a)	5. (c)	6. (b)	7. (d)	8. (d)	9. (c)	10. (d)
11. (e)	12. (a)	13. (d)	14. (c)	15. (c)	16. (d)	17. (c)	18. (c)	19. (c)	20. (b)

BRAIN STORMING PROBLEMS

1. Which of the following structures corresponds to the product expected, when excess of C_6H_6 reacts with CH_2Cl_2 in presence of anhydrous $AlCl_3$?

(a) 

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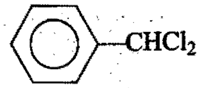
(b) 

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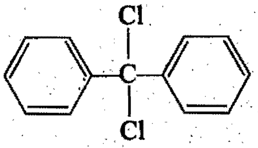
(c) 

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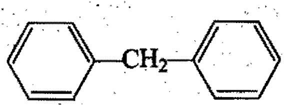
(d) 

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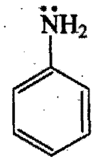
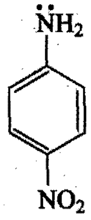
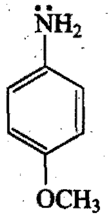
2. The correct order of decreasing basicity of the following compounds is:



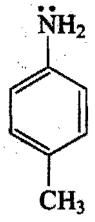
(I)



(II)



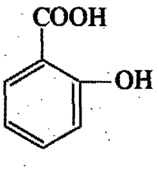
(III)



(IV)

(a) I > II > III > IV ☐ (b) II > I > III > IV ☐
(c) III > IV > I > II ☐ (d) II > I > IV > III ☐

3. Which of the following has lowest pK_a value?

(a) 

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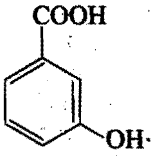
(b) 

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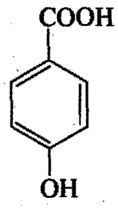
(c) 

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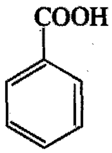
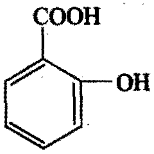
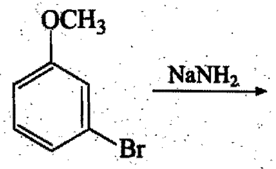
(d) 

☐

[Hint : Closer is the electron withdrawing group to the carboxylic group, greater is the acidic character of the compound.

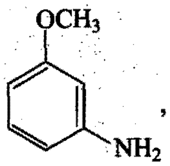
Thus, 

has lowest pK_a value.]

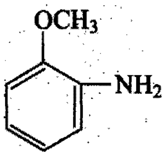
4. 

Product '*A*' by reaction '*R*'.

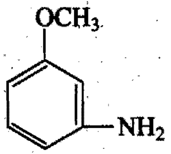
'*A*' and '*R*' are :

(a) 

, elimination addition ☐

(b) 

, elimination addition ☐

(c) 

, nucleophilic substitution ☐

(d) none of the above ☐

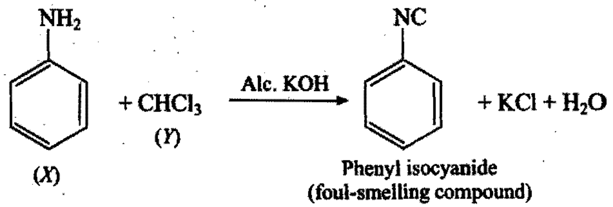
5. Which of the following does not undergo Friedel-Crafts reaction?
(a) Aniline ☐ (b) Phenol ☐
(c) Nitrobenzene ☐ (d) All of these ☐

6. Which of the following groups deactivates the benzene ring towards electrophilic substitution?
(a) —NH*R* ☐ (b) —OH ☐
(c) —COO*R* ☐ (d) —O*R* ☐

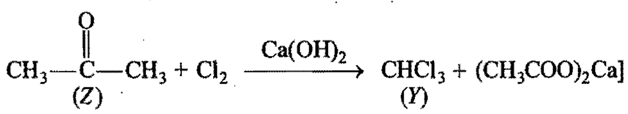
7. Benzene reacts with CCl_4 in presence of anhydrous $AlCl_3$ to give :
(a) tetraphenyl methane ☐
(b) chlorobenzene ☐
(c) tetrachlorobenzene ☐
(d) triphenyl methyl chloride ☐

8. An aromatic amine (X) was treated with alcoholic potash and another compound (Y) when a foul-smelling gas was formed with formula C_6H_5NC, (Y) was formed by reacting a compound (Z) with Cl_2 in presence of slaked lime. The compound (Z) is :
(a) $C_6H_5NH_2$ ☐ (b) CH_3OH ☐
(c) CH_3COCH_3 ☐ (d) $CHCl_3$ ☐

[Hint :



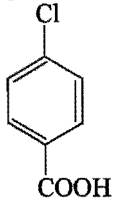
Phenyl isocyanide
(foul-smelling compound)

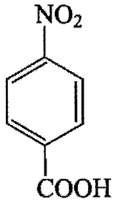


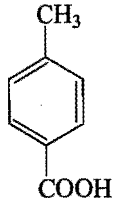
$$\underset{(Z)}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + Cl_2 \xrightarrow{Ca(OH)_2} \underset{(Y)}{CHCl_3} + (CH_3COO)_2Ca]$$

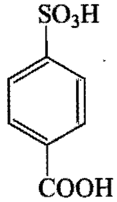
9. Which xylene is most readily nitrated?
(a) *Ortho* xylene ☐ (b) *Para* xylene ☐
(c) *Meta* xylene ☐ (d) All at the same rate ☐

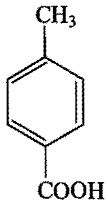
10. Which of the following compounds is a weaker acid as compared to benzoic acid?

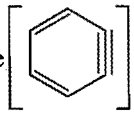
(a)  ☐

(b)  ☐

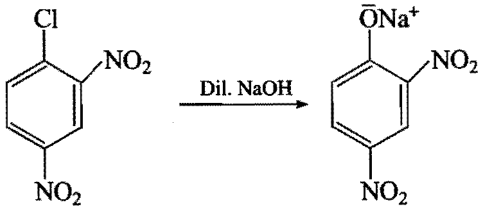
(c)  ☐

(d)  ☐

[**Hint :**  is weaker acid than benzoic acid because +*I* group (—CH_3) lowers the acidic character of carboxylic group.]

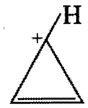
11. In benzyne  intermediate, the triple bond consists of :
(a) one *sp*-*sp* sigma bond and two *p*-*p* pi-bonds ☐
(b) one sp^2-sp^2 sigma bond and two *p*-*p* pi-bonds ☐
(c) two *sp*-*sp* sigma bonds and one *p*-*p* pi-bond ☐
(d) one sp^2-sp^2 sigma bond, one sp^2-sp^2 pi-bond and one *p*-*p* pi-bond ☐

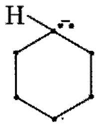
12.

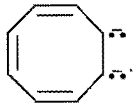


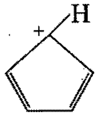
The above reaction proceeds through :
(a) electrophilic addition ☐
(b) benzyne intermediate ☐
(c) activated nucleophilic substitution ☐
(d) oxirane ☐

13. Which of the following is/are aromatic?

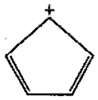
(a)  ☐

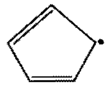
(b)  ☐

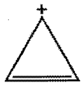
(c)  ☐

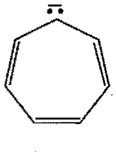
(d)  ☐

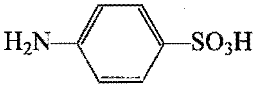
14. Which of the following species is aromatic?

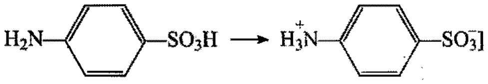
(a)  ☐

(b)  ☐

(c)  ☐

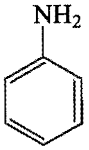
(d)  ☐

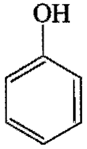
15. Sulphanilic acid  has high melting point. This is due to :
(a) the molecule exists as Zwitter ion ☐
(b) intramolecular hydrogen bonding takes place ☐
(c) the compound is purely ionic in character ☐
(d) none of the above ☐

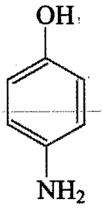
[**Hint :** ]

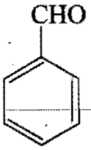
Zwitter ion

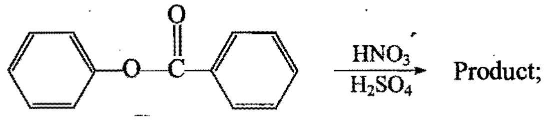
16. Oxidation of (*A*) gives *para* benzoquinone. (*A*) is :

(a)  ☐

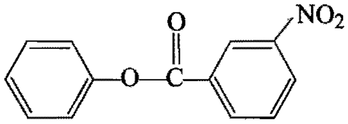
(b)  ☐

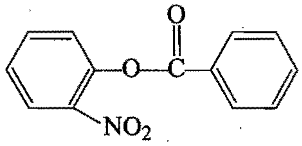
(c)  ☐

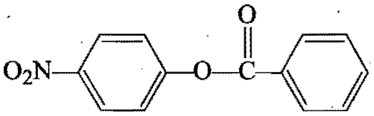
(d)  ☐

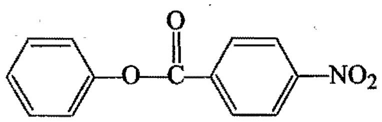
17.  Product;

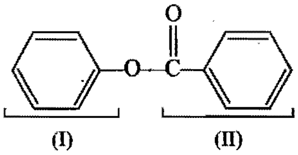
Product of this reaction will be :

(a)  ☐

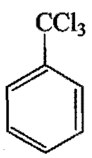
(b)  ☐

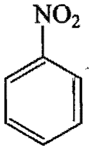
(c)  ☐

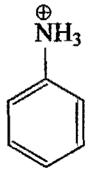
(d)  ☐

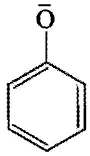
[Hint: 
(i) Activating and *ortho-para*-directing
(ii) Deactivating and *meta*-directing]

18. In which of the following cases, the nitration will take place at *meta*-position?


(I)

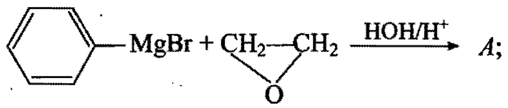

(II)


(III)

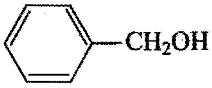

(IV)

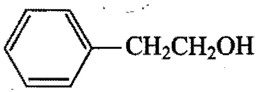
(a) II and IV ☐ (b) I, II and III ☐
(c) II and III ☐ (d) I only ☐

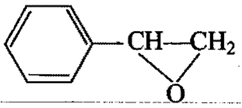
19. In the reaction



compound 'A' is :

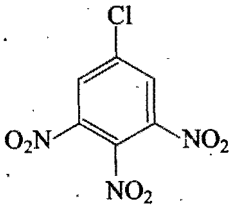
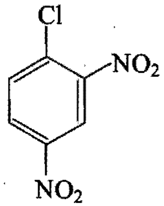
(a)  ☐

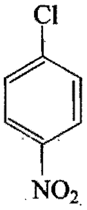
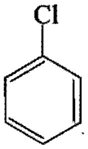
(b)  ☐

(c)  ☐

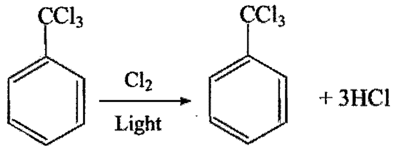
(d) no reaction ☐

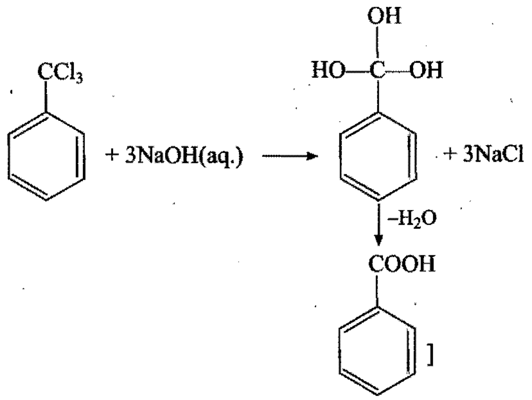
20. Which undergoes hydrolysis most easily?

(a)  ☐ (b)  ☐

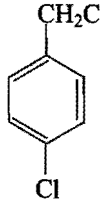
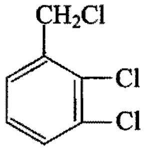
(c)  ☐ (d)  ☐

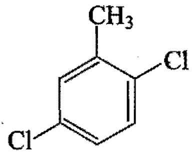
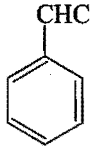
21. Chlorination of boiling toluene in presence of light followed by treatment with aqueous NaOH gives :
(a) *ortho* cresol ☐ (b) *para* cresol ☐
(c) 2,4-dihydroxy toluene ☐ (d) benzoic acid ☐

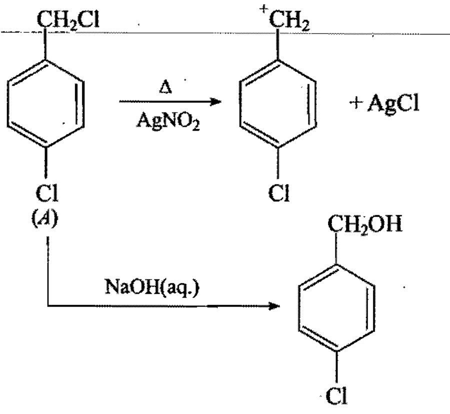
[Hint : 

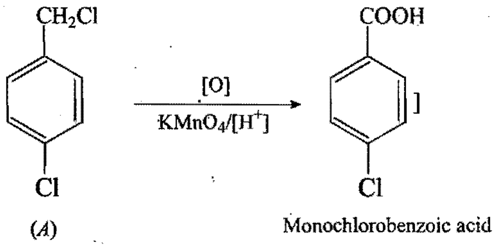


22. An aromatic compound $C_7H_6Cl_2$ (A), gives AgCl on boiling with alcoholic $AgNO_2$ solution and yields C_7H_7OCl on treatment with sodium hydroxide. (A) on oxidation gives monochlorobenzoic acid. The compound (A) is :

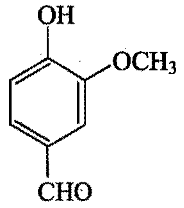
(a)  ☐ (b)  ☐

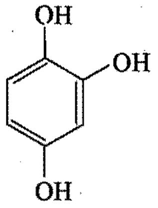
(c)  ☐ (d)  ☐

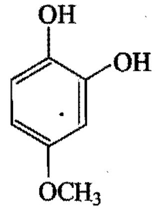
[Hint : 

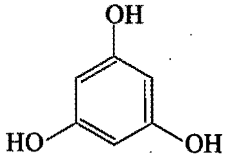


23. Oil of vanilla bean is :

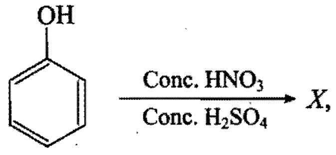
(a)  ☐

(b)  ☐

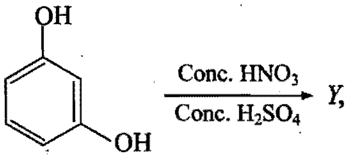
(c)  ☐

(d)  ☐

24. Consider the following reactions I and II,

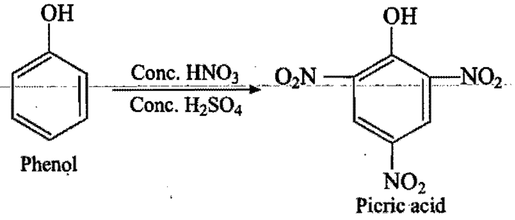
I 

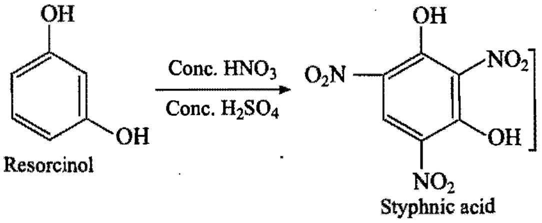
Phenol

II 

Products '*X*' and '*Y*' are respectively :

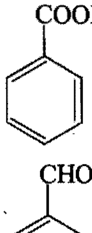
(a) picric acid, styphnic acid ☐
(b) styphnic acid, picric acid ☐
(c) picric acid, benzoic acid ☐
(d) picric acid, salicylic acid ☐

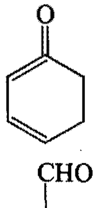
[**Hint:** 

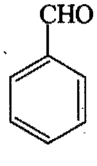


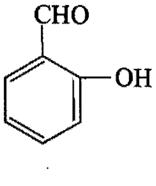
.]

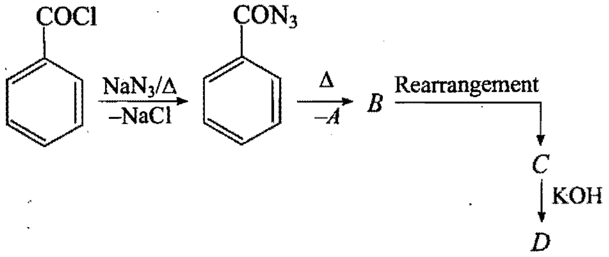
25. Oil of bitter almonds is :

(a)  ☐

(b)  ☐

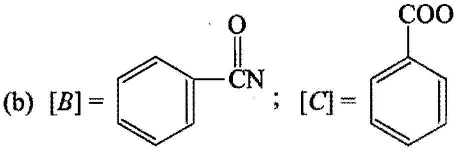
(c)  ☐

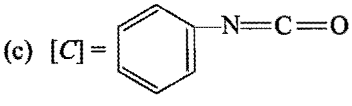
(d)  ☐

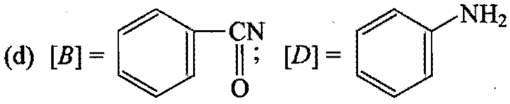
26. 

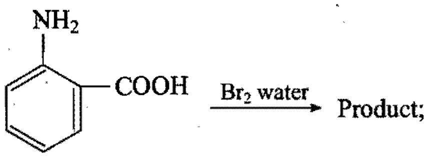
then :

(a) $[A] = N_2$ ☐

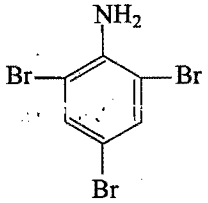
(b)  ☐

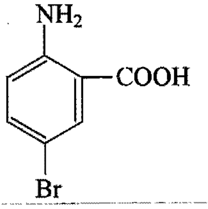
(c)  ☐

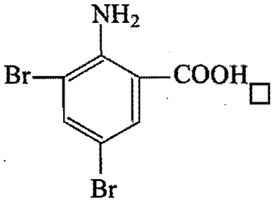
(d)  ☐

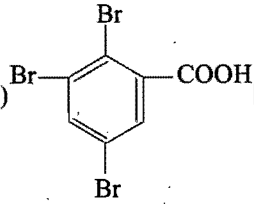
27. 

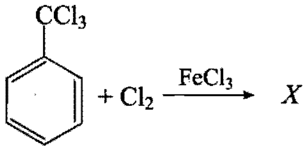
The product formed in above reaction is :

(a)  ☐

(b)  ☐

(c)  ☐

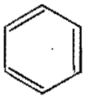
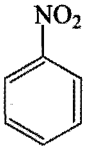
(d)  ☐

28. 

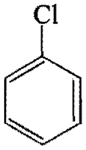
'*X*' is :

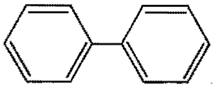
(a) *ortho* chlorobenzotrichloride ☐
(b) *para* chlorobenzotrichloride ☐
(c) *meta* chlorobenzotrichloride ☐
(d) none of the above ☐

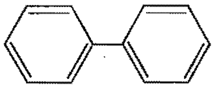
29. Which of the following is most reactive towards electrophilic substitution reaction?

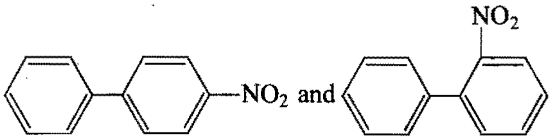
(a)  ☐ (b) 

☐

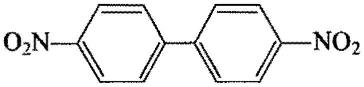
(c) 

☐ (d)  ☐

30. When  is treated with nitrating mixture ($HNO_3 + H_2SO_4$), we get :

(a) 

☐

(b) 

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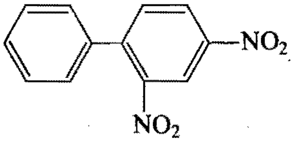
(c) 

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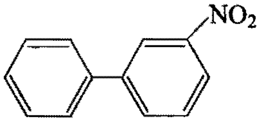
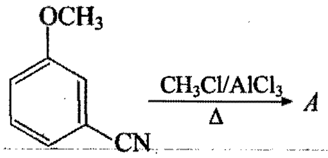
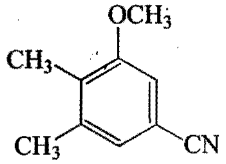
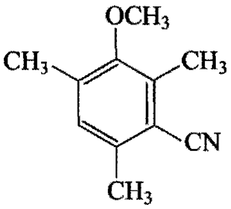
(d) 

☐

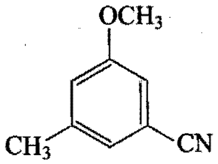
31. 

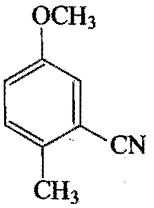
Here, the product '*A*' will be :

(a) 

☐ (b) 

☐

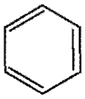
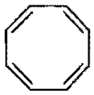
(c) 

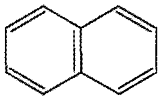
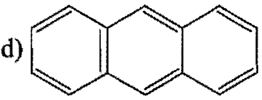
☐ (d) 

☐

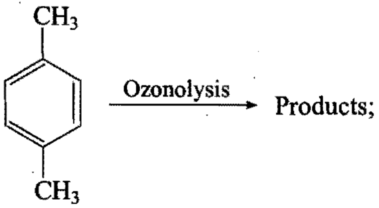
[**Hint :** —OCH$_3$ is *ortho, para*-directing and activating group while —CN is *meta*-directing and deactivating. Thus, electrophilic substitution will take place at *para*-position with respect to —OCH$_3$ group. *Ortho* product will not be preferred due to steric hindrance.]

32. Which of the following will have lowest heat of hydrogenation per mole of compound?

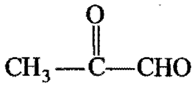
(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

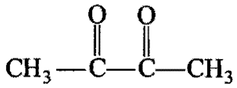
[**Hint :** Benzene has lowest heat of hydrogenation because it has least number of π-bonds.]

33. 

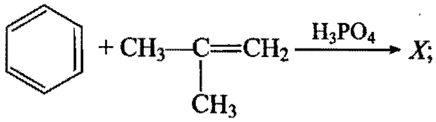
The products formed are :

(a) 
$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CHO}$ ☐

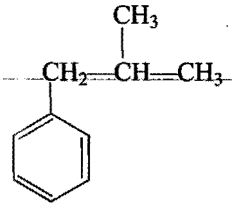
(b) CHO—CHO ☐

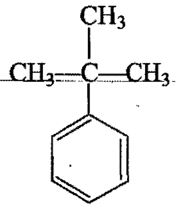
(c) 
$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3}$ ☐

(d) HCOOH ☐

34. 

The compound '*X*' is :

(a) 

☐ (b) 

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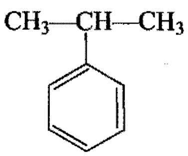
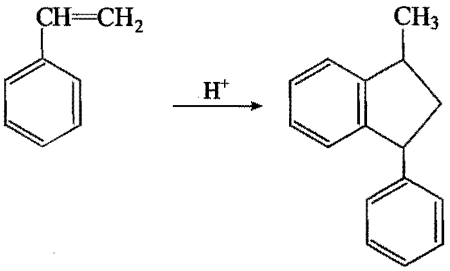
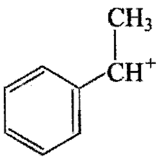
(c) 

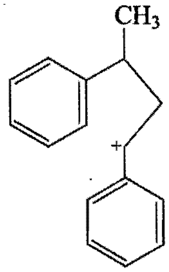
☐ (d) none of these ☐

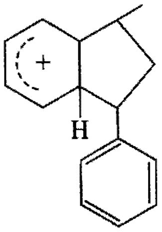
35. Styrene undergoes following reaction in acid medium :

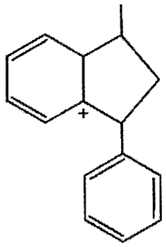


The various intermediates formed are :

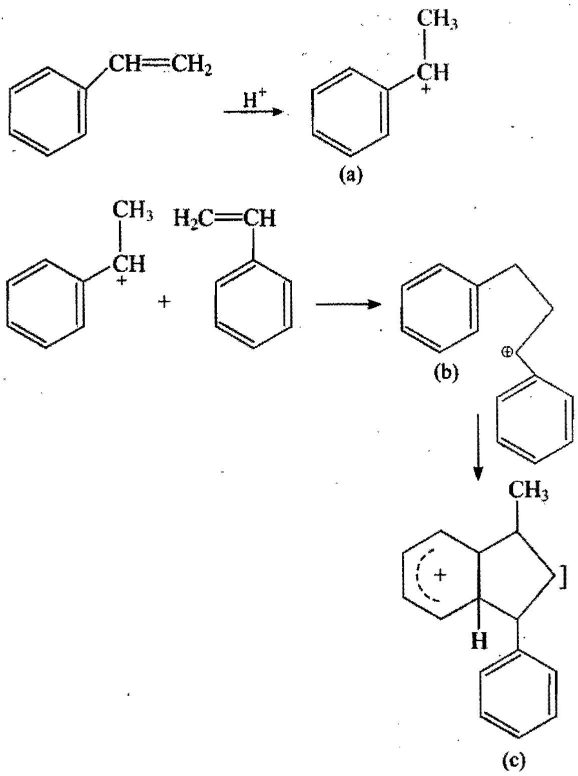
(a)  ☐

(b)  ☐

(c)  ☐

(d)  ☐

[Hint :



ANSWERS : BRAIN STORMING PROBLEMS

1. (d)	**2.** (c)	**3.** (a)	**4.** (c)	**5.** (c)	**6.** (c)	**7.** (a)	**8.** (c)	**9.** (c)	**10.** (c)
11. (d)	**12.** (b)	**13.** (a,c)	**14.** (c)	**15.** (a)	**16.** (a,b,c)	**17.** (c)	**18.** (b)	**19.** (b)	**20.** (a)
21. (d)	**22.** (a)	**23.** (a)	**24.** (a)	**25.** (c)	**26.** (a,c,d)	**27.** (a)	**28.** (c)	**29.** (a)	**30.** (a)
31. (d)	**32.** (a)	**33.** (a,b)	**34.** (b)	**35.** (a,b,c)					

LINKED COMPREHENSION TYPE QUESTIONS

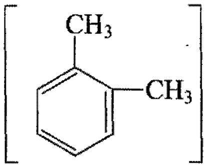
Passage 1

In the electrophilic substitution of benzene ring, the second substituent is directed by the group already present. Electron releasing groups (+*I* and +*M*) are *ortho-para*-directing and activating, whereas the electron withdrawing groups (–*I* and –*M*) are *meta*-directing and deactivating.

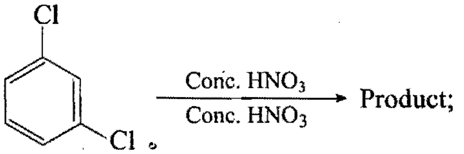
Halogens are placed under the category of +T (Tautomeric) groups because they have –Inductive and +Mesomeric effect. These groups are deactivating but *ortho-para*-directing.

In the introduction of third group to the benzene ring, the product of minimum steric hindrance is formed.

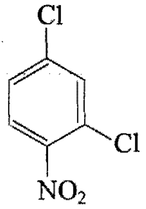
Answer the following questions :

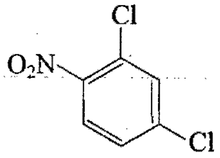
1. *Ortho*-xylene 

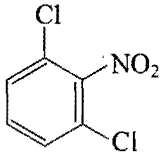
on mono nitration gives :
   (a) two products (b) three products
   (c) one product (d) four products
2. In the reaction,

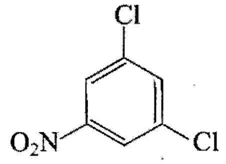


Which of the following products is not formed at all?

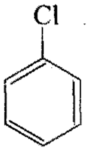
(a) 

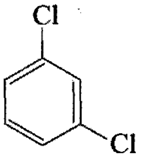
(b) 

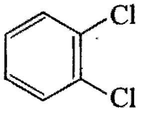
(c) 

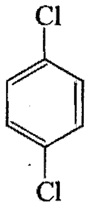
(d) 

3. Which of the following is not an *ortho, para*-directing group?
   (a) —F (b) —NC
   (c) —$OCOCH_3$ (d) —CCl_3
4. Which of the following substituted benzene derivatives would furnish three isomers when one more substituent is introduced?

(a) 

(b) 

(c) 

(d) 

5. A deactivating group in electrophilic substitution reaction :
   (a) deactivates only *ortho*- and *para*-positions
   (b) deactivates only *meta*-position
   (c) deactivates *meta*-position more than *ortho*- and *para*-positions
   (d) deactivates *ortho*- and *para*-positions more than *meta*-position

Passage 2

An aromatic compound (*A*), $C_9H_{12}O$ was subjected to a series of test in the laboratory. It was found that this compound :

(i) does not form silver mirror with Tollens' reagent.

(ii) rotates the plane of polarised light.

(iii) reacts with sodium metal to evolve hydrogen gas.

(iv) does not decolourise pink colour of bromine water.

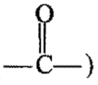
(v) reacts with hot $KMnO_4$ to form monocarboxylic acid '*B*' which on decarboxylation gives benzene.

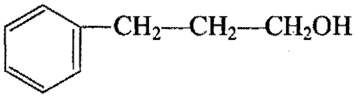
(vi) reacts with Lucas reagent in about 5 min.

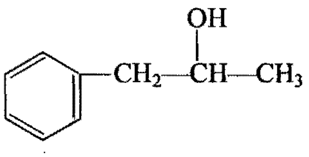
(vii) reacts with I_2 and NaOH to produce yellow coloured precipitate of the compound (*C*).

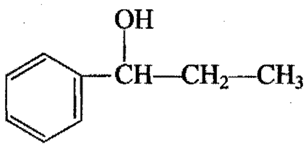
(viii) loses its optical activity due to formation of compound (*D*) on reaction with Red P and HI.

Answer the following questions:

1. The functional groups present in the compound (*A*) is:
   (a) aldehydic (—CHO) (b) ketonic ( $\overset{O}{\overset{\|}{—C—}}$)
   (c) alcoholic (—OH) (d) alkoxy group (—O*R*)
2. Structure of the compound (*A*) will be :

(a) 

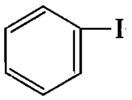
(b) 

(c) 

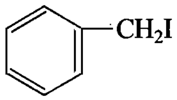
(d) none of the above

3. Molecular formula of the compound (C) will be :

(a) CH_3I

(b)


(c) CHI_3

(d)


4. Monocarboxylic acid (B) will be :

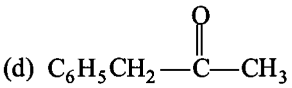
(a) $HCOOH$ (b) C_6H_5COOH

(c) $C_6H_5—CH_2—COOH$ (d) CH_3COOH

5. The compound (D) will be :

(a) $C_6H_5CH_2CH_2CH_3$ (b) $C_6H_5CH_2CH_2COOH$

(c) $C_6H_5CH_2CH_2CHO$

(d)

$C_6H_5CH_2—\overset{O}{\overset{\|}{C}}—CH_3$

Passage 3

A compound (A) called vanillin is isolated from vanilla seeds. Molecular formula of vanillin is $C_8H_8O_3$. Vanillin gives violet colour on treatment with neutral $FeCl_3$. It also gives silver mirror with Tollens' reagent. Each mole of vanillin gives one mole of AgI when subjected to Zeisel's active methoxy estimation.

$$\text{Vanillin} \xrightarrow{\text{Conc. HBr}} \text{compound } (B);$$

Compound (B) can also be obtained from catechol by Gattermann-Koch reaction.

Answer the following questions :

1. Which of the following functional groups is not present in vanillin?

(a) —COOH (b) —CHO

(c) —OH (d) $—OCH_3$

2. Vanillin contains :

(a) —Cl (b) $—CONH_2$

(c) —CHO (d) —COOH

3. Vanillin contains :

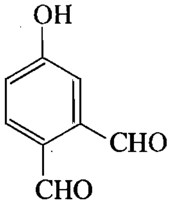
(a) a phenolic group

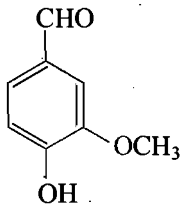
(b) an alcoholic group

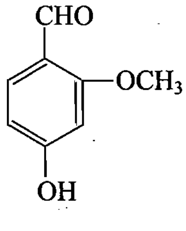
(c) both phenolic and alcoholic groups

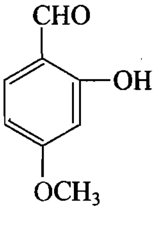
(d) two phenolic groups

4. Structure of vanillin should be :

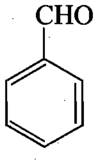
(a)


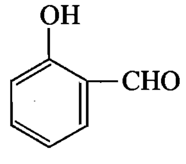
(b)


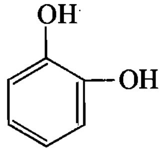
(c)


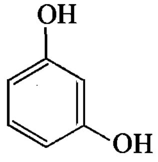
(d)


5. Compound (B) when heated with zinc dust will give :

(a)


(b)


(c)


(d)


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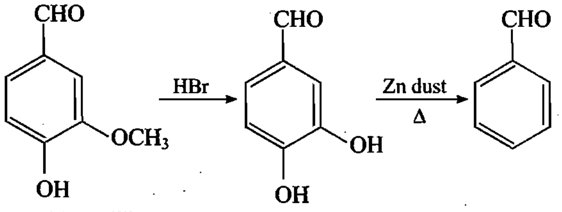
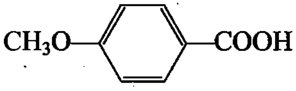


(A) Vanillin (B)]

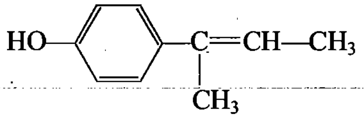
Passage 4

Two isomeric compounds 'A' and 'B' are isolated from vegetable origin, both have molecular formula $C_{10}H_{12}O$. Both these compounds are insoluble in water. These compounds decolourise Br_2/CCl_4 and pink colour of Baeyer's reagent.

On vigorous oxidation both isomers give same compound, *i.e., para* anisic acid,


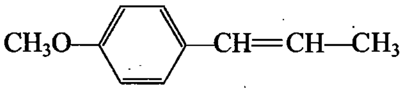
Indicate whether the following statements are true or false :

1. One of the two isomers may be :

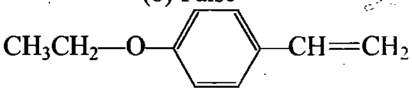


(a) True (b) False

2. If two isomers 'A' and 'B' on catalytic hydrogenation give same product then these isomers may be :

Cis or *trans*


(a) True (b) False

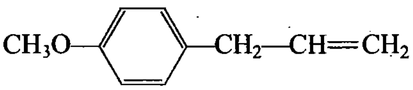
3. The compound


on oxidation gives *para* anisic acid.

(a) True (b) False

4. One of the two isomers can be synthesized as follows :

$$p\text{-bromoanisole} + \text{Mg} + \text{ether} \xrightarrow{\text{Allyl bromide}} 'A' \text{ or } 'B';$$



Then the isomer will be :

(a) True (b) False

5. Both '*A*' and '*B*' are geometrical isomers :

(a) True (b) False

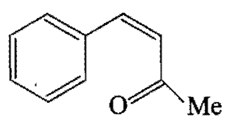
Passage 5

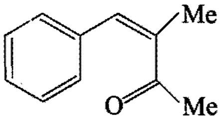
A carbonyl compound *P*, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin *Q*. Ozonolysis of *Q* leads to a dicarbonyl compound *R*, which undergoes intramolecular aldol reaction to give predominantly *S*.

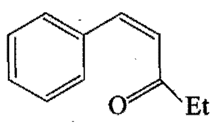
$$P \xrightarrow[\substack{2.\ H^+,\ H_2O\\ 3.\ H_2SO_4,\ \Delta}]{1.\ \text{MeMgBr}} Q \xrightarrow[2.\ \text{Zn},\ H_2O]{1.\ O_3} R \xrightarrow[2.\ \Delta]{1.\ OH^-} S$$

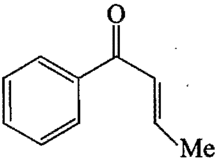
[IIT 2009]

1. The structure of the carbonyl compound *P* is:

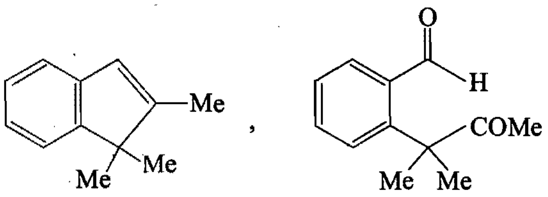
(a) 

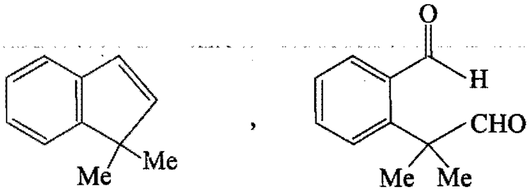
(b) 

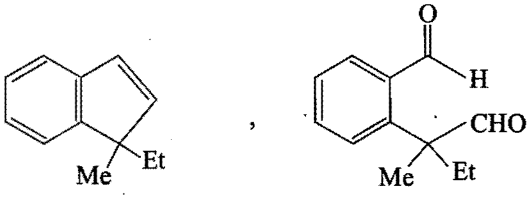
(c) 

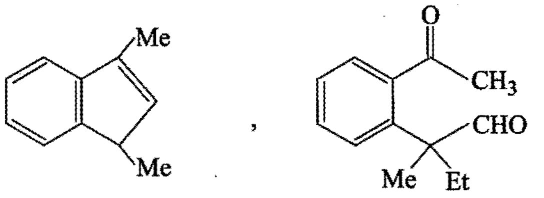
(d) 

2. The structures of the products *Q* and *R*, respectively, are:

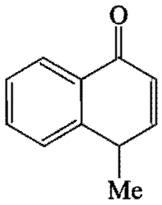
(a) 

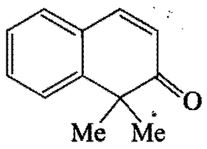
(b) 

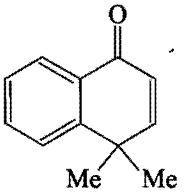
(c) 

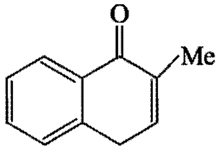
(d) 

3. The structure of the product *S* is:

(a) 

(b) 

(c) 

(d) 

Passage 6

p-Amino-*N*,*N*-dimethylaniline is added to a strongly acidic solution of *X*. The resulting solution is treated with a few drops of aqueous solution of *Y* to yield blue coloration due to the formation of methylene blue. Treatment of the aqueous solution of *Y* with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of *Y* with the solution of potassium hexacyanoferrate(III) leads to a brown coloration due to the formation of *Z*. **[IIT 2009]**

1. The compound *X* is:

(a) $NaNO_3$ (b) NaCl

(c) Na_2SO_4 (d) Na_2S

2. The compound *Y* is:

(a) $MgCl_2$ (b) $FeCl_2$

(c) $FeCl_3$ (d) $ZnCl_2$

3. The compound *Z* is:

(a) $Mg_2[Fe(CN)_6]$ (b) $Fe[Fe(CN)_6]$

(c) $Fe_4[Fe(CN)_6]_3$ (d) $K_2Zn_3[Fe(CN)_6]_2$

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	**1.** (a)	**2.** (d)	**3.** (d)	**4.** (a,b)	**5.** (d)
Passage 2	**1.** (c)	**2.** (b)	**3.** (c)	**4.** (b)	**5.** (a)
Passage 3	**1.** (a)	**2.** (c)	**3.** (a)	**4.** (b)	**5.** (a)
Passage 4	**1.** (b)	**2.** (a)	**3.** (b)	**4.** (a)	**5.** (a)
Passage 5	**1.** (b)	**2.** (a)	**3.** (b)		
Passage 6	**1.** (d)	**2.** (c)	**3.** (b)		

17

ORGANIC COMPOUNDS IN THE SERVICE OF MANKIND

Mankind owes much to chemistry. The main aim of chemistry has been to improve the quality of human life. Organic compounds are so closely related with our daily activities that in their absence our survival is not possible. Organic compounds are used in various fields of human effort such as agriculture, textiles, medicines and drugs, power and transportation, plastics, dyes, soaps, photography, etc. In this chapter, we shall study the chemistry of organic compounds used as polymers, dyes and medicines.

17.1 POLYMERS AND POLYMERIZATION

When ethylene is heated under pressure with oxygen, there is obtained a compound of high molecular mass (about 20,000) which is essentially an alkane with a very long chain. This compound is made up of many ethylene units and hence is called **polyethylene** (poly = many).

$$nH_2C{=}CH_2 \xrightarrow[\text{Pressure}]{O_2,\ \text{heat}} \ldots CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—\ldots$$

$$\text{or} \qquad \underset{\text{Polyethylene}}{(—CH_2—CH_2—)_n}$$

Polyethylene is a polymer and its formation is an example of the process termed polymerization.

Polymers are, thus, high molecular mass compounds whose structures are composed of a large number of simple repeating units. The repeating structural units are usually obtained from low molecular mass simple compounds called monomers (mono = one). The process of joining together of a large number of simple small molecules (monomers) to make high molecular mass ($10^3 - 10^7$ u) polymer through covalent bonds (polymers : poly + mers = many parts) is termed polymerization. Polymers are also called macromolecules (macro = large), which have very high molecular masses.

Smaller species formed by the process of polymerization of a monomer are referred to as **dimer, trimer, tetramer, pentamer .... polymer,** etc., depending on the number of monomer units.

Monomer		A
Dimer	Two monomer units	$A—A$
Trimer	Three monomer units	$A—A—A$
Tetramer	Four monomer units	$A—A—A—A$
Pentamer	Five monomer units	$A—A—A—A—A$
... ...	... ...	... ...
... ...	... ...	... ...
Polymer	Large no. of monomer units	$(A)_n$

HOMOPOLYMERS AND CO-POLYMERS

Polymers are divided into two categories depending upon the nature of the repeating structural units.

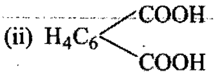
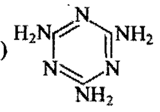
(i) Homopolymer and (ii) Co-polymer

A polymer which is obtained from only one type of monomer molecules is known as a **homopolymer.** On the other hand, a polymer made from more than one type of monomer molecules is referred to as a **co-polymer.** Few examples of common homopolymers and copolymers are given in the ahead tables:

Table 17.1—HOMOPOLYMERS

Common name of the homopolymer	Monomer	Uses
1. Polyethylene	$H_2C{=}CH_2$ Ethylene	In the manufacture of pipes, toys, bags, wire insulators, bottles, etc.
2. Polyvinyl chloride (PVC)	$H_2C{=}CHCl$ Vinyl chloride	In the manufacture of sheets, water pipes, hoses, hand bags, etc.
3. Polystyrene	$C_6H_5CH{=}CH_2$ Styrene	In the manufacture of combs, toys, radio and television cabinets, etc.
4. Polyacrylonitrile (PAN)	$H_2C{=}CH{-}CN$ Acrylonitrile	In the manufacture of orlon (fibre) and acrilon films.
5. Teflon (Polytetrafluoroethene)	$F_2C{=}CF_2$ Tetrafluoro ethylene	In the manufacture of insulators, gaskets, etc.
6. Buna rubber	$H_2C{=}CH{-}CH{=}CH_2$ Buta-1,3-diene	In the manufacture of tyres, hoses, etc.
7. Polyvinyl acetate	$H_2C{=}CHOOCCH_3$ Vinyl acetate	In the manufacture of latex paint.

Table 17.2—CO-POLYMERS

Common name of the co-polymer	Monomer	Uses
1. Synthetic rubber or styrene butadiene rubber (SBR) or (Buna-S)	(i) $C_6H_5CH{=}CH_2$ Styrene (ii) $H_2C{=}CH{-}CH{=}CH_2$ Buta-1,3-diene	In the manufacture of light duty tyres, belting, hoses and rubber soles.
2. Dacron or Terylene (Polyester)	(i) $HOCH_2{-}CH_2OH$ Ethylene glycol (ii) $H_3COOC(C_6H_4)COOCH_3$ Dimethyl terephthalate	In the manufacture of fabrics and magnetic recording tapes.
3. Glyptal (Polyester)	(i) $HOCH_2{-}CH_2OH$ Ethylene glycol (ii)  $H_4C_6(COOH)_2$ Phthalic acid	In the manufacture of paints and lacquers.
4. Nylon-6,6 (Polyamide)	(i) $H_2N(CH_2)_6NH_2$ Hexamethylene diamine (ii) $HOOC(CH_2)_4COOH$ Adipic acid	In the manufacture of fabrics, tyre cords, ropes, carpets, etc.
5. Bakelite (Formaldehyde resin)	(i) HCHO Formaldehyde (ii) C_6H_5OH Phenol	In the manufacture of electrical goods, phonograph records, fountain pen barrels, combs, etc.
6. Melamine-formaldehyde resin or Melamine (Formaldehyde resin)	(i) HCHO Formaldehyde (ii)  Melamine	In the manufacture of plastic crockery.
7. Polyurethane	(i) $HOCH_2{-}CH_2OH$ Ethylene glycol (ii) $O{=}C{=}N{-}CH{=}CH{-}N{=}C{=}O$ Ethylene di-isocyanate	In the manufacture of fibres, paints and heat insulators.

17.2 CLASSIFICATION OF POLYMERS

The polymers may be classified in a number of ways depending upon one criterion or the other as described below:

1. Classification based upon source or origin,
2. Classification based upon synthesis,
3. Classification based upon mechanism,
4. Classification based upon structure,
5. Classification based upon molecular forces.

1. Classification based upon source or origin : On the basis of their origin, polymers may be classified into three groups:

(i) Natural polymers
(ii) Semi-synthetic polymers and
(iii) Synthetic polymers.

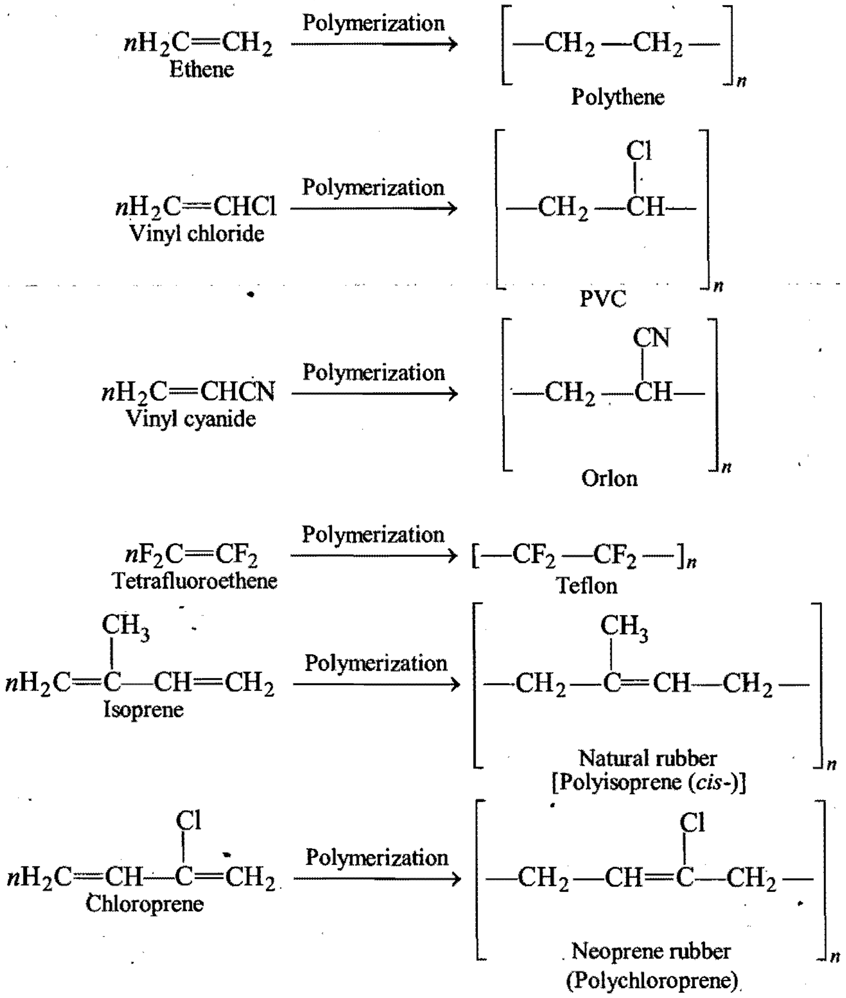
(i) Natural polymers : These are substances of natural origin, *i.e.*, these are found in nature mainly in plants and animals. The well known natural polymers are proteins (polymers of amino acids), polysaccharides (polymers of monosaccharides) and rubber (polymer of isoprene, *i.e.*, 2-methylbuta-1,3-diene). Silk, wool, starch, cellulose, enzymes, natural rubber, haemoglobin, etc., are the examples of natural polymers.

(ii) Semi-synthetic polymers : These are the substances which are obtained by using natural polymers, *i.e.*, some modifications are made in natural polymers by artificial means. Nitrocellulose, cellulose acetate, vulcanized rubber, gun cotton (cellulose trinitrate) and cellulose xanthate, etc., belong to this class of polymers.

(iii) Synthetic polymers : These are man-made polymers, *i.e.*, polymers synthesised in laboratory. A list of important synthetic polymers has been given in Tables 17.1 and 17.2.

2. Classification based upon synthesis : On the basis of mode of synthesis, polymers are classified into two categories.

(i) Addition polymers (or Chain growth polymers) : These are polymers formed by the addition together of the molecules of the monomer or monomers to form a macromolecule without elimination of anything. The process of the formation of addition polymers is termed **addition polymerization.** The addition polymers are formed by monomers which are unsaturated compounds, *e.g.*, ethene and derivatives of ethene. An addition polymer has the same empirical formula as the monomer. Ethene, vinyl chloride and vinyl cyanide are some of the compounds which undergo addition polymerization.



$$n\underset{\text{Ethene}}{H_2C{=}CH_2} \xrightarrow{\text{Polymerization}} \underset{\text{Polythene}}{\left[-CH_2-CH_2-\right]_n}$$

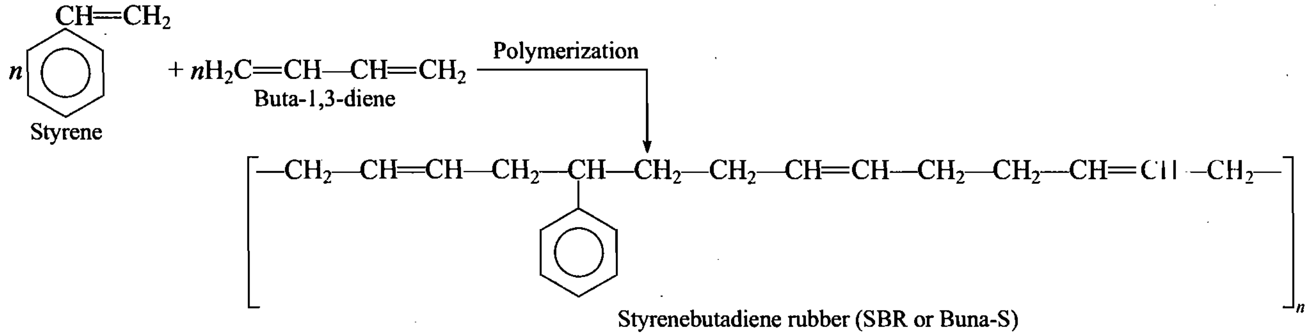
$$n\underset{\text{Vinyl chloride}}{H_2C{=}CHCl} \xrightarrow{\text{Polymerization}} \underset{\text{PVC}}{\left[-CH_2-\overset{Cl}{\overset{|}{C}}H-\right]_n}$$

$$n\underset{\text{Vinyl cyanide}}{H_2C{=}CHCN} \xrightarrow{\text{Polymerization}} \underset{\text{Orlon}}{\left[-CH_2-\overset{CN}{\overset{|}{C}}H-\right]_n}$$

$$n\underset{\text{Tetrafluoroethene}}{F_2C{=}CF_2} \xrightarrow{\text{Polymerization}} \underset{\text{Teflon}}{\left[-CF_2-CF_2-\right]_n}$$

$$n\underset{\text{Isoprene}}{H_2C{=}\overset{CH_3}{\overset{|}{C}}-CH{=}CH_2} \xrightarrow{\text{Polymerization}} \underset{\substack{\text{Natural rubber}\\ \text{[Polyisoprene (}cis\text{-)]}}}{\left[-CH_2-\overset{CH_3}{\overset{|}{C}}{=}CH-CH_2-\right]_n}$$

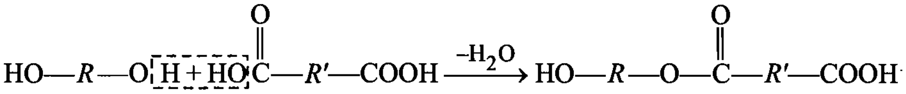
$$n\underset{\text{Chloroprene}}{H_2C{=}CH-\overset{Cl}{\overset{|}{C}}{=}CH_2} \xrightarrow{\text{Polymerization}} \underset{\substack{\text{Neoprene rubber}\\ \text{(Polychloroprene)}}}{\left[-CH_2-CH{=}\overset{Cl}{\overset{|}{C}}-CH_2-\right]_n}$$



Styrenebutadiene rubber (SBR or Buna-S)

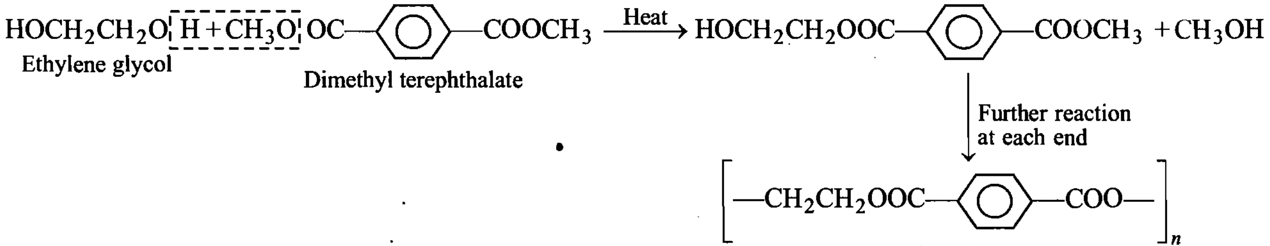
(ii) Condensation polymers (or Step-growth polymers) : Condensation polymers are formed by the combination of monomers with the elimination of simple molecules such as water, alcohol, NH_3, HCl, CO_2, etc. This process of formation of polymers is called **condensation polymerization.** Condensation polymers are generally formed by reaction between polyfunctional monomers. Proteins, starch, cellulose, etc., are the examples of natural condensation polymers. Amongst the synthetic polymers, two main types of condensation polymers are : polyesters and polyamides. These are also called **step-growth polymers** since, they are formed as a result of stepwise reaction.

Polyester—(Terylene or Dacron) : The long chain of condensation polymers consists of ester linkages formed by condensation of an hydroxy group and carboxylic group with elimination of water molecules.



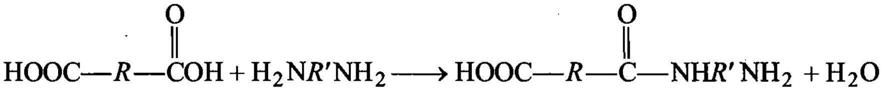
$$HO—R—O\boxed{H + HO}\overset{\overset{O}{\|}}{C}—R'—COOH \xrightarrow{-H_2O} HO—R—O—\overset{\overset{O}{\|}}{C}—R'—COOH$$

Terylene is the most important example of this group. It is made by heating ethylene glycol with dimethyl terephthalate.



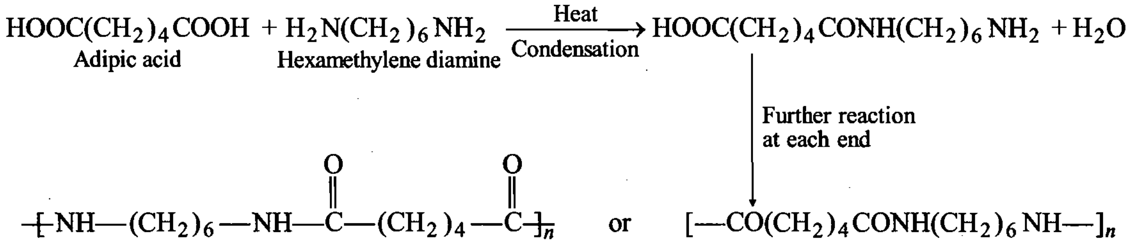
Terylene (Dacron)

Polyamide (Nylon-6,6)* : The long chain of condensation polymers consists of amide linkages formed by condensation of an amino group and carboxylic group with elimination of water molecules. Nylon-6,6 is the most important amide.



$$HOOC—R—\overset{\overset{O}{\|}}{C}OH + H_2NR'NH_2 \longrightarrow HOOC—R—\overset{\overset{O}{\|}}{C}—NHR'NH_2 + H_2O$$

Nylon-6,6 is formed by condensation of adipic acid and hexamethylene diamine.



$$\underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} + \underset{\text{Hexamethylene diamine}}{H_2N(CH_2)_6NH_2} \xrightarrow[\text{Condensation}]{\text{Heat}} HOOC(CH_2)_4CONH(CH_2)_6NH_2 + H_2O$$

$$\downarrow \text{Further reaction at each end}$$

$$\left[NH—(CH_2)_6—NH—\overset{\overset{O}{\|}}{C}—(CH_2)_4—\overset{\overset{O}{\|}}{C}\right]_n \quad \text{or} \quad [—CO(CH_2)_4CONH(CH_2)_6NH—]_n$$

Nylon-6,6

3. Classification based upon mechanism : Polymers and polymerization process may also be classified according to the mechanism of combination of monomer units.

(A) Chain growth addition polymerization : It involves a series of reactions each of which consumes a reactive particle and produces another similar one. The reactive particles may be free radicals or ions (cations or anions) to which monomers get added by a chain reaction. The polymers thus, formed are known as chain growth polymers. Chain growth addition polymerization

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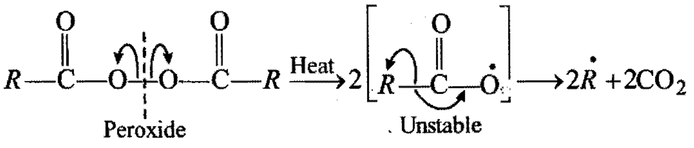
*Nylon-6,6 gets its name from its two constituents, adipic acid and hexamethylene diamine, both of which have six carbon atoms each.

is an important reaction of alkenes and conjugated dienes or indeed of all kinds of compounds that contain carbon-carbon double bonds. Polythene, polypropylene, polybutadiene, teflon (PTFE), polyvinyl chloride (PVC), polystyrene are some examples of chain growth polymers.

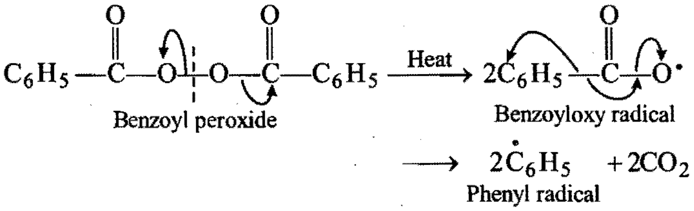
(a) Free radical mechanism : Free radical polymerization is initiated by organic peroxide or other reagents which decompose to give free radicals. Following steps are involved:

(i) Chain initiation : Organic peroxides undergo homolytic fission to form free radicals.



$$\underset{\text{Peroxide}}{R\text{—}\overset{O}{\overset{\|}{C}}\text{—}O\text{—}O\text{—}\overset{O}{\overset{\|}{C}}\text{—}R} \xrightarrow{\text{Heat}} 2\underset{\text{Unstable}}{\left[R\text{—}\overset{O}{\overset{\|}{C}}\text{—}\dot{O}\right]} \longrightarrow 2\dot{R} + 2CO_2$$

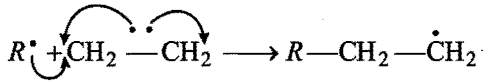
In case of benzoyl peroxide, the free radical formed is benzoyloxy radical and then phenyl free radical.



$$\underset{\text{Benzoyl peroxide}}{C_6H_5\text{—}\overset{O}{\overset{\|}{C}}\text{—}O\text{—}O\text{—}\overset{O}{\overset{\|}{C}}\text{—}C_6H_5} \xrightarrow{\text{Heat}} \underset{\text{Benzoyloxy radical}}{2C_6H_5\text{—}\overset{O}{\overset{\|}{C}}\text{—}\dot{O}}$$

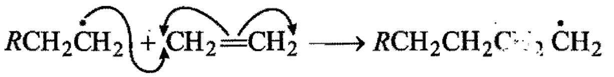
$$\longrightarrow \underset{\text{Phenyl radical}}{2\dot{C}_6H_5} + 2CO_2$$

(ii) Chain propagation : Free radical adds to an alkene (ethene) molecule to form a new free radical.



$$R\dot{} + CH_2\text{—}CH_2 \longrightarrow R\text{—}CH_2\text{—}\dot{C}H_2$$

The free radical formed attacks another alkene molecule and the process continues in building a long chain.



$$RCH_2\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow RCH_2CH_2CH_2\dot{C}H_2$$

(iii) Chain termination : The chain reaction comes to halt when two free radical chains combine.

$$2R(CH_2CH_2)_nCH_2\dot{C}H_2 \longrightarrow$$

$$R(CH_2CH_2)_nCH_2CH_2{:}CH_2CH_2(CH_2CH_2)_nR$$

Note : Benzoyl or *t*-butyl peroxide are common initiators, used.

Free radical polymerization can also be initiated by a mixture of ferrous sulphate and hydrogen peroxide ($FeSO_4 + H_2O_2$).

$$2C_6H_5(CH_2CH_2)_nCH_2\dot{C}H_2 \longrightarrow C_6H_5(CH_2CH_2)_n$$

$$\text{—}CH_2CH_2\text{—}CH_2CH_2\text{—}(CH_2CH_2)_nC_6H_5$$

or they can undergo disproportionation by accepting one hydrogen free radical or by one free radical from the other which is converted to an alkene.

(iv) Disproportionation :

$$2C_6H_5(CH_2CH_2)_nCH_2\dot{C}H_2 \longrightarrow$$

$$\underset{\text{Alkene}}{C_6H_5(CH_2CH_2)_nCH{=}CH_2} + \underset{\text{Alkane}}{C_6H_5(CH_2CH_2)_nCH_2CH_3}$$

(b) Cationic mechanism : Cationic addition polymerization is initiated by use of strong Lewis acids such as H_2SO_4, HF, $AlCl_3$, $SnCl_4$, $TiCl_4$ or BF_3 in H_2O. The following steps are involved:

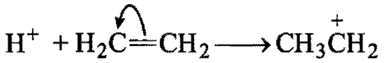
(i) Chain initiation : The acid furnishes proton.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

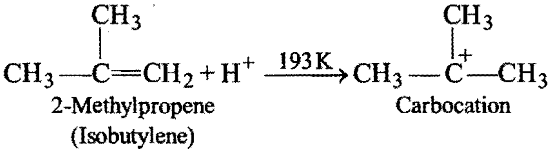
$$HF \rightleftharpoons H^+ + F^-$$

$$BF_3 + H_2O \rightleftharpoons H^+ + BF_3(OH)^-$$

The proton adds to the carbon of the double bond of the alkene to form a carbocation.

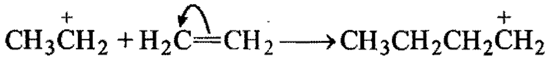


$$H^+ + H_2C{=}CH_2 \longrightarrow CH_3\overset{+}{C}H_2$$



$$\underset{\substack{\text{2-Methylpropene}\\ \text{(Isobutylene)}}}{CH_3\text{—}\overset{CH_3}{\overset{|}{C}}{=}CH_2} + H^+ \xrightarrow{193\,K} \underset{\text{Carbocation}}{CH_3\text{—}\overset{CH_3}{\overset{|}{\overset{+}{C}}}\text{—}CH_3}$$

(ii) Chain propagation : The carbocation combines with another molecule of alkene to form a new carbocation and the process continues to form a long chain.

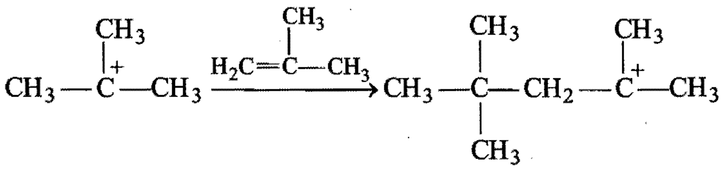


$$CH_3\overset{+}{C}H_2 + H_2C{=}CH_2 \longrightarrow CH_3CH_2CH_2\overset{+}{C}H_2$$

$$CH_3CH_2CH_2\overset{+}{C}H_2 + nH_2C{=}CH_2 \longrightarrow$$

$$CH_3CH_2(CH_2CH_2)_nCH_2\overset{+}{C}H_2$$

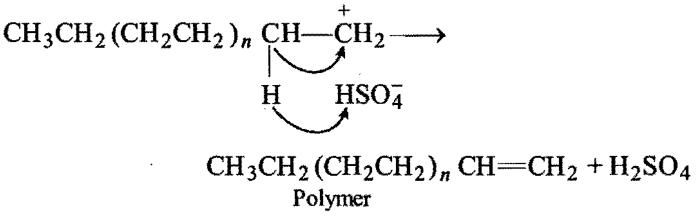
Similarly,



$$CH_3\text{—}\overset{CH_3}{\overset{|}{\overset{+}{C}}}\text{—}CH_3 \xrightarrow{H_2C=\overset{CH_3}{\overset{|}{C}}\text{—}CH_3} CH_3\text{—}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{—}CH_2\text{—}\overset{CH_3}{\overset{|}{\overset{+}{C}}}\text{—}CH_3$$

$$\longrightarrow (CH_3)_3C\text{—}[CH_2\text{—}C(CH_3)_2]_n\text{—}CH_2\text{—}C^+(CH_3)_2\text{—}$$

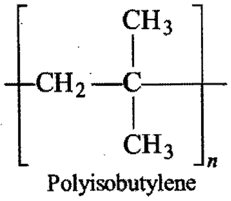
(iii) Chain termination : The chain may be terminated by combination with a negative ion or loss of a proton.



$$CH_3CH_2(CH_2CH_2)_n\underset{H}{\underset{|}{C}H}\text{—}\overset{+}{C}H_2 \longrightarrow \quad HSO_4^-$$

$$\underset{\text{Polymer}}{CH_3CH_2(CH_2CH_2)_nCH{=}CH_2} + H_2SO_4$$

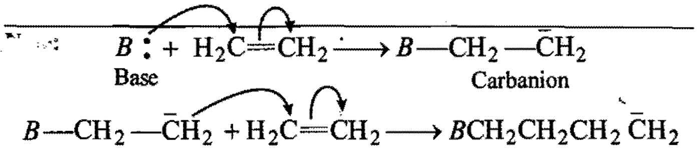
$$(CH_3)_3C\text{—}[CH_2\text{—}C(CH_3)_2]_n\text{—}CH_2\text{—}C^+(CH_3)_2 \longrightarrow$$



$$\underset{\text{Polyisobutylene}}{\left[\text{—}CH_2\text{—}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{—}\right]_n}$$

The special feature of cationic addition polymerization is that they proceed at high speeds (few seconds only) even at very low temperature. Polyisobutylene is used for the manufacture of truck tyre inner tubes. Some common examples of alkenes (monomers) undergoing cationic polymerization are ethylene, propylene, isobutylene, styrene, vinyl ethers and butadiene, etc.

(c) Anionic mechanism : The **anionic addition polymerization** is initiated by strong bases such as $\overset{+}{K}NH_2^-$, $\overset{+}{Na}NH_2^-$, C_4H_9Li and Grignard reagent, etc. In the chain initiation step, carbanion is formed which then reacts with alkenes molecule to form another carbanion and the process continues.



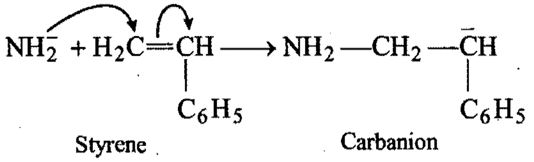
$$\underset{\text{Base}}{B\,\colon} + H_2C{=}CH_2 \longrightarrow \underset{\text{Carbanion}}{B{-}CH_2{-}\bar{C}H_2}$$

$$B{-}CH_2{-}\bar{C}H_2 + H_2C{=}CH_2 \longrightarrow BCH_2CH_2CH_2\bar{C}H_2$$

The nucleophilic attack on an alkene is not an easy reaction because alkenes themselves are electron rich. Thus, the initiator to be used must be a very strong nucleophile. In these polymerizations, the chain carriers are negatively charged carbanions and involve the following steps:

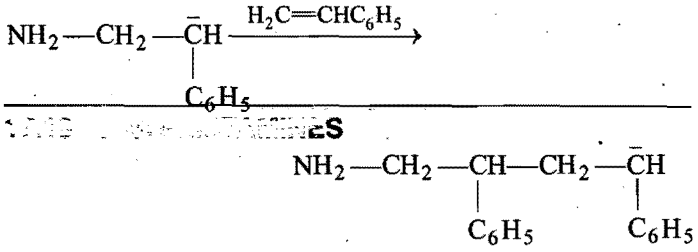
(i) Chain initiation : The base furnishes an anion.

$$K^+NH_2^- \longrightarrow K^+ + NH_2^-$$



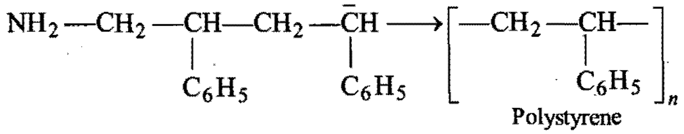
$$NH_2^- + \underset{\text{Styrene}}{H_2C{=}\underset{C_6H_5}{\underset{|}{C}H}} \longrightarrow \underset{\text{Carbanion}}{NH_2{-}CH_2{-}\underset{C_6H_5}{\underset{|}{\bar{C}H}}}$$

(ii) Chain propagation :



$$NH_2{-}CH_2{-}\underset{C_6H_5}{\underset{|}{\bar{C}H}} \xrightarrow{H_2C{=}CHC_6H_5} NH_2{-}CH_2{-}\underset{C_6H_5}{\underset{|}{CH}}{-}CH_2{-}\underset{C_6H_5}{\underset{|}{\bar{C}H}}$$

(iii) Chain termination :



$$NH_2{-}CH_2{-}\underset{C_6H_5}{\underset{|}{CH}}{-}CH_2{-}\underset{C_6H_5}{\underset{|}{\bar{C}H}} \longrightarrow \underset{\text{Polystyrene}}{\left[{-}CH_2{-}\underset{C_6H_5}{\underset{|}{CH}}{-}\right]_n}$$

Anionic addition polymerization is more favourable with the monomers which have electron withdrawing substituents (*e.g.*, —CN and —COO*R*) because these groups decrease the electron density and stabilize the intermediate anion to facilitate attack by a nucleophile. Some common examples of monomers undergoing anionic polymerization are acrylonitrile, styrene, methyl α-cyano acrylate, vinyl chloride and methyl methylacrylate, etc.

(B) Step growth polymerization : It involves a series of reactions each of which is essentially independent of the preceding one. Formation of polymer is possible simply because monomer happens to undergo reaction at more than one functional group. This type of polymerization proceeds by stepwise intermolecular condensation with the loss of simple molecules like H_2O, NH_3, HCl, etc., and does not depend upon chain carrying free radicals or ions. The polymers thus, formed are called **step growth polymers.** Formation of nylon, terylene, bakelite, etc., are the examples of step growth polymerization.

Let us illustrate the process of step growth polymerization in the simplest way involving two monomer units *A* and *B*.

$$\underset{\text{Monomer}}{A + B} \xrightarrow[\text{Step I}]{\text{Condense}} \underset{\text{Dimer}}{A{-}B}$$

$$A{-}B + A \xrightarrow[\text{Step II}]{\text{Condense}} A{-}B{-}A$$

$$\vdots$$

$$A{-}B{-}A + B \xrightarrow[\text{Step III}]{\text{Condense}} \underset{\text{Tetramer}}{A{-}B{-}A{-}B}{-}{-}{-}{-}\underset{\text{Polymer}}{(A{-}B)_n}$$

So, it should be noted that an **addition polymerization occurs through chain-growth mechanism** whereas **condensation polymerization is through step-growth mechanism (Distinction).**

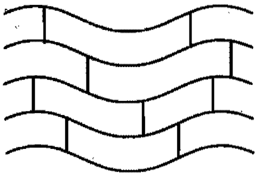
4. Classification based on structure : On the basis of structure, polymers are of three types:

(i) Linear polymers : These are the polymers in which the monomers are joined together to form long straight chains. The various polymeric chains are then stacked over one another to give a well packed structure **[Fig. 17.1 (a)].** As a result of close packing, such polymers have high melting points, high densities **(HDP)** and high tensile strength. The examples of such type of polymers are polythene, **PVC,** polyesters and nylons, etc. These may be termed as **one dimensional polymers.**

(ii) Branched chain polymers : In these polymers, the monomeric units are joined to produce long chains (called the main chain) along with side-chains of different lengths which produce branches **[Fig. 17.1 (b)].** Branched chain polymers are irregularly packed and as a result they have lower melting points, low density **(LDP)** and lower tensile strength as compared to linear polymers. Some common examples of branched chain polymers are amylopectin and glycogen, etc. Their molecules are **two dimensional.**

(iii) Cross-linked polymers : In these polymers, the initially formed linear polymer chains are joined together to form a **three dimensional** network structure **[Fig. 17.1 (c)].** The links involved are called cross-links and these polymers are called **cross-linked polymers.** These polymers are hard, rigid and brittle because of their network structure. Solids are termed as three dimensional polymers. Examples are: bakelite, urea-formaldehyde polymer, melamine formaldehyde **(melmac)** resins, etc.

(a) Linear chain (b) Branched chain



(c) Cross-linked

Fig. 17.1

5. Classification based upon molecular forces : The utility of polymers in various fields is due to their mechanical properties like tensile strength, elasticity, toughness, etc. These properties mainly depend upon the intermolecular forces like van der Waals' forces and hydrogen bonding operating in polymer molecules. Polymers have been classified into four types on the basis of the magnitude of intermolecular forces present in them.

(i) Elastomers : These are the polymers having **very weak intermolecular forces** of attraction between the polymer chains. The weak forces permit the polymer to be stretched out about 10 times their normal length. Few chemical bonds are introduced between the randomly coiled molecular chains which act as cross-links. These cross-links help the polymer to come to its original position after the force is released. Elastomers thus, possess elastic character. Vulcanized rubber is a very important example of an elastomer and other examples are natural rubber, Buna-S or SBR (a copolymer of butadiene 75% and styrene 25%).

Highly vulcanized rubber containing 20–30% sulphur is called **ebonite.**

(ii) Fibres : These are the polymers which have quite **strong intermolecular forces** such as hydrogen bonding. These polymers can be used for making fibre as their molecules are long and thread like. Nylon-6,6 polyester (terylene or dacron) and polyacrylo nitrile (orlon), etc., are some important examples of this type.

(iii) Thermoplastics : These are the polymers in which intermolecular forces of attraction are neither very strong nor very weak and there are no cross-links between the chains. These can be easily moulded by heating, *i.e.*, a thermoplastic polymer is one which softens on heating and becomes hard on cooling. Polyethylene, polypropylene, polystyrene, PVC and teflon are the examples of thermoplastics.

[**Plasticisers :** Substances, which are sometimes added to plastics to impart viscosity, flexibility, softness or other properties to finished products, are called plasticisers.]

(iv) Thermosetting polymers : These are polymers in which extensive cross-links are formed between polymer chains on heating. A thermosetting polymer becomes hard on heating. Such polymers are prepared in two steps. The first step is the formation of long chain molecules which are capable of further reaction with each other. The second step is the application of heat which causes a reaction to occur between the chains, thus, producing a complex cross-linked polymer. Bakelite is an example of thermosetting polymers.

Difference between Thermoplastic and Thermosetting Polymers

Thermoplastic polymers	Thermosetting polymers
1. These soften and melt on heating.	These do not soften on heating but rather become hard. In case prolonged heating is done, these start burning.
2. These can be remoulded, recast and reshaped.	These cannot be remoulded or reshaped.
3. These are less brittle and soluble in some organic solvents.	These are more brittle and insoluble in organic solvents.
4. These are formed by addition polymerization.	These are formed by condensation polymerization.
5. These have usually linear structures.	These have three dimensional cross-linked structures.
6. **Examples :** Polyethylene, PVC, Teflon, Nylon, etc.	**Examples :** Bakelite, Urea-formaldehyde, Resin, Terylene, etc.

CO-POLYMERIZATION

When two or more different monomers unite together to polymerize, the resulting product is called a **co-polymer** and the process is termed **co-polymerization.**

The properties of a copolymer are entirely different from a physical mixture of the two individual polymers. Copolymers have better physical and mechanical properties. For example, Buna-S or SBR (Styrenebutadiene rubber) is a co-polymer of styrene and buta-1,3-diene. Polystyrene is easily breakable but polybutadiene is flexible. The co-polymer, SBR is more flexible than polybutadiene and tougher than polystyrene. The properties could be changed by varying the amounts of each monomer.

Types of co-polymer : Depending upon the distribution of monomer units, the following four types of co-polymers are possible:

(i) Alternating co-polymer : The two monomer units (A and B) are linked in an alternate manner throughout the polymer chain.

$$A—B—A—B—A—B—A—B—A—B\ldots$$

(ii) Random co-polymer : The distribution of monomer units is random throughout the chain.

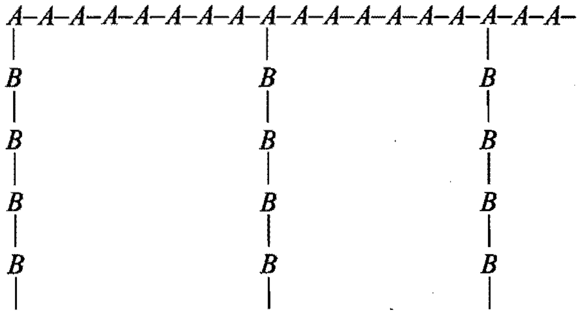
A—B—B—B—A—A—B—A—A—B—B—A—B
—B—A—A—A—A—B—B—B...

(iii) Block co-polymer : In this kind, there are blocks of each kind of monomer units; *i.e.*, it consists of blocks of one type of monomer units alternate with blocks of another type.

—B—B...A—A—A—A—A—A—B—B—B—B—B
—B—A—A—

Block co-polymers can be prepared by initiating the radical polymerization of one monomer to give homopolymer chains, followed by addition of an excess of the second monomer.

(iv) Graft co-polymer : It consists of a linear polymer chain of one type to which has been grafted side-chains (branches) of another type of monomer units.



The formation of graft co-polymer can be brought about by either of the two general methods:

(a) Initiation of chain growth of monomer (*B*) on an existing polymer molecule formed from monomer (*A*) or

(b) Termination of chain growth of polymer (*B*) by an existing polymer molecule formed from monomer (*A*).

17.3 SOME IMPORTANT POLYMERS

The various commercially important addition and condensation polymers are as follows:

[A] Addition Polymers

1. Polyethylene or Polythene $(\text{—CH}_2\text{—CH}_2\text{—})_n$: This polymer is an addition polymer and is obtained by polymerizing ethylene. Now-a-days, two types of polythenes are manufactured which have widely different properties.

(i) Low density polythene (LDPE) : It is prepared by heating very pure ethylene at 190–210°C under a pressure of about 1500 atmospheres in the presence of traces of oxygen (0.03–0.1%). The polymer produced consists of highly branched chain molecules. The branching does not allow the polymer molecules to undergo close packing and thus, the density of the polymer is low and it has low melting point (384 K).

$$\underset{\text{Ethene}}{n\text{H}_2\text{C}{=}\text{CH}_2} \xrightarrow[\text{(Oxygen)}]{200^\circ\text{C, 1500 atm.}} \underset{\text{Polythene}}{\text{—(H}_2\text{C—CH}_2\text{)—}_n}$$

It is chemically inert, tough but flexible. It is a poor electrical conductor. It is used for packaging, cable insulation and in the manufacture of pipes, squeeze bottles and toys.

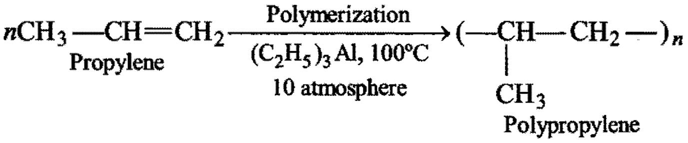
(ii) High density polythene (HDPE) : It is manufactured by the coordination polymerization of ethylene in a hydrocarbon solvent at 60–70°C under a pressure 6–7 atmosphere in the presence of a catalyst such as triethyl aluminium and titanium tetrachloride (Zeigler-Natta catalyst).

$$\underset{\text{Ethene}}{n\text{H}_2\text{C}{=}\text{CH}_2} \xrightarrow[\text{[TiCl}_4 + \text{Al(C}_2\text{H}_5)_3\text{]}]{60\text{-}70^\circ\text{C, 6 atm.}} \underset{\text{Polythene}}{\text{—(H}_2\text{C—CH}_2\text{)—}_n}$$

The polymer thus, produced, consists of practically linear molecules which get packed closely and thus, density is high.

It is chemically inert but more tougher and harder. Its tensile strength is more also than low density polythene. It is used in making housewares such as buckets, containers, dustbins, bottles, pipes, toys, etc.

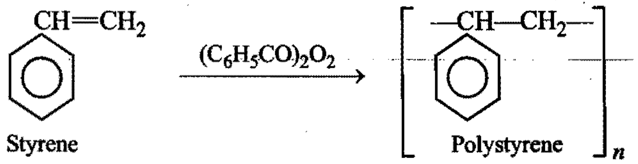
2. Polypropylene : It is prepared by passing propylene through *n*-hexane containing triethyl aluminium at 100°C under 10 atmospheric pressure.



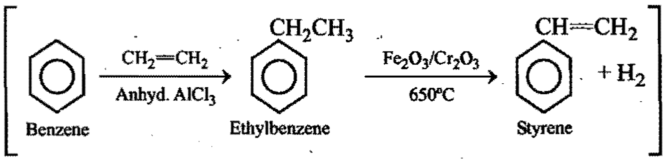
$$\underset{\text{Propylene}}{n\text{CH}_3\text{—CH}{=}\text{CH}_2} \xrightarrow[\substack{(\text{C}_2\text{H}_5)_3\text{Al, }100^\circ\text{C}\\ \text{10 atmosphere}}]{\text{Polymerization}} \underset{\text{Polypropylene}}{(\text{—}\underset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{—CH}_2\text{—})_n}$$

It is used in the manufacture of housewares, medical equipment, electronic components, toys, pipes, fibres, etc. It is also used as an electrical insulator and coating on electrical wires.

3. Polystyrene (Styron) : It is manufactured by polymerization of styrene in presence of benzoyl peroxide.



Note : Styrene is obtained from benzene as follows:



Polystyrene is used in the manufacture of food containers, cosmetic bottles, television and radio cabinets, plastic cups, packaging and toys.

4. Teflon—Polytetrafluoroethylene (PTFE) : It is manufactured by heating tetrafluoroethylene under pressure in the presence of ammonium peroxydisulphate.

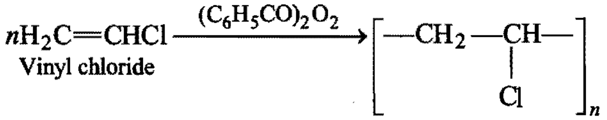
$$n\text{F}_2\text{C}{=}\text{CF}_2 \xrightarrow[\text{High pressure}]{(\text{NH}_4)_2\text{S}_2\text{O}_8} \underset{\text{Teflon PTFE}}{[\text{—CF}_2\text{—CF}_2\text{—}]_n}$$

It is chemically inert and heat resistant polymer. It is very tough and electrical resistant. It is used in making seals and gaskets which have to withstand high temperature. It is also used for insulation of electrical items and for making non-stick surface coating and lubricant particularly for cooking utensils.

Similarly, polymonochlorotrifluoroethylene (PCTFE) can also be used at the place of teflon.

$$\underset{\text{Chlorotrifluoroethylene}}{n\text{ClFC}{=}\text{CF}_2} \longrightarrow \underset{\text{PCTFE}}{(\text{—ClFC—CF}_2\text{—})_n}$$

5. Polyvinyl chloride (PVC) : It is obtained by heating vinyl chloride in an inert solvent in the presence of benzoyl peroxide.



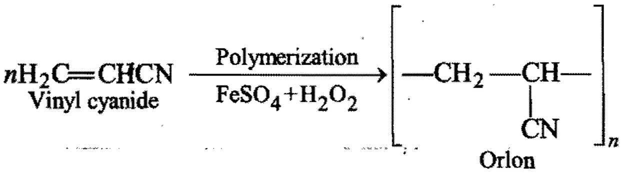
$$\underset{\text{Vinyl chloride}}{n\text{H}_2\text{C}{=}\text{CHCl}} \xrightarrow{(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2} \left[\text{—CH}_2\text{—}\underset{\text{Cl}}{\underset{|}{\text{CH}}}\text{—}\right]_n$$

Polyvinyl chloride

It is a thermoplastic and its plasticity can be increased by addition of a plasticiser (esters of phthalic acid). It is an electrical insulator and is resistant to fire and chemicals.

It is used in making sheets, pipes, waterproof outer clothing (rain coats), hand bags, table clothes, plastic dolls, gramophone records, floor covering and electrical insulating coating on electrical cables.

6. Polyacrylonitrile (Orlon): It is prepared by polymerization of acrylonitrile (vinyl cyanide) in presence of ferrous sulphate and hydrogen peroxide.

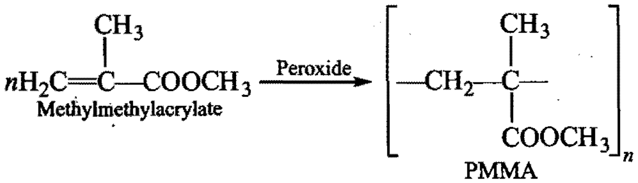


$$\underset{\text{Vinyl cyanide}}{n\text{H}_2\text{C}{=}\text{CHCN}} \xrightarrow[\text{FeSO}_4+\text{H}_2\text{O}_2]{\text{Polymerization}} \left[\text{—CH}_2\text{—}\underset{\text{CN}}{\underset{|}{\text{CH}}}\text{—}\right]_n$$

Orlon

Orlon is also named **acrilanor** courtelle. This polymer forms water resistant and quick drying fibre. The fibre can be worn or knitted. It can also be blended with wool. It is used for clothes, carpets, blankets, etc.

7. Polymethylmethylacrylate, (PMMA): It is prepared by polymerization of methylmethylacrylate in the presence of organic peroxide.

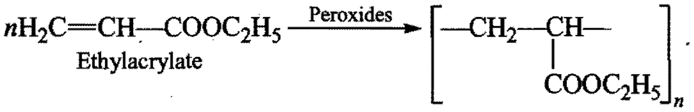


$$\underset{\text{Methylmethylacrylate}}{n\text{H}_2\text{C}{=}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{—COOCH}_3} \xrightarrow{\text{Peroxide}} \left[\text{—CH}_2\text{—}\overset{\text{CH}_3}{\overset{|}{\underset{\text{COOCH}_3}{\underset{|}{\text{C}}}}}\text{—}\right]_n$$

PMMA

It is a hard and transparent polymer. It is commercially known as **plexiglas.** It is used for making lenses, photosensitive, aircraft windows, skylights, plastic jewellery, etc.

Similarly, polyethylacrylate **(PEA)** is also formed. It is tough and also used as alternative of rubber. Mainly it is used in blankets and carpets.

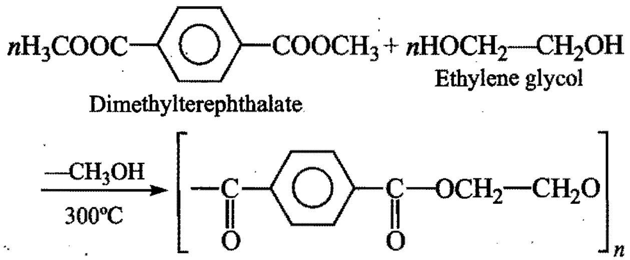


$$\underset{\text{Ethylacrylate}}{n\text{H}_2\text{C}{=}\text{CH—COOC}_2\text{H}_5} \xrightarrow{\text{Peroxides}} \left[\text{—CH}_2\text{—}\underset{\text{COOC}_2\text{H}_5}{\underset{|}{\text{CH}}}\text{—}\right]_n$$

Polyethylacrylate

[B] Condensation Polymers

1. Terylene (Dacron): Terylene or Dacron is also called a polyester as it contains ester groups. It is prepared by condensing dimethylterephthalate and ethylene glycol in presence of a weak base, (calcium acetate). Methanol is eliminated during condensation.

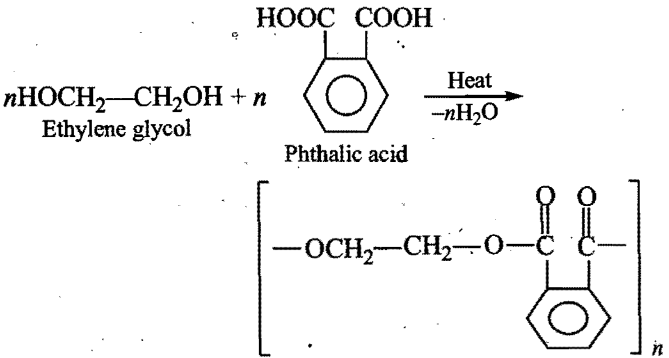


Terylene

It is the most important polyester. Its melt can be spun into fibres. It can be mixed with cotton and wool. It is highly resistant to the action of chemicals. It has a low degree of moisture absorption and dries up very rapidly. The terylene fibre is strong, flexible and durable. Its clothes retain creases.

As a film, this polymer has a high tensile strength and resistant to tearing. The film is used for making magnetic recording tapes.

2. Glyptal or Alkyds : It is a three dimensional polyester having cross-links and is a thermosetting plastic. It is obtained by condensation of ethylene glycol and phthalic acid or glycerol and phthalic acid.



(Glyptal)
Poly (ethylene glycol phthalate)

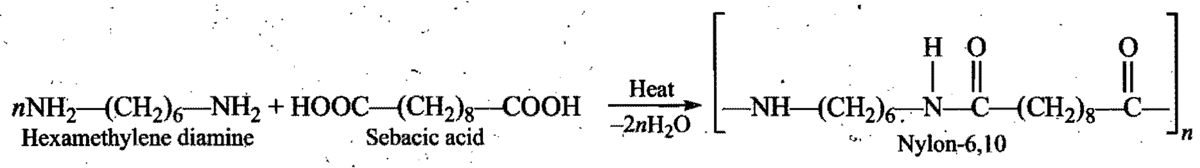
When its solution in a suitable solvent is evaporated, it leaves a tough but non-flexible film. It is, therefore, used in the manufacture of paints and lacquers.

3. Nylon : Nylon is used as a general name for all synthetic fibres forming polyamides, *i.e.*, having a protein like structure. These are the condensation polymers of diamines and dibasic acids. A number is usually suffixed with the name nylon which refers to the number of carbon atoms present in the diamine and the dibasic acid respectively.

Nylon-6,6 (read as nylon six, six) is obtained by condensation polymerization of hexamethylene diamine (a diamine with six carbon atoms) and adipic acid (a dibasic acid having 6 carbon atoms).

$$\underset{\text{Adipic acid}}{n\text{HOOC(CH}_2)_4\text{COOH}} + \underset{\text{Hexamethylene diamine}}{n\text{H}_2\text{N(CH}_2)_6\text{NH}_2} \xrightarrow[\text{High pressure } -n\text{H}_2\text{O}]{280^\circ\text{C}} \underset{\text{Nylon}-6,6}{\left[-\text{OC(CH}_2)_4\text{CONH(CH}_2)_6\text{NH}-\right]_n}$$

Nylon-6,10 (read as nylon six, ten) is obtained by condensation polymerization of hexamethylene diamine (six carbon atoms) and sebacic acid (a dibasic acid with 10 carbon atoms).

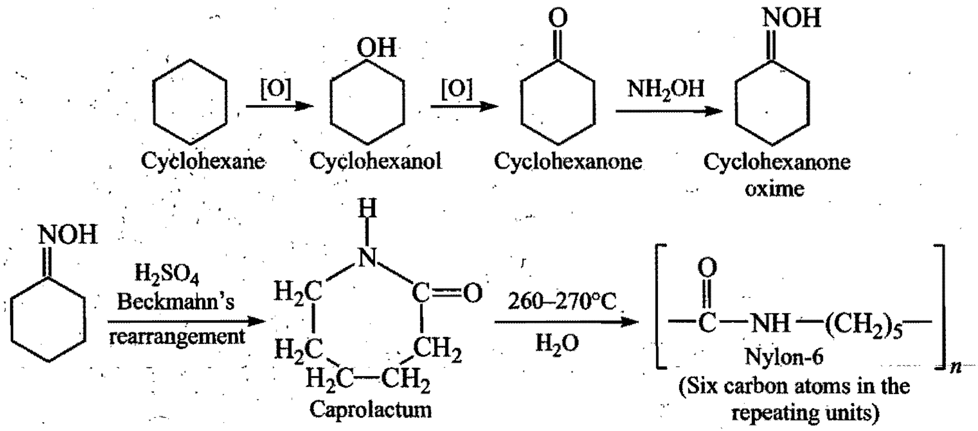


$$\underset{\text{Hexamethylene diamine}}{n\text{NH}_2\text{—(CH}_2)_6\text{—NH}_2} + \underset{\text{Sebacic acid}}{\text{HOOC—(CH}_2)_8\text{—COOH}} \xrightarrow[-2n\text{H}_2\text{O}]{\text{Heat}} \underset{\text{Nylon-6,10}}{\left[\text{—NH—(CH}_2)_6\text{—}\overset{\text{H}}{\text{N}}\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—(CH}_2)_8\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—}\right]_n}$$

Nylon fibres are stronger than natural fibres and so are used in making cords and ropes. The fibres are elastic, light, very strong and flexible. They have drip dry property and retain creases. It is inert towards chemicals and biological agents. It can be blended with wool. Nylon fibres are used in making carpets, fabrics, tyres, cords, ropes, etc.

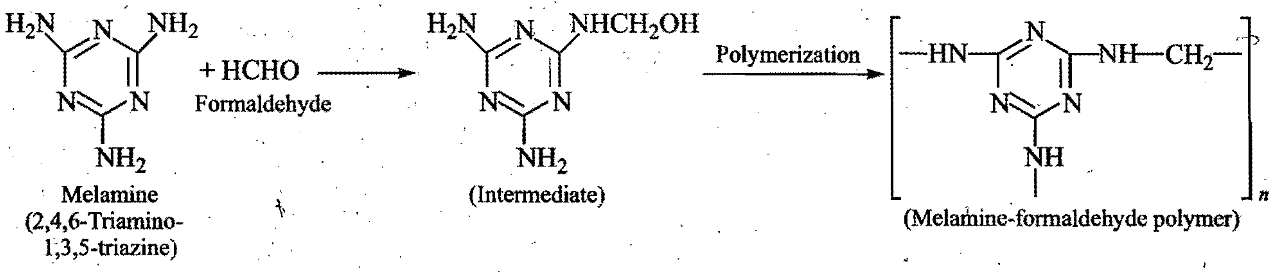
Nylon-6 or Perlon L: A polyamide closely related to nylon known as **Perlon L** (Germany) or **Nylon-6** (USA), is prepared by prolonged heating of caprolactum at 260-270°C.

Caprolactum is obtained by Beckmann's rearrangement of cyclohexanone oxime.



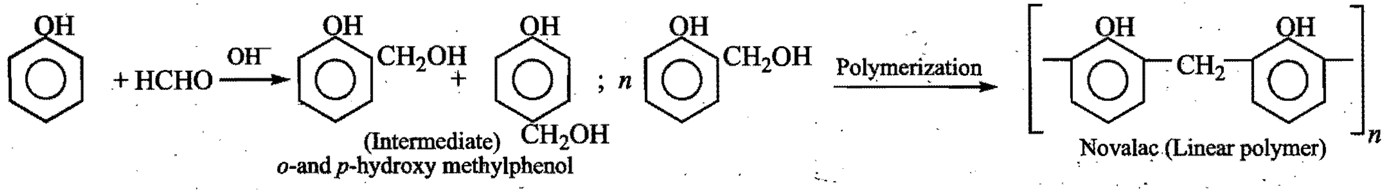
The fibre is practically identical to nylon-6,6 in properties.

4. Melamine-formaldehyde resin: This resin is formed by condensation co-polymerization of melamine and formaldehyde.

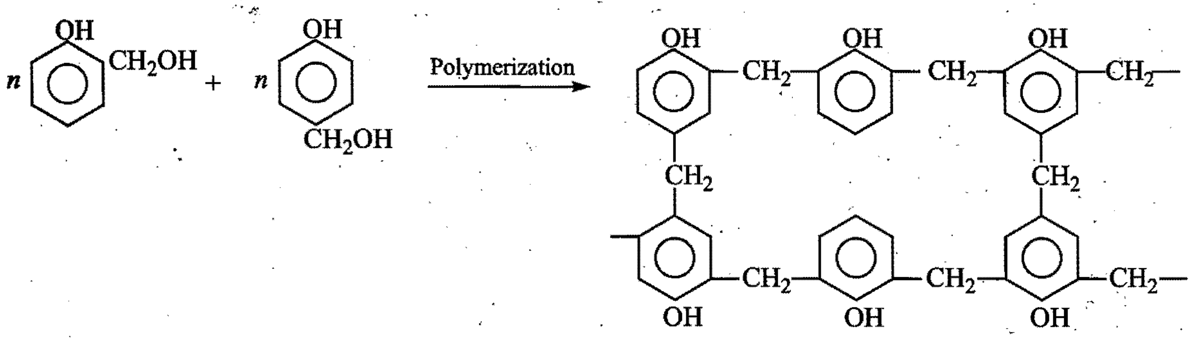


It is a quite hard polymer and is used widely for making plastic crockery under the name **melamine.** The articles made from this polymer do not break even dropped from considerable height.

5. Phenol-formaldehyde resin (Bakelite): Phenol-formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of a basic catalyst. The reaction involves the formation of methylene bridges in *ortho*, *para* or both *ortho* and *para* positions. The initial product is a linear polymer called **Novalac** which is used in paints.



Novalac on heating with HCHO undergo cross-linkage to form an infusible solid called **bakelite.**



Cross-linked polymer (Bakelite)

Bakelite is used for making combs, fountain pens, phonograph records, electrical goods, etc. Soft bakelites with low degree of polymerization are used as binding glue for laminated, wooden plants and in varnishes and lacquers. Sulphonated bakelites are used as ion-exchange resins.

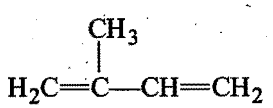
17.4 RUBBER

It is a polymer which is capable of returning to its original length, shape or size after being stretched or deformed. Rubber is a common example of an elastomer. The rubber obtained from natural sources is called **natural rubber** and polymers prepared in laboratory which are similar to natural rubber are known as synthetic rubbers.

(i) Natural rubber: Natural rubber is a polymer which is obtained from rubber trees in the form of a milky sap known as **latex.** The latex is coagulated with acetic acid or formic acid. The coagulated mass is then squeezed.

The raw natural rubber is a soft, gummy and sticky mass. It is insoluble in water, dilute acids and alkalies but soluble in benzene, chloroform, ether, petrol and carbon disulphide. It absorbs a large amount of water. It has low elasticity and low tensile strength. It breaks when too much stretched.

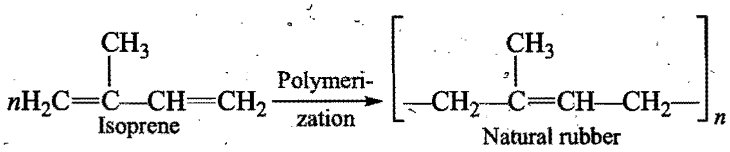
Natural rubber is a hydrocarbon polymer. It has the composition $(C_5H_8)_n$. Destructive distillation of natural rubber gives mainly isoprene (2-methyl buta-1,3-diene).



$$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2$$

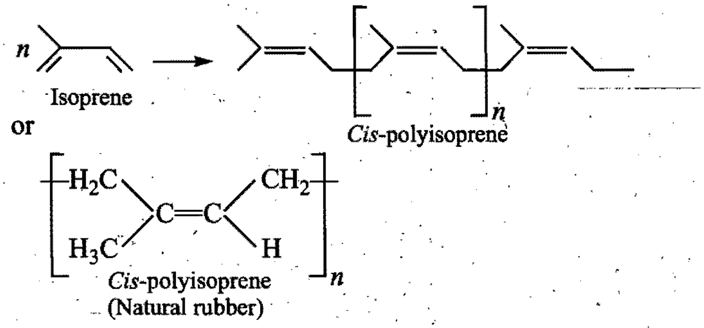
Isoprene
(2-methyl buta-1,3-diene)

Thus, isoprene is a monomer of natural rubber.

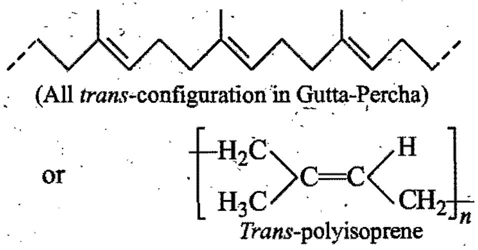


Natural rubber is a linear 1,4-addition polymer of isoprene. On the average, it contains 5000 isoprene units.

Natural rubber is *cis*-1,4-polyisoprene and has only *cis* configuration about the double bond as shown below:

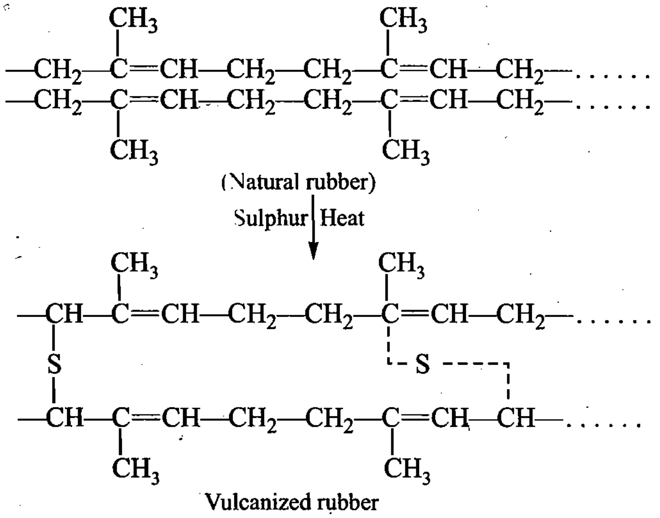


There are weak van der Waals' forces and therefore, it is elastic and non-crystalline. **Gutta-Percha** (*getah* means gum and *percha* means tree) is a naturally occurring isomer of rubber in which all the double bonds are *trans*. So, **Gutta-Percha is all trans-polyisoprene.** It is non-elastic and non-crystalline.



Vulcanization of rubber

Natural rubber is soft and sticky and therefore, in order to give strength and elasticity natural rubber is **vulcanized.** Vulcanization is a process of treating natural rubber with sulphur or some compounds of sulphur (like SF_6) under heat as to modify its properties, *i.e.*, to render it non-plastic and to give greater elasticity and ductility. The sulphur reacts with the polymer molecules forming a cross-linked network. This cross-linking gives mechanical strength to the rubber. In addition, fillers, such as carbon black and zinc oxide are usually added to the crude rubber before vulcanization in order to improve its wearing characteristics.

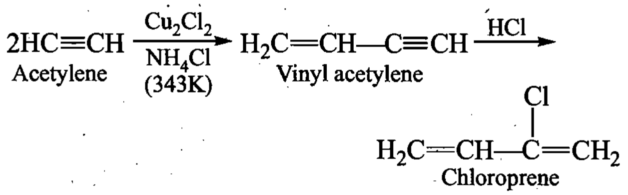


Natural rubber is used for making shoes, waterproof coats and golf balls. Vulcanized rubber is used for manufacturing rubber bands, gloves, tubing, conveyor belts and car tyres.

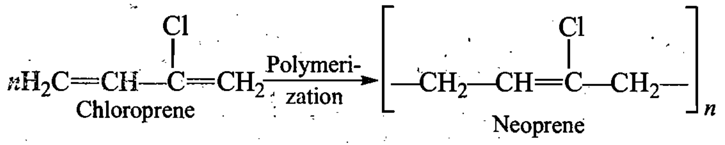
(ii) Synthetic rubber: They are also more flexible, tougher and durable than natural rubber. Neoprene, thiokol, buna-S and *cis* polybuta-1,3-diene are some examples of synthetic rubber.

(a) Neoprene: It was the first synthetic rubber manufactured on large scale. It is also called **diepreńe.** Its monomer, chloroprene (2-chlorobuta-1,3-diene) is prepared from acetylene.

Chloroprene undergoes free radical polymerization to form neoprene (polychloroprene). It polymerizes very rapidly (700 times faster than isoprene) and the reaction occurs by 1,4 addition of one chloroprene molecule to the other.

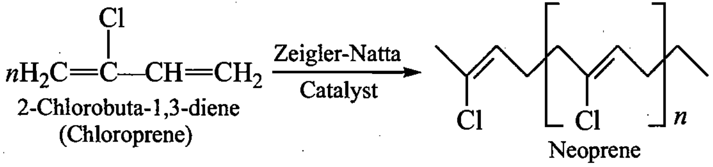


$$\underset{\text{Acetylene}}{2HC\equiv CH}\xrightarrow[NH_4Cl\ (343K)]{Cu_2Cl_2}\underset{\text{Vinyl acetylene}}{H_2C=CH-C\equiv CH}\xrightarrow{HCl}\underset{\text{Chloroprene}}{H_2C=CH-\overset{\overset{Cl}{|}}{C}=CH_2}$$



$$\underset{\text{Chloroprene}}{nH_2C=CH-\overset{\overset{Cl}{|}}{C}=CH_2}\xrightarrow{\text{Polymerization}}\underset{\text{Neoprene}}{\left[-CH_2-CH=\overset{\overset{Cl}{|}}{C}-CH_2-\right]_n}$$

or



$$\underset{\substack{\text{2-Chlorobuta-1,3-diene}\\ \text{(Chloroprene)}}}{nH_2C=\overset{\overset{Cl}{|}}{C}-CH=CH_2}\xrightarrow[\text{Catalyst}]{\text{Zeigler-Natta}}$$

Many of the properties of neoprene are similar to natural rubber, but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non-inflammable.

It is therefore, used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

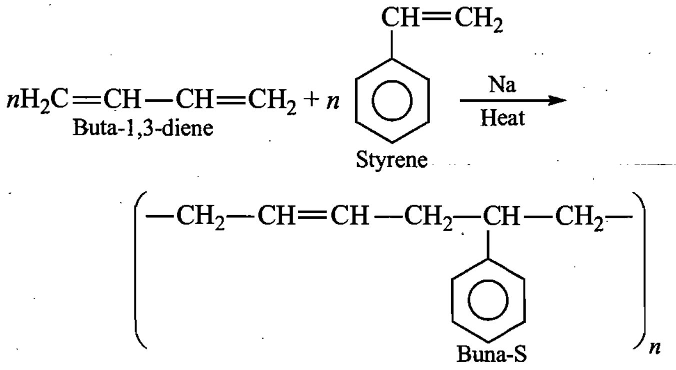
(b) Thiokol: Thiokol is made by polymerizing ethylene chloride and sodium polysulphide.

$$ClCH_2-CH_2Cl + Na-S-S-Na + ClCH_2-CH_2Cl$$
$$\Big\downarrow \text{Polymerization}$$
$$\underset{\text{Thiokol rubber}}{-CH_2-CH_2-S-S-CH_2-CH_2-S-S-CH_2-CH_2-}$$

The repeating unit is $-CH_2-S-S-CH_2-$.

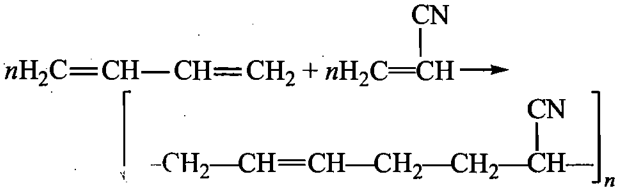
Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

(c) Buna-S (SBR—Styrene butadiene rubber): Buna-S rubber is a co-polymer of three moles of butadiene and one mole of styrene. In Buna-S, 'Bu' stands for butadiene, 'na' for symbol of sodium (Na) which is polymerizing agent and 'S' stands for styrene. It is an elastomer, (General purpose styrene rubber or GRS).



Buna-S is generally compounded with carbon black and vulcanized with sulphur. It is extremely resistant to wear and tear and therefore, used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical co-polymerization of its monomers.

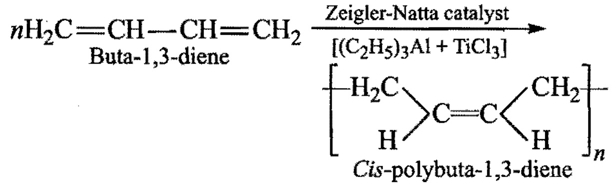
Buna-N: It is obtained by co-polymerization of butadiene and acrylonitrile, (General purpose Rubber Acrylonitrile or GRA).



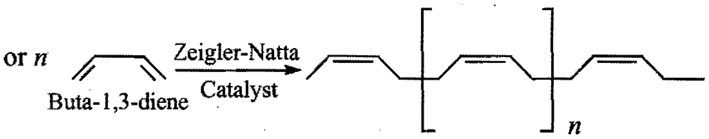
$$nH_2C=CH-CH=CH_2 + nH_2C=\overset{\overset{CN}{|}}{CH}\longrightarrow\left[-CH_2-CH=CH-CH_2-CH_2-\overset{\overset{CN}{|}}{CH}-\right]_n$$

It is very rigid and is very resistant to action of petrol, lubricating oil and many organic solvents. It is mainly used for making fuel tanks].

(d) *Cis*-polybuta-l, 3-diene: Buta-1,3-diene on polymerization in presence of Zeigler-Natta Catalyst (*i.e.*, a mixture of triethyl aluminium and titanium trichloride or tetrachloride) gives *cis*-polybuta-1,3-diene in which 1,4-addition takes place in each butadiene molecule and the remaining doubled bonds are *cis*.



Cis-polybuta-1,3-diene



Cis-polybuta-1,3-diene
(Synthetic rubber)

17.5 MOLECULAR MASS OF POLYMERS

Polymerization is quite complicated in nature. During the formation of polymers, the degree of polymerization or the length of the polymer chain depends upon the availability of the monomer molecules near the growing polymer chain and also the reaction conditions employed. As a result in the synthetic polymers, the chains of different lengths may unite with one another. Hence, an average value of molecular mass is taken. But the same is not true for the natural polymers such as proteins, where the chains are of identical lengths and hence their molecular masses are singular and not average in nature.

Types of average molecular mass: There are two types of average molecular masses of polymers.

(i) Number-average molecular mass ($\overline{M}_n$).

(ii) Weight (mass)-average molecular mass ($\overline{M}_w$).

The two types of molecular masses are defined and calculated as follows:

(i) Number-average molecular mass ($\overline{M}_n$): When the total mass of all the molecules of a sample is divided by the total number of molecules, the result obtained is called the number-average molecular mass. For example:

Let N_1 molecules have molecular mass = M_1 each
Let N_2 molecules have molecular mass = M_2 each
Let N_3 molecules have molecular mass = M_3 each
Then, Total mass of N_1 molecules = N_1M_1
Total mass of N_2 molecules = N_2M_2
Total mass of N_3 molecules = N_3M_3 and so on.

So, the total mass of all the molecules

$$= N_1M_1 + N_2M_2 + N_3M_3 + \ldots$$
$$= \Sigma N_iM_i$$

where N_i is the total number of molecules of *i*th type with molecular mass M_i.

Total number of all the molecules = $N_1 + N_2 + N_3 \ldots$
$= \Sigma N_i$

Therefore, **the Number average molecular mass ($\overline{M}_n$)**

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 \ldots}{N_1 + N_2 + N_3 \ldots}$$

$$\overline{M}_n = \frac{\Sigma N_iM_i}{\Sigma N_i}$$

$\overline{M}_n$ is generally determined by osmotic pressure measurement.

(ii) Weight (mass)-average molecular mass ($\overline{M}_w$): It is average of the molecular mass of the groups of the molecules having particular molecular masses multiplied by their respective molecular masses. For example, as before that N_1, N_2, N_3, etc., molecules have molecular masses M_1, M_2, M_3, etc., respectively.

Then, Total mass of N_1 molecules = N_1M_1
Total mass of N_2 molecules = N_2M_2
Total mass of N_3 molecules = N_3M_3 and so on.

The products with their respective molecular masses will be:

$(N_1M_1 \times M_1), (N_2M_2 \times M_2), (N_3M_3 \times M_3)$, etc.
i.e., $N_1M_1^2, N_2M_2^2, N_3M_3^2$, etc.,

Sum of the products = $N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \ldots$
$= \Sigma N_iM_i^2$

Total mass of the molecules

$$= N_1M_1 + N_2M_2 + N_3M_3 + \ldots$$
$$= \Sigma N_iM_i$$

Hence, the **weight-average molecular mass ($\overline{M}_w$)** is calculated by multiplying the total molecular mass of groups of molecules having different molecular masses with their respective molecular masses, adding the products and then by dividing the sum by the total mass of all the molecules. Therefore,

$$\overline{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \ldots}{N_1M_1 + N_2M_2 + N_3M_3 + \ldots}$$

$$\overline{M}_w = \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i}$$

$\overline{M}_w$ is generally determined by using methods which depend upon the masses of individual molecules, *viz.*, light scattering, ultra centrifuge or sedimentation, etc.

Polydispersity Index (PDI) : The ratio of weight average molecular mass and number-average molecular mass is called **Polydispersity Index (PDI)**, *e.g.*,

$$\text{PDI} = \frac{\overline{M}_w}{\overline{M}_n}$$

PDI is used to determine the homogeneity of a polymer. In general, there are two different types of polymeric substance depending on the basis of values of PDI.

(i) Monodisperse polymers: Polymers whose molecules have same or narrow range of molecular masses are called **monodisperse polymers.**

In **natural polymers,** PDI is usually equal to one (*i.e.*, $\overline{M}_w = \overline{M}_n$) which means that they are monodispersed and hence, are **more homogeneous** (PDI = 1).

(ii) Polydisperse polymers : Polymers whose molecules have a wide range of molecular masses are called **polydisperse polymers.**

In **synthetic polymers,** PDI is greater than unity (*i.e.*, $\overline{M}_w > \overline{M}_n$) which means that they are polydispersed and hence, are **less homogeneous** (PDI > 1).

Example 1. *In a polymer sample,* 30% *molecules have molecular mass* 20,000; 40% *have molecular mass* 30,000 *and the rest* 30% *have* 60,000. *Calculate their number-average and mass-average molecular masses.* **[PMT (Kerala) 2006]**

[**Hint:** $$\overline{M}_n = \frac{(30\times 20{,}000)+(40\times 30{,}000)+(30\times 60{,}000)}{30+40+30} = 36{,}000$$

$$\overline{M}_w = \frac{30(20{,}000)^2 + 40(30{,}000)^2 + 30(60{,}000)^2}{30\times 20{,}000 + 40\times 30{,}000 + 30\times 60{,}000} = 43{,}333]$$

Example 2. *A sample of polymer contains* 200 *molecules of molecular mass* 10^3*; each* 300 *molecules have* 10^4 *each; and* 500 *molecules have* 10^5 *each. Calculate their number-average and weight-average molecular masses.*

[**Hint:** $$\overline{M}_n = \frac{(200\times 10^3)+(300\times 10^4)+(500\times 10^5)}{200+300+500}$$

$$= \frac{(2+30+500)10^5}{1000} = 53{,}200$$

$$\overline{M}_w = \frac{200\times(10^3)^2 + 300\times(10^4)^2 + 500\times(10^5)^2}{200\times 10^3 + 300\times 10^4 + 500\times 10^5}$$

$$= \frac{10^8(2+300+50000)}{10^5(2+30+500)} = \frac{10^3\times 50302}{532} = 94{,}553]$$

17.6 BIOPOLYMERS AND BIODEGRADABLE POLYMERS

Nature provides many polymeric species which are essential for life and can be produced by biological systems such as micro-organism, plants and animals. They can also be synthesised chemically. Starch and cellulose (polysaccharides), proteins, peptides, PHBV (Poly β-hydroxyl butyrate β-hydroxyl valerate), R.N.A. and D.N.A. (nucleic acids) which control the various life processes are called **Biopolymers.** (Details about their characteristics are given in unit 15 of biomolecules).

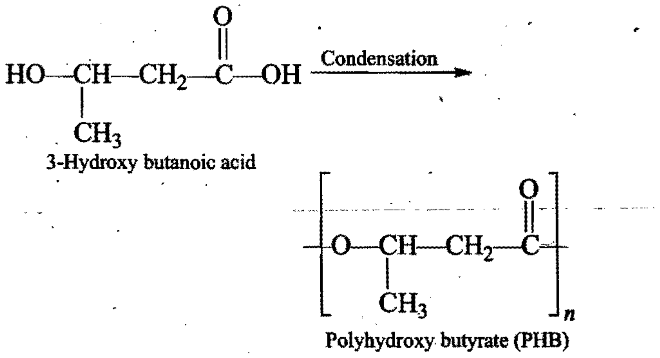
All these biopolymers can be broken into component parts either by enzyme-catalysed reaction or themselves during a certain period of time and hence, are biodegradable. They are non-toxic and do not cause pollution, hence, a better alternative to petroleum based polymers such as plastics which are non-biodegradable and are the source of major pollution. In biological systems, biopolymers degrade mainly by enzymatic hydrolysis and to some extent by oxidation. One of the best method of making a polymer biodegradable is by inserting hydrolysable ester group into the polymer.

Biopolymers have several functional uses, *i.e.*, they act as stabilizers, thickners, binders, lubricants and adhesives, etc. Since, biopolymers are biodegradable and are from renewable sources, they have a major scope in industry such as in cosmetics, pharmaceuticals, packing papers and textiles, etc.

In view of the disposal problem of polymers waste and for developing polymers for other safe uses in human system, biodegradable synthetic polymers have been developed. These synthetic polymers mostly have functional groups prevalent in biopolymers and lipids.

Among these the most important class of biodegradable polymers are aliphatic polyesters and polyamides. Some of these briefly discussed below:

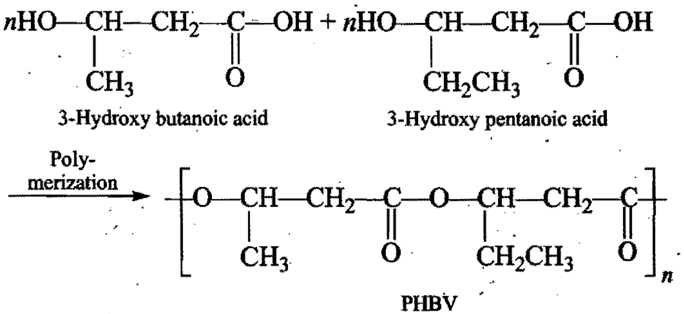
(a) Polyhydroxy butyrate (PHB): It is obtained from hydroxy butyric acid (3-hydroxy butanoic acid.).



$$\underset{\text{3-Hydroxy butanoic acid}}{\text{HO}-\underset{\substack{|\\ \text{CH}_3}}{\text{CH}}-\text{CH}_2-\overset{\substack{\text{O}\\ \|}}{\text{C}}-\text{OH}} \xrightarrow{\text{Condensation}} \left[-\text{O}-\underset{\substack{|\\ \text{CH}_3}}{\text{CH}}-\text{CH}_2-\overset{\substack{\text{O}\\ \|}}{\text{C}}-\right]_n$$

Polyhydroxy butyrate (PHB)

(b) Poly-β-hydroxy butyrate-CO-β-hydroxyvalerate (PHBV): It is a copolymer of 3-hydroxy butanoic acid and 3-hydroxy pentanoic acid, in which the two monomer units are joined by ester linkages.



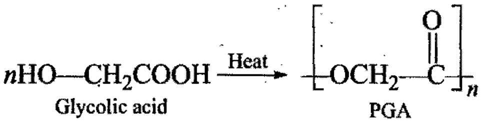
$$n\text{HO}-\underset{\substack{|\\ \text{CH}_3}}{\text{CH}}-\text{CH}_2-\underset{\substack{\|\\ \text{O}}}{\text{C}}-\text{OH} + n\text{HO}-\underset{\substack{|\\ \text{CH}_2\text{CH}_3}}{\text{CH}}-\text{CH}_2-\underset{\substack{\|\\ \text{O}}}{\text{C}}-\text{OH} \xrightarrow{\text{Poly-merization}} \left[-\text{O}-\underset{\substack{|\\ \text{CH}_3}}{\text{CH}}-\text{CH}_2-\underset{\substack{\|\\ \text{O}}}{\text{C}}-\text{O}-\underset{\substack{|\\ \text{CH}_2\text{CH}_3}}{\text{CH}}-\text{CH}_2-\underset{\substack{\|\\ \text{O}}}{\text{C}}-\right]_n$$

PHBV

The properties of PHBV vary according to the ratio of both the acids (monomers). 3-Hydroxy butanoic acid provides stiffness while 3-hydroxy pentanoic acid gives flexibility to the copolymer.

PHB and PHBV have been used for making films for packaging and into moulded items. When a drug is enclosed in a capsule of **PHBV**, it is released only when the polymer is degraded in the body. **PHBV** also undergoes bacterial degradation in the environment.

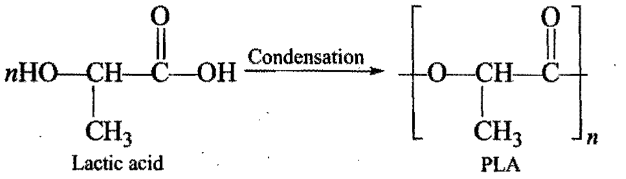
(c) Poly glycolic acid (PGA) and poly lactic acid (PLA): This copolymer is commercially called **dextron.** PGA is obtained by the chain polymerization of cyclic dimer of glycolic acid.



$$n\mathrm{HO{-}CH_2COOH} \xrightarrow{\text{Heat}} \left[\mathrm{O{-}CH_2{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\right]_n$$

Glycolic acid PGA

PLA is obtained by polymerization of cyclic dimer of lactic acid or by microbiological synthesis of lactic acid followed by polycondensation and removal of water by evaporation.

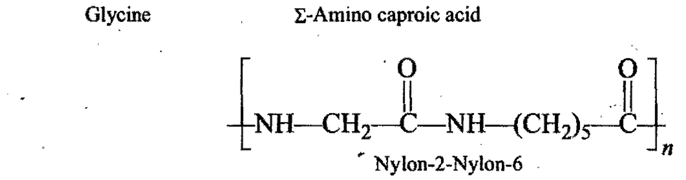


$$n\mathrm{HO{-}}\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{CH}}\mathrm{{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}OH} \xrightarrow{\text{Condensation}} \left[\mathrm{O{-}}\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{CH}}\mathrm{{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\right]_n$$

Lactic acid PLA

A copolymer of PGA and PLA (90 : 10) was the first biodegradable polyester used for stitching of wounds after operation. This polymer gets completely degraded and absorbed by the body within 15 days to one month of the surgery.

(d) Nylon-2-Nylon-6: It is an alternating polyamide of glycine (containing two carbon atoms) and 5 (or Σ) amino caproic acid (containing six carbon atoms).



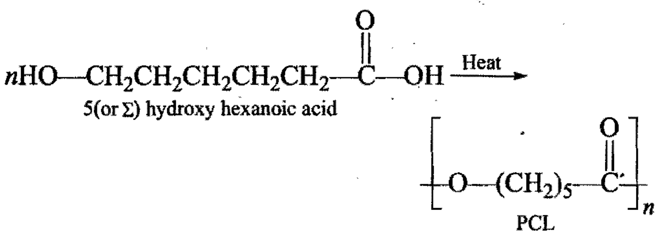
$$n\mathrm{H_2N{-}CH_2{-}COOH} + n\mathrm{H_2N{-}(CH_2)_5{-}COOH} \xrightarrow{\text{Heat}} \left[\mathrm{NH{-}CH_2{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}NH{-}(CH_2)_5{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\right]_n$$

Glycine Σ-Amino caproic acid

Nylon-2-Nylon-6

It is a biodegradable step-growth co-polymer.

(e) Poly Σ-caprolactone lactone (PCL): It is obtained by chain polymerization of the lactone of 5 (or Σ) hydroxy hexanoic acid.



$$n\mathrm{HO{-}CH_2CH_2CH_2CH_2CH_2{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}OH} \xrightarrow{\text{Heat}} \left[\mathrm{O{-}(CH_2)_5{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\right]_n$$

5(or Σ) hydroxy hexanoic acid

PCL

17.7 WHY DO WE SEE COLOUR

Visible light consists of electromagnetic radiations of wavelengths 400-750 nm (4000-7500 Å). Each wavelength is associated with definite energy and produces characteristic colour sensation when it strikes the retina of our eye. Light possessing all the wavelengths from 400-750 nm (visible range) appears white. The white light is actually made of seven colours. These are violet, indigo, blue, green, yellow, orange and red (VIBGYOR). When white light falls on a substance, three things may occur:

(i) Totally reflected, *i.e.*, nothing is absorbed or,

(ii) Partially reflected and partially absorbed or,

(iii) Totally absorbed, *i.e.*, nothing is reflected.

The substance appears white when light is totally reflected or black when it is totally absorbed. But when a part of light is reflected and rest absorbed, the substance looks coloured. If only a single band is absorbed, the substance will have the complementary colour of the absorbed band. The table given below correlates the wavelengths absorbed with complementary (visible) colours observed:

Wavelength absorbed (nm)	Colour absorbed	Complementary colour
400–435	violet	yellow-green
435–480	blue	yellow
480–490	blue-green	orange
490–500	green-blue	red
500–560	green	purple
560–580	yellow-green	violet
580–595	yellow	blue
595–605	orange	green-blue
605–750	red	blue-green

In case, only one band is reflected and rest are absorbed, the colour of the substance is that of the reflected band. Thus, the substance may appear red,

(a) either because it absorbs only the green-blue band (490–500 nm) from the white light and reflects all the rest.

(b) or because it absorbs all the bands except red (605–750 nm), which it reflects.

17.8 DYES

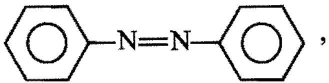
Dye is a natural or synthetic colouring matter which is used in solution to stain materials especially fabrics. All the coloured substances are not dyes. A coloured substance is termed as a dye if it fulfils the following conditions:

(i) It must have a suitable colour.

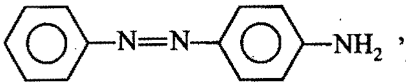
(ii) It can be fixed on the fabric either directly or with the help of mordant.

(iii) When fixed it must be fast to light and washing, *i.e.*, it must be resistant to the action of water, acids and alkalies, particularly to alkalies as washing soda and soap have alkaline nature.

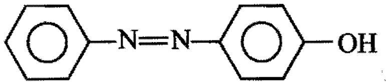
The following examples show that all coloured substances are not necessarily dyes. Azobenzene is a highly coloured substance but does not act as a dye because it does not fix itself on a fabric while two similar compounds *p*-aminoazobenzene and *p*-hydroxyazobenzene act as dyes.



Azobenzene



p-Aminoazobenzene

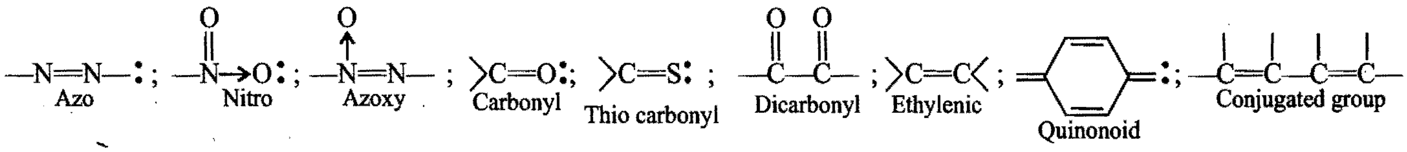


p-Hydroxy azobenzene

A dye consists of a chromophore group and a salt forming group called anchoric group.

In 1876, Otto **Witt** put forth a theory as to correlate colour with molecular structure (constitution). The theory is named **'The Chromophore Auxochrome Theory'** and its main postulates are:

(i) The colour of the organic compounds is due to the presence of certain multiple bonded groups called **chromophores.** Important **chromophores** are:



[Chromophore-Greek word, *Chroma* = colour, *Phorein* = to bear]

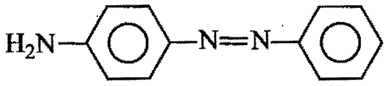
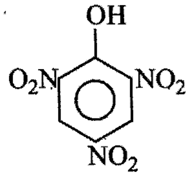
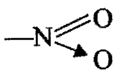
The presence of chromophore is not necessarily sufficient for colour. To make a substance coloured, the chromophore has to be conjugated with an extensive system of alternate single and double bonds as exists in aromatic compounds.

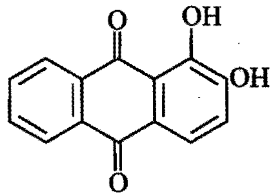
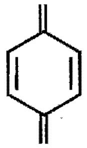
The chromophore part of the coloured substance (dye) absorbs some wavelengths from white light and reflects back the complementary colour. A coloured compound having a chromophore is known as **chromogen.**

(ii) Certain groups, while not producing colour themselves, when present along with a chromophore in an organic substance, intensify the colour. Such colour assisting groups are called **auxochromes** (Greek word, *Auxanien* = to increase; *Chrome* = colour), *i.e.*, they make the colour deep and fast and fix the dye to the fabric. The **auxochromes** are acidic or basic functional groups. The important auxochromes are:

Acidic :	$-OH$,	$-SO_3H$,	$-COOH$	**Basic :**	$-NH_2$,	$-NHR$,	$-NR_2$
	Hydroxy	Sulphonic	Carboxylic		Amino	Alkylamino	Dialkylamino

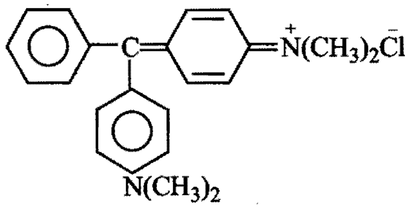
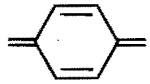
Examples :

Dye	**Chromophore**	**Auxochrome**
1. *p*-Aminoazobenzene  (Orange) ,	$-N=N-$,	$-NH_2$
2. Picric acid  (Yellow) ,	 ,	$-OH$

3. Alizarin  ,  , —OH

(Purple solution in alkali)

4. Malachite green

 ,  , $—N(CH_3)_2$

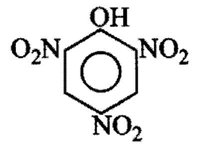
However, Otto **Witt** chromophore-auxochrome concept fails to explain the colour of certain dye stuffs like indigo.

17.9 CLASSIFICATION OF DYES

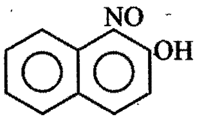
Dyes are classified to their chemical constitution or by their application to the fibre. Chemists prefer to classify dyes according to their structures but the dyers classify them according to their application.

Classification of Dyes According to their Chemical Structures

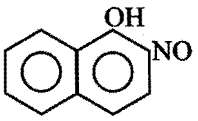
(i) Nitro and nitroso dyes : These dyes contain nitro or nitroso groups as the chromophores and —OH as auxochrome. A few examples are:



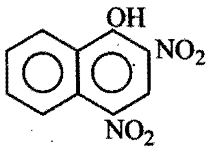
Picric acid
(2,4,6-Trinitrophenol)



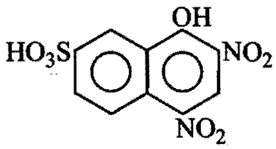
1-Nitroso-2-naphthol
(Gambine-*Y*)



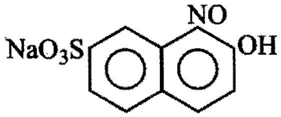
2-Nitroso-1-naphthol
(Gambine-*R*)



Martius yellow

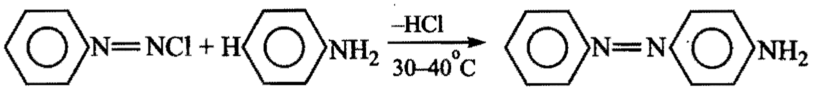


Naphthol yellow-S

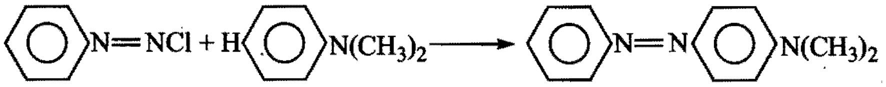


Naphthol green-B

(ii) Azo dyes : The azo dyes contain one or more azo groups —N═N—, as the chromophore. Azo dyes constitute the largest and the most important group of synthetic dyes. These can be prepared by diazotising an aromatic amine and subsequent coupling with a suitable aromatic phenol or amine.

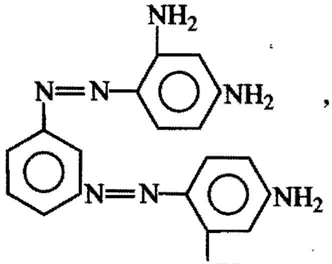


p-Amino azobenzene(Aniline yellow)

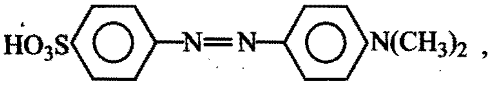


p-Dimethyl amino azobenzene
(Butter yellow)

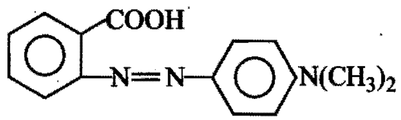
The important azo dyes are the following:



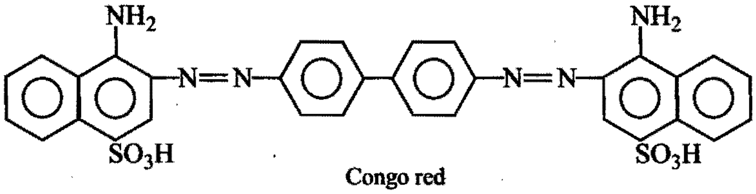
Bismark brown



Methyl orange



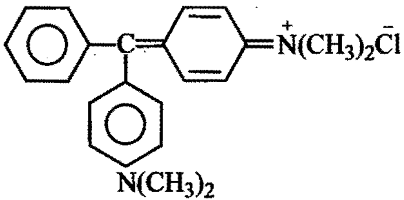
Methyl red



Congo red

Azo dyes are highly coloured. Azo dyes can be further divided into acid, basic, direct, ingrain or developed dyes, etc., on the basis of mode of application.

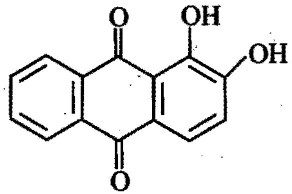
(iii) Triarylmethane dyes : In these dyes, the central carbon is bonded to three aromatic rings. One of which is in the quinonoid form (the chromophore). Malachite green is the typical example of this class.



Malachite green

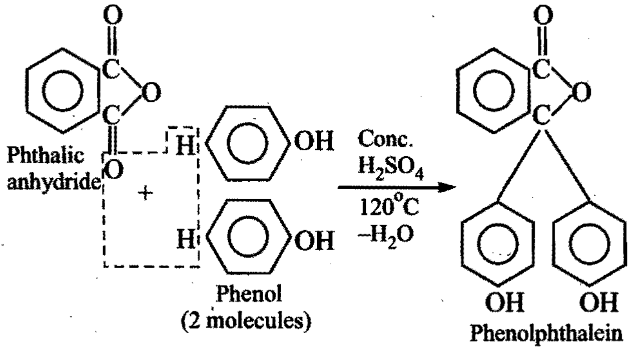
Rosaniline and crystal violet are other two important dyes of this class.

(iv) Anthraquinone dyes : *Para* quinonoid chromophore is present in these anthracene type dyes. Alizarin is a typical anthraquinone dye.



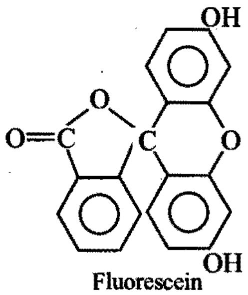
Alizarin

(v) Phthaleins: Products obtained by condensation of phthalic anhydride with phenols in presence of dehydrating agents like conc. H_2SO_4 or anhydrous zinc chloride are called phthaleins.

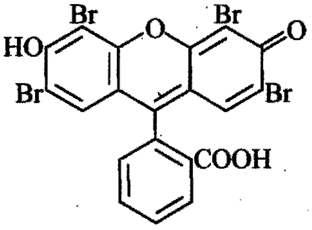


Phenolphthalein

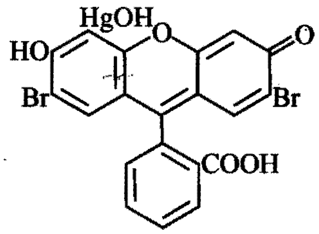
The other important dyes of this class are:



Fluorescein

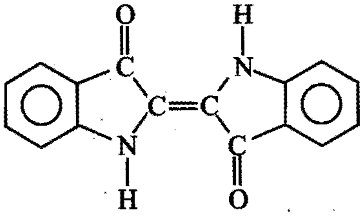


Eosin



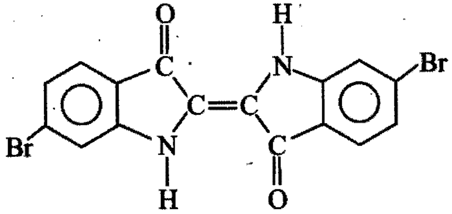
Mercurochrome

(vi) Indigo dyes : These dyes contain the carbonyl chromophore. Indigo is the oldest known dye.



Indigo (Dark blue crystalline powder)

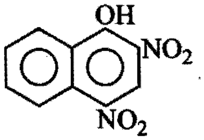
Another indigo dye is royal blue in colour which is dibromo derivative of indigo. It is called Tyrian blue.



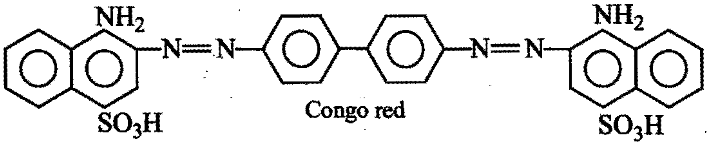
Tyrian purple

Classification of Dyes According to their Application

(i) Direct dyes : Direct dyes can be directly applied to the fibre, both animal and vegetable, by dipping in hot aqueous solution of the dye. These dyes are most useful for those fabrics which can form hydrogen bonds, *i.e.*, for cotton, rayon, wool, silk and nylon. Martius yellow and congo red act as direct dyes.

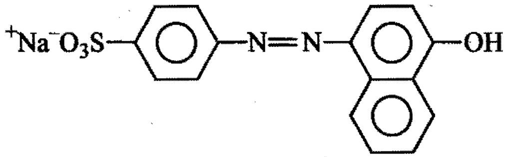


Martius yellow



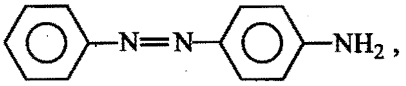
Congo red

(ii) Acid dyes : These are usually salts of sulphonic acids and can be applied to wool, silk and nylon. The presence of sulphonic acid group makes them water soluble. These dyes are applied from an acidic bath. The polar acidic groups interact with the basic groups of the fabric. Orange-1 is an excellent acid dye.

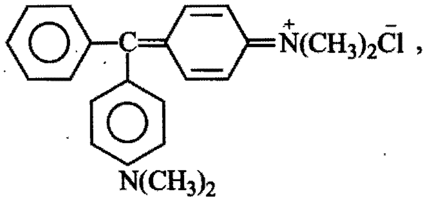


Orange-1(Azo dye)

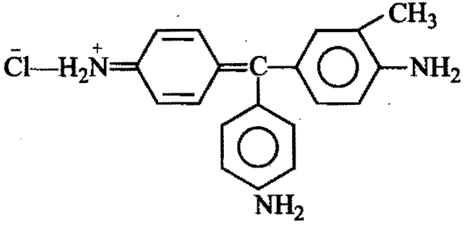
(iii) Basic dyes : These are the hydrochlorides or zinc chloride salts of colour bases having basic groups. These dyes react with anionic sites present on the fabric to attach themselves. These dyes colour fibres of nylons and polyesters. Aniline yellow, butter yellow, magenta (rosaniline) and malachite green are the examples of basic dyes.



Aniline yellow



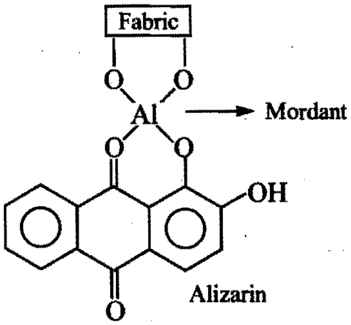
Malachite green



Magenta

Note: Acid and basic dyes are actually direct dyes.

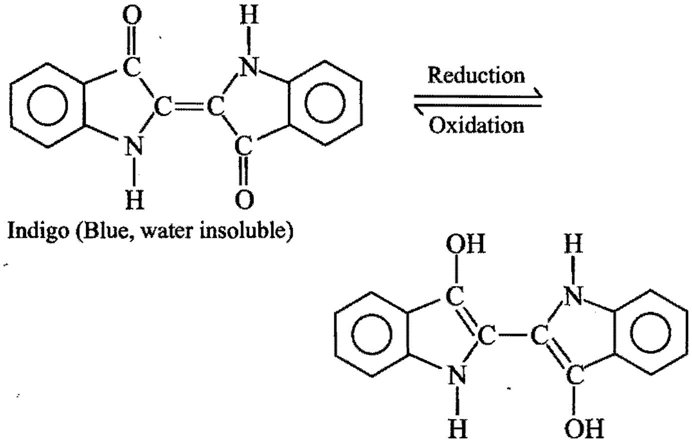
(iv) Mordant dyes : These dyes have no natural affinity for the fabric and are applied to it with the help of certain additional substances known as mordants. A mordant (Latin mordere = *to bite*) is any substance which can be fixed to fabric and reacts with the dye to produce colours on fabric. Three types of mordants are commonly used: (i) acidic mordants like tannic acid which are used with basic dyes; (ii) basic mordants such as metallic hydroxides or albumin which are used with acidic dyes and (iii) metallic mordants like salts of aluminium, chromium, iron, tin, etc., which are used with acidic dyes. Actually the mordant forms an insoluble coordination compound between the fabric and the dye and binds the two. Alizarin is a typical mordant dye. It gives different colours depending on the metal ion used. For example, with Al^{3+}, alizarin gives a rose red colour; with Ba^{2+}, a blue colour; with Fe^{3+}, a violet colour and with Cr^{3-}, a brownish red colour.



Coordination compound of Alizarin with Al^{3+}

The process of mordant dyeing consists in impregnating the fabric with mordant in presence of wetting agent followed by soaking of the fabric into the solution of dye.

(v) Vat dyes: These dyes are insoluble in water and cannot be applied directly. These dyes on reduction with sodium hydrosulphite ($NaHSO_3$) in a vat form, a soluble compound which has great affinity for cotton and other cellulose fibres. The cloth is soaked in the solution of a reduced dye and then hung in air or treated with oxidants like perboric acid. As a result, the colourless compound is oxidised to insoluble dye which is now bound to the fabric. So, the dyes which are applied to the fabric in the colourless reduced state and then oxidised to coloured state, are called **vat dyes.** The colourless and reduced state of the dye is called the **leuco base.** The common examples of vat dyes are indigo and tyrian purple. These are mostly used on cotton.



Indigo (Blue, water insoluble)

Indigo-white, Leucobase
(Colourless, water soluble)

(vi) Ingrain dyes (Developed dyes): Ingrain dyes are those which are synthesised directly on the fabric. Examples of this type are azo dyes. The fabric is immersed in the solution of coupling reagent (usually a phenol or naphthol). Then it is dipped in the solution of suitable diazonium salt. Both react to form the dye whose molecules are adsorbed on the surface of fabric. The ingrain dyeing is particularly suitable for cotton fabrics.

(vii) Disperse dyes: These dyes are used to colour synthetic fabrics such as nylon, orlon, polyesters and cellulose acetate which have tightly packed structures. The dyes are dispersed in a colloidal form in water. The fabric is immersed in the colloidal dispersion of the dye when fine dye particles are trapped within the polymer structure of the fabric. Examples of this type are monoazodye and anthraquinone dye.

17.10 INTRODUCTION TO DRUGS AND CHEMOTHERAPY

The word drug is derived from the French word *drogue* which means a dry herb. In a general way, the drug may be defined as substance used in the prevention, diagnosis, treatment or cure of disease in man or other animals. Drugs may be a single chemical substance or a combination of two or more different substances. An ideal drug should satisfy the requirements given ahead:

(i) When administrated to the ailing individual or host, its action should be localised at the site where it is desired to act. In actual practice, there is no drug which behaves in this manner.

(ii) It should act on a system with efficiency and safety.

(iii) It should have minimum side effects.

(iv) It should not injure host tissues or physiological processes.

(v) The cells should not acquire resistance to the drug after sometime.

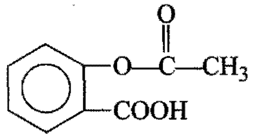
Very few drugs satisfy all the above requirements. Each drug has an optimum dose, below which it has no action and above this level it becomes a poison.

The term *chemotherapy,* which literally means chemical therapy or chemical treatment was coined in 1913 by **Paul Ehrlich,** the father of modern chemotherapy. **He defined chemotherapy as the use of chemicals (drugs) to injure or destroy infectious microorganisms without causing any injury to the host.** According to Ehrlich, chemotherapeutic agents are chemical substances which have selective toxicity, being harmful as much as possible to the invading or infectious organisms but harmless to the host. Chemotherapy has developed into a vast subject today and efforts are being continuously made to search new drugs as to free human beings from various types of diseases. Chemicals (drugs) used in chemotherapy are usually classified according to their action.

17.11 ANTIPYRETICS AND ANALGESICS

An antipyretic is a drug which is responsible for lowering the temperature of the feverish organism to normal but has no effect on normal temperature states. This causes body to lose heat and subsequently lowers the body temperature.

Aspirin is an important antipyretic. The other antipyretics are phenacetin, paracetamol, novalgin, phenyl butazone, methacetin and butazolidine etc.

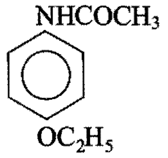


Aspirin
(Acetyl salicylic acid)
or (2-Acetoxy benzoic acid)

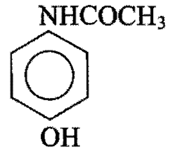
Aspirin is absorbed from gastrointestinal tract. The stomach acid causes a partial hydrolysis of the ester. The ester circulates in the blood and further hydrolysis occurs into salicylic acid which is the active component. It causes several side effects. It may cause minute ulcers in the stomach and cause bleeding. Aspirin should not be taken empty stomach. Some persons are allergic to aspirin. The usual allergic reaction is rashes on skin, lowering of blood pressure, profuse sweating, intense thirst, nausea and vomiting. Calcium and sodium salts of aspirin are more soluble and less harmful. Aspirin is also used to prevent heart stroke because it acts as vaso-dialator.

Because of these shortcomings in aspirin, the other analgesics like ibuprofen, naproxen, diclofenac sodium or potassium find use as alternatives.

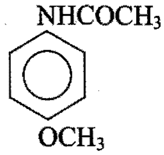
The derivatives of *p*-aminophenol are used as antipyretic. The main limitation of these derivatives is that they may act on red blood cells and thus, they may be harmful in moderate doses. The important derivatives are:



Phenacetin (4-Ethoxy-acetanilide)

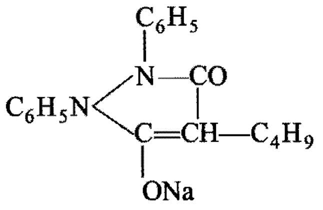


Paracetamol (4-Acetamido-phenol)



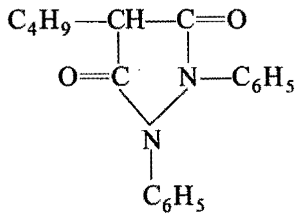
Methacetin (4-Methoxy-acetanilide)

Phenyl butazone is a pyrazolone derivative. Its structure is:



Phenyl butazone

or

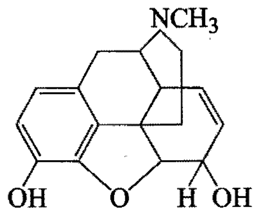


Butazolidine

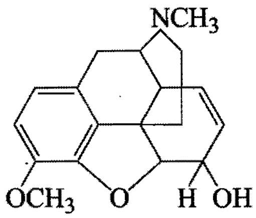
It is highly toxic and hence not considered as a safe drug. Oxyphenyl butazone is less toxic and is used in place of phenyl butazone.

Analgesics: Medicines which relieve or decrease pain are termed analgesics. These are of two types:

(i) Narcotic (addictive) drugs: These are mainly opium and its products such as morphine, codeine, marijuana and heroin. These produce analgesia and sleep and in high doses cause unconsciousness. They are very potent drugs and their chronic use leads to addiction.

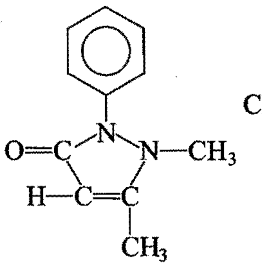


Morphine

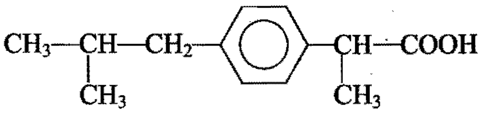


Codeine

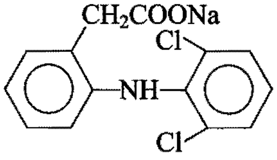
(ii) Non-narcotic (non-addictive) drugs: These are the drugs which are not potent and do not cause addiction. Common drugs are aspirin, analgin, novalgin, butazolidine (phenyl butazone) and brufen (ibuprofen), etc. They are quite effective and give immediate relief from pain and fever. These drugs also have antipyretic properties.



Analgin



Ibuprofen or Brufen (*p*-Isobutyl phenyl-2-propanoic acid)



Diclofenac sodium

Aspirin, novalgin, phenacetin and combiflam act both as antipyretic as well as analgesic. They are quite effective and give immediate relief from pain and fever.

17.12 ANTISEPTICS AND DISINFECTANTS

The chemicals used for sterilisation are classified under two headings : (i) Antiseptics and (ii) Disinfectants.

(i) Antiseptics : The term 'septic' is derived from the Greek word *septikos* which means putrify or rot. In medicine, it indicates the state of being infected with pus forming organisms. Anti-infective agents which are applied locally, *i.e.,* applied directly to the skin wounds, cuts, ulcers and diseased skin surfaces, etc., are known as antiseptics.

Chemical substances which prevent the growth of microorganisms or kill them but are not harmful to the living human tissues are called antiseptics. Some common examples of antiseptics are : Dettol, savlon, acriflavin, gentian violet, mercurochrome, boric acid, chloramine-T, tincture of iodine (an alcohol-water solution containing 2-3% iodine), iodoform, potassium permanganate, etc.

(ii) Disinfectants : These **substances kill the micro-organisms or stop their growth but are harmful to the human tissues.** These are used for sterilisation of inanimate objects like instruments, utensils, clothes, floors, sanitary fittings, sputum and excreta. These are harmful to living tissues and cannot be used on the skin. The examples are : phenol, methyl phenols, hydrogen peroxide, chlorine, bleaching powder, sulphur dioxide, etc.

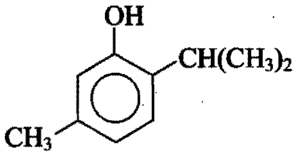
The same substance can act as antiseptic or disinfectant depending upon the concentration of the substance in solution. In smaller concentrations, it is an antiseptic while in higher concentrations it becomes disinfectant. 0.2% solution of phenol acts as an antiseptic and its 1% solution is a disinfectant.

Some common examples are:

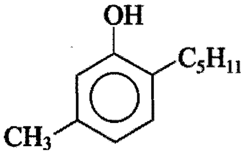
(a) Chlorine (Cl_2) is used to disinfect drinking water. It is used as 0.2 to 0.4 ppm (parts per million) concentrated solution.

(b) Hexachlorophene is mainly used in soaps, creams, dusting powders and emulsions.

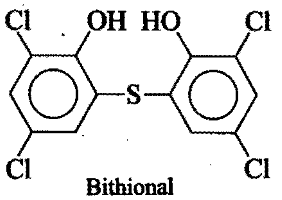
(c) Thymol, a natural derivative of phenol is a powerful disinfectant.



(d) Amyl meta cresol (5-methyl-2-pentyl phenol) is used as antiseptic in mouthwash or gargles in infections of the mouth and throat.

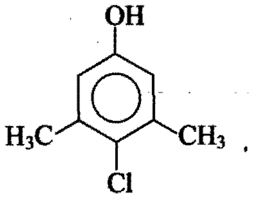


(e) Bithional is also used as an antiseptic in medicated soap. Such soaps are used to reduce undesirable odours due to bacterial action on skin surface.

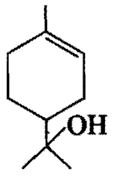


Bithional

(f) Dettol is one of the most commonly used antiseptic in the world. It is a mixture of **chloroxylenol** and **α-terpeneol** in a suitable solvent. Chloroxylenol (4-chloro-3,5-dimethyl phenol) is used both as an antiseptic and disinfectant. *p*-Chlorometaxylenol is also used as a body deodorant.



Chloroxylenol



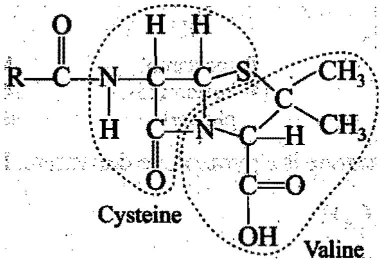
α-Terpineol

(g) Gention violet and methylene blue are organic dyes but used as effective antiseptic.

17.13 ANTIBIOTICS

The term antibiotics has been derived from the word ‘Antibiosis’ which means survival of fittest, *i.e.*, a process in which one organism may destroy another to preserve itself. **It is a chemical substance produced by or derived from living cells which is capable of inhibiting the life processes or even destroying microorganism.**

The first antibiotic, discovered by Alexander Fleming in 1929 from the mould *penicillium notatum,* was penicillin. In 1938, Ernst Chain and Howard Florey isolated penicillin in pure form and proved its effectiveness as an antibiotic. It was introduced into medical practice in 1941. Penicillin is used against large number of infections caused by various cocci, gram positive bacteria, etc. It is an effective drug for pneumonia, bronchitis, sore throat and abcesses.



General structure of penicillin

Several naturally occurring penicillins have been isolated. All of these have the empirical formula,

$$C_9H_{11}O_4SN_2R$$

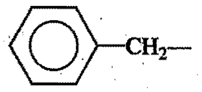
In penicillin, a four membered ring is fused to another five membered ring. Structures of individual penicillins are given in the table. Penicillin-G is the most commonly used.

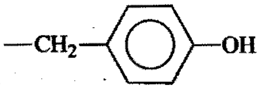
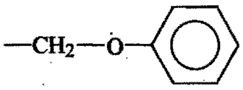
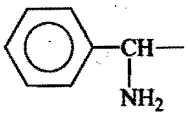
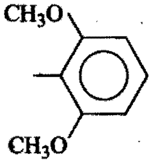
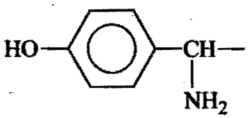
The penicillins are only sparingly soluble in water. However, their sodium or potassium salts are soluble in water. Penicillins are found to be active against gram positive stains. However, these are ineffective against gram negative organisms. Organisms sometimes develop resistance to penicillins. Penicillins generally have low toxicity in comparison to sulpha drugs. However, in some cases allergic reactions may result in. Penicillin is thus, given after a test prick.

The antibiotics can either be bactericidal or bacteriostatic. Examples are:

Bactericidal : The drugs which kill the organism in the body. For example, penicillin, oxloxacin, aminoglycosiders.

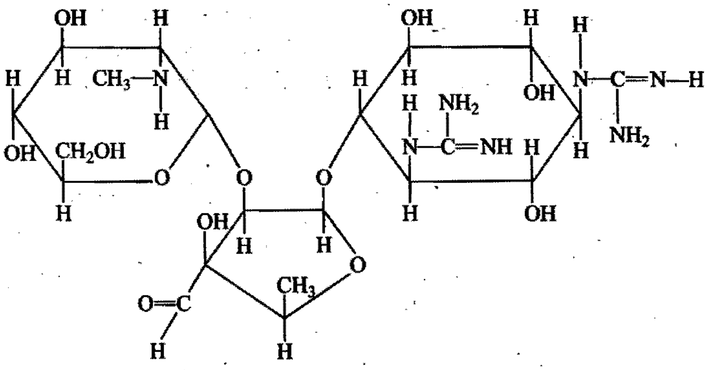
Bacteriostatic : The drugs which inhibit or check the growth of the organism in the body. For example, tetracycline, chloramphenicol and erythromycin.

	Name	Value of *R*	Chemical name
1.	Penicillin-G or II,		Benzyl penicillin
2.	Penicillin-F or I,	$—CH_2—CH=CH—CH_2—CH_3$	2-Pentenyl penicillin
3.	Penicillin-K or IV,	$—(CH_2)_6—CH_3$	*n*-Heptyl penicillin

	Name	Value of R	Chemical name
4.	Penicillin-X or III,		p-Hydroxy benzyl penicillin
5.	Penicillin-Y or V,		Phenoxy methyl penicillin
6.	Ampicillin		
7.	Methicillin		
8.	Amoxycillin		

Scientists have discovered a number of other antibiotics. These have proved to be as effective as penicillin but some of these are broad spectrum and are more effective. The commonly used are:

(i) Streptomycin : It was discovered in 1944 by Waksman. It is effective against tuberculosis (TB). It is also used for other common infections like throat, lungs, ears and kidney. It is very effective in the treatment of meningitis and pneumonia. Streptomycin is an amino base and forms salts that are very soluble in water. The sulphate and calcium chloride double salts are white amorphous powders. The molecule contains two strongly basic quanido groups and a weakly basic methylamino group.

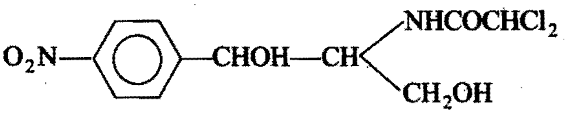


Streptomycin

Streptomycin is rapidly absorbed after an intramuscular injection. Oral administration of streptomycin is of no value in the treatment.

PAS (p-amino salicylic acid) and **INH** (isonicotin hydrazine or isoniazid) are also used for the treatment of tuberculosis.

(ii) Chloramphenicol : It is a broad spectrum antibiotic. It was first isolated from a species of *streptomyces*. It has been produced synthetically on commercial basis. It is white or greyish white needle like crystalline substance. It has a bitter taste. One gram of chloramphenicol is soluble in about 400 mL of water. It is freely soluble in alcohol.

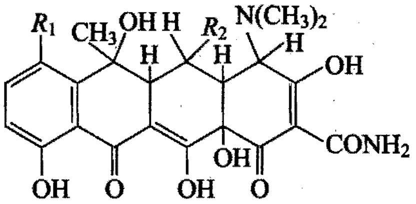


Chloramphenicol

It is effective against certain gram-positive and gram-negative bacteria, some rickettsiae and viruses. It is very effective in the treatment of typhoid fever, para-typhoid fevers, diarrhoea and dysentery. It is also specific for influenza, meningitis, pneumonia, whooping cough and urinary tract infection.

Chloramphenicol may cause serious complications and hence it should not be used indiscriminately or for minor infections. Chloramphenicol in high concentrations inhibits the growth of animal and plant cells.

(iii) Tetracyclines : The tetracyclines contain hydronaphthacene skeleton as the characteristic structural unit. The structures of tetracyclines are given below:



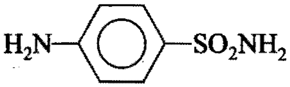
Chlorotetracycline (Aureomycin)	$R_1 = Cl, R_2 = H$
Oxytetracycline (Terramycin)	$R_1 = H, R_2 = OH$
Tetracycline	$R_1 = R_2 = H$

Tetracyclines are broad spectrum antibiotics and are effective against a number of types of bacteria, larger viruses, protozoa, parasites and typhus fever. These can be given orally.

17.14 ANTIMICROBIALS

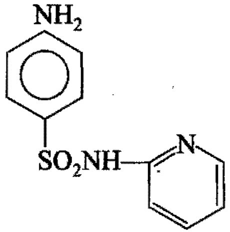
Chemical substances used to cure diseases caused by bacteria. fungi and viruses are called antimicrobials. These include antibacterials, antifungal and antiviral agents. Some important examples of antibacterial drugs are sulpha drugs, antibiotics and quinolones, etc.

Sulpha drugs : A group of drugs which are derivatives of *p*-amino benzene sulphonamide (Sulphanilamide) are called sulpha drugs.

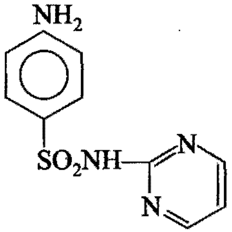


p-Amino benzene sulphonamide
(Sulphanilamide)

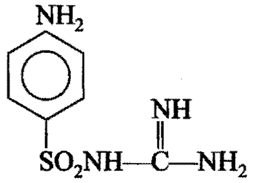
These were the first effective chemotherapeutic agents to be widely used for the cure of bacterial infections in humans. They have also been found to be active against gram-positive and gram-negative cocci, bacilli and protozoa. At present sulphanilamides have been largely replaced by antibiotics for the treatment of most of the bacterial diseases. Some successful sulphanilamides are given below:



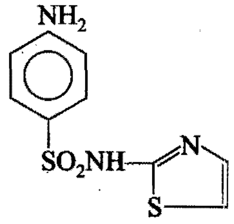
Sulphapyridine



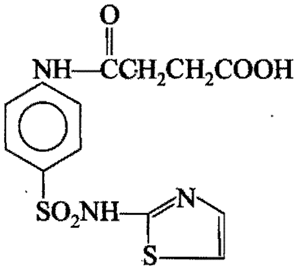
Sulphadiazine



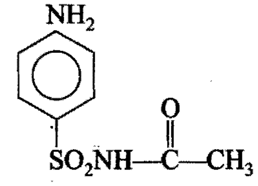
Sulphaguanidine



Sulphathiazol



Succinyl sulphathiazole



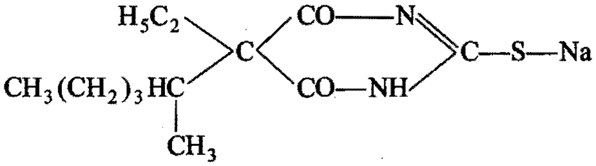
Sulpha acetamide

Sulphapyridine	:	used to cure pneumonia.
Sulphadiazine	:	used to cure pneumonia, throat infections, meningitis, etc.
Sulphaguanidine	:	used to cure bacillary dysentery.
Sulphathiazole	:	useful against staphylococcal infections and bubonic plague.
Succinyl sulphathiazole	:	useful in intestinal infections such as bacillary dysentery and cholera.
Sulpha acetamide	:	used to cure urinary tract infections.

17.15 ANAESTHETICS

Anaesthetics may be defined as those **drugs which produce insensibility to the vital functions of all types of cells especially of nervous system.** The effect produced by anaesthetic is reversible, *i.e.*, affected organs return to the normal state as soon as the concentration of the anaesthetic is decreased. Thus, anaesthetic produces temporary insensibility to pain or feeling in the whole body or a particular organ. Anaesthetics may be classified into two groups on the basis of their applications.

(i) General anaesthetics : These depress the central nervous system to such an extent that all sensitivity to pain or feeling is lost, *i.e.*, they produce unconsciousness all over the body. These are used for major surgical operations. These may be used in the form of a gas, *e.g.*, nitrous oxide, cyclopropane, ethylene, ether or may be given in the injection form, *e.g.*, sodium pentothal.



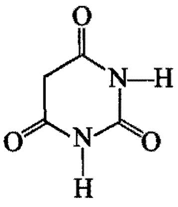
Sodium pentothal

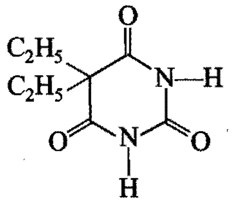
(ii) Local anaesthetics : These affect only a part of the body to make it insensitive to pain or feeling. Common local anaesthetics are : xylocaine (used in jelly form), ethyl chloride (used in spray form) and procaine (used in injection). These are used for small surgical operations like tooth extraction, stitching of a wound or incision of an abscess. Some other modern local anaesthetics are : α-eucaine, orthocaine (orthoform) and dimethisoquin.

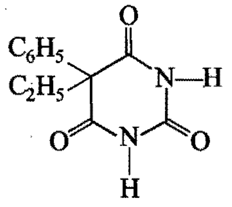
17.16 TRANQUILLIZER OR HYPNOTICS

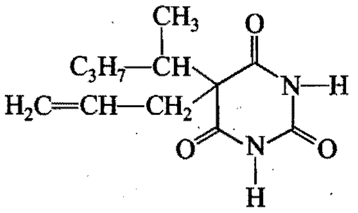
The chemicals which **bring about reduced mental tension, relieve anxiety** and result in a more calm outlook without producing any marked degree of sedation or hypnosis or without grossly altering the level of consciousness are called tranquillizers. Tranquillizers are effective in such mental disorders when ordinary hypnotics or sedatives fail. These are also called as **psychotherapeutic drugs.**

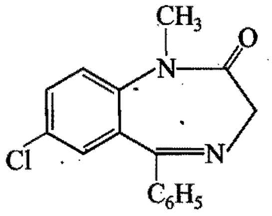
Two powerful drugs called reserpine (an alkaloid) and chlorpromazine were introduced simultaneously. The other drugs in common use are barbituric acid and its 5,5-disubstituted derivatives (barbiturates) such as veronal, amytal, luminal, equanil, seconal, librium, diazepam (valium, calmpose), etc.

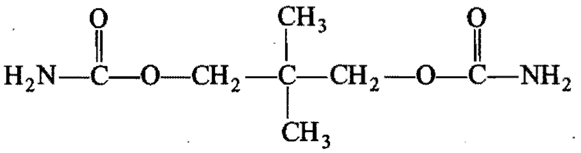

Barbituric acid


Veronal or (Barbital)


Luminal


Seconal


Valium (Diazepam)



$$H_2N-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-NH_2$$

Equanil

Note : Equanil is an important medicine used in depression and hypertension.

Drugs used in the treatment of mental disease can be classified as:

(i) Narcotics : These are used as *analgesic* and *depressant*. It reduces anxiety and tension, *e.g.*, pethidine, heroin, opium, etc.

(ii) Hypnotics : These are tranquillizers, used to reduce anxiety and mental tension.

(iii) Sedatives : It reduce the action of central nervous system. These are also called as depressant. These are used for the violent mental patients. It induces the feeling or relaxation, calmness and drowsiness. Some common sedatives are *valium* and *barbiturates.*

(iv) Antidepressants : These drugs are given to the patients having lack of confidence. These are also called mood boosters. It induces the feeling of well being. Some examples are *vitalin*, *methadrine* and *cocain.*

17.17 ANTI-MALARIALS

Medicines used to bring down the body temperature during malaria fever are called anti-malarials. Originally quinine (an alkaloid) was the only drug known to be effective against malaria.

Malaria is a highly widespread infectious disease, caused by sporozoa of genus *Plasmodium*. It is characterised clinically by periodic fever, anaemia and enlargement of liver and spleen. The four species, *Plasmodium vivax, Plasmodium malariae, Plasmodium ovale* and *Plasmodium falciparum* are responsible for malaria in humans. Thus, there are four types of malaria:

Protozoa	**Malaria caused**
Plasmodium vivax	Fever on alternate days
Plasmodium malariae	Fever once in three days
Plasmodium ovale	Fever once in three days
Plasmodium falciparum	Fever once in four days

The chemotherapy of malaria is connected with different stages in the cycle of malarial parasite. The mosquito injects the parasite into the blood of a human being. It immediately goes to the liver cells where it multiplies. Once the parasites have grown in number, these come to blood and enter the red blood corpuscles where they also multiply. Eventually, the red cells burst liberating the parasites as well as toxins. These toxins cause fever, chills and rigour. The liberated parasites attack the fresh red cells and the cycle continues. Depending upon the periodicity of this cycle in the red cells fever comes on alternate days, once in three days or once in four days. Some of the liberated parasites go back to liver and continue the cycle there.

Choice of an anti-malarial drug depends on the point of its action on the life cycle of the malarial parasite. Various drugs used are:

1. Primaquine : It destroys sporozites in the liver. It is too toxic and its long term use is not advisable.

2. Chloroquine, proquanil and pyrimethamine: These kill the parasites in blood.

17.18 ANTACIDS

Intestine is acidic due to the formation of HCl during digestion. Excessive acidity in the intestine creates problem of intestinal ulcer, gastric reflux and oesophagitis. **The**

compounds which reduce or neutralise acidity are called antacids. Some commonly used antacids are discussed below:

(i) Baking soda containing $NaHCO_3$ and $KHCO_3$.

(ii) MgO, $Mg(OH)_2$, $MgCO_3$ and magnesium trisilicate

(iii) $CaCO_3$

(iv) $Al(OH)_3$, $AlPO_4$ and aluminium amino acetate. Above compounds are basic and thereby neutralise HCl, *e.g.*,

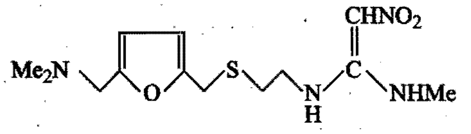
$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

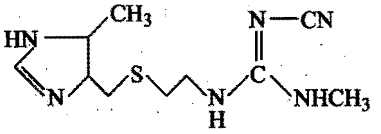
$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$$

Antacid can be used in the form of liquid (solution) and in the form of tablets, but solution is more effective antacid.

Note: (i) **Rantidine** and **Cimetidine** are used in the treatment of peptic ulcers.

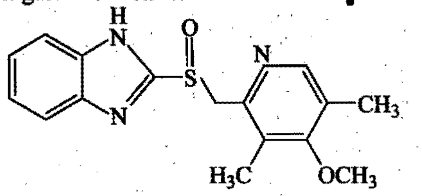


Ranitidine (Zantac)



Cimetidine (Tegamet)

(ii) **Pentaprazole** and **Omiprazole** are the new drugs used to inhibit gastric secretion.



Omeprazole

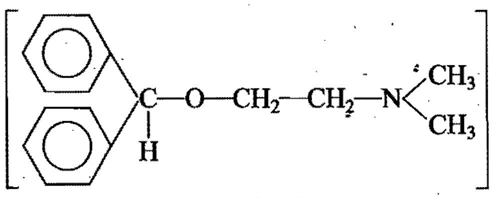
17.19 ANTI-HISTAMINES

Antigens from environment and food create allergic reactions to our body. In this situation **histamines** are released from certain cells in our body.

Anti-histamines are the drugs which diminish or abolish the effects of histamine, a chemical released by mast cells during an allergic reaction.

Some commonly used anti-histamines are:

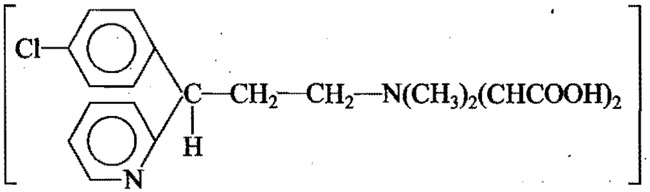
(i) Diphenhydramine (Benadryl)



Diphenhydramine

(ii) Pheniramine maleate (Avil and cough syrups)

(iii) Chloropheniramine maleate (Zeet)



(iv) Triprolidine (Acididil)

(v) Phenothiazine, Promethazine (Phenargan)

(vi) Dimethindene (Foristal)

(vii) Antazoline (Antistine)

(viii) Chlorotheopyllinate salt (Avomine)

These drugs are used in the treatment of hay fever, mild asthma, insect bites, cold etc.

17.20 CHEMICALS IN FOOD

The chemicals used in food are preservatives, edible colours, artificial sweetening agents and antioxidants. Such chemicals are discussed below in short.

1. Preservatives : According to British Food and Drug Act of 1928, a preservative may be defined as *the substance which is capable and inhibiting or arresting the process of fermentation, acidification or any other decomposition of food.*

Preservatives are classified into the following three categories depending upon course of action:

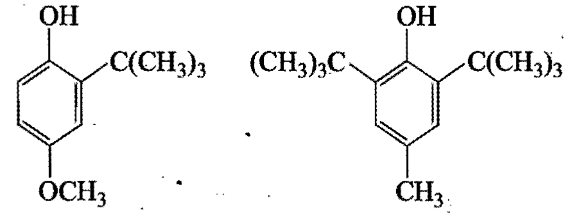
(a) Antioxidant preservatives : These are the substances that retard the chemical reactions and break down of foods when they come in contact with oxygen, light, heat and certain metals. These chemicals also stabilize some of the vitamins and amino acids present in food. Examples of antioxidant preservatives are:

(i) Butylated Hydroxy Anisole (BHA)

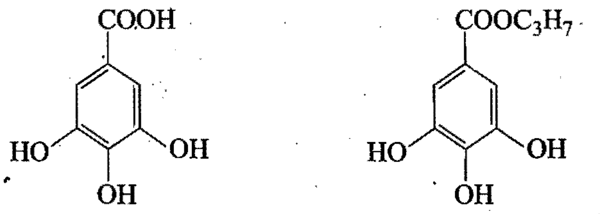
(ii) Butylated Hydroxy Toluene (BHT)

(iii) Tertiary butyl hydroquinone

(iv) Propyl gallate



Butylated hydroxy anisole (BHA) Butylated hydroxy toluene (BHT)



Gallic acid Propyl gallate

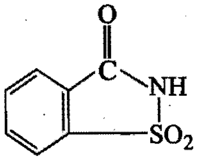
(Antioxidants)

(b) Antiripening agents : These are used to preserve food specially fruits and vegetables. These chemicals attack the enzymes which metabolize the food after harvesting. Example of antiripening agents are : citric acid, ascorbic acid and disodium salt of ethylene diamine tetraacetic acid (EDTA).

(c) Antimicrobial preservatives : Such chemicals inhibit the growth of yeast, bacteria or moulds. Examples of such preservatives are : sorbates and esters of *p*-hydroxy benzoic acid, sodium nitrite, sodium sulphite, calcium propionate and benzoates, etc.

Note : In addition to sugar and salt the substances such as vinegar, oils, spices and citric acid are also used to preserve jam, pickles, ketchups and squashes, etc.

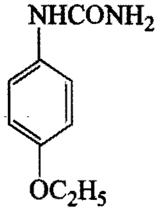
(2) Artificial sweetening agents : Artificial sweeteners have been in use since the discovery of saccharin in the 1880s. Its structure (*o*-Sulphobenzoic imide) is given below:



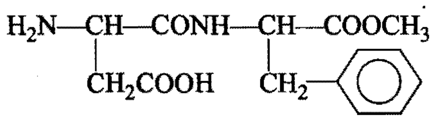
(Saccharin; 1,2-benzisothiazolin-3-one, 1,1-dioxide)

Saccharin is 500 times sweeter than sucrose. Sodium salt of saccharin is water soluble and more palatable. Examples of some other artificial sweetener are: sucralose, dulcin, nitroanilines, aspartame and acesulfame-potassium.

Artificial sweeteners are also called as low calorie sweeteners because these chemicals pass through human body unmetabolised. A polyhydroxy compound called xylitol is used as a sweeteners in sugarless gum.



Dulcin
(*p*-phenethyl urea)



Aspartame

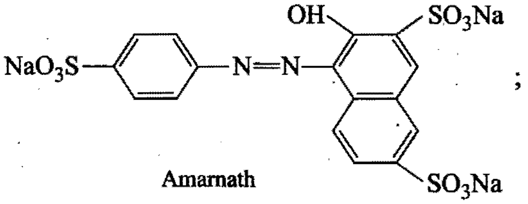
Note : Aspartame breaks down in the body into menthol and naturally occurring amino acid.

(3) Edible colours : The colours that can be added to the food without harmful side effects are known as edible colours. The colours increase the eye appeal and compliment a definite flavour. Edible colours should be stable to acids, alkalies, light and high temperature. Edible colours may be of natural or synthetic origin.

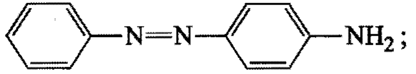
The commonly used natural colours are:

(i) Chlorophyll (green colouring matter from leaves)
(ii) Saffron (prepared from saffron flowers)
(iii) Turmeric (dried roots)
(iv) Caramel (prepared by strongly heating the sugar)
(v) Cochineal or caramine (obtained from dried female insects)
(vi) β-carotene (from carrot)
(vii) Alizarine, Indigo (dyes from plant origin)

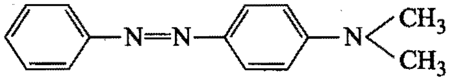
Synthetic edible colours are also frequently used. Aniline dyes, azodyes replace natural colours. For example, **amarnath, aniline yellow, butter yellow** are frequently used azo dyes. Amarnath gives magenta colour in aqueous medium.



Amarnath



Aniline yellow



Butter yellow

Some other synthetic edible colours are tabulated below:

Common name of colour	Colour
Erythrosine	bluish pink
Allura red	yellowish red
Sunset yellow	reddish yellow
Tetrazine	lemon yellow
Indigoline	deep blue
Carmoisine	fast red
Ponceau	fast green

17.21 ROCKET PROPELLANTS

A number of satellites have been launched by different countries. India launched its first successful satellite vehicle, SLV-3 from Sriharikota on July 18, 1980. In order to push these rocket satellites into the space, some chemical substances are used. These **substances (fuels) used for launching rockets are called rocket propellants.** A propellant is a combination of an **oxidiser** and a **fuel** which when ignited undergoes combustion to release large volume of hot gases. When these hot gases are passed through a narrow nozzle of the rocket motor, it provides the necessary thrust for the rocket uplift in accordance with Newton's third law of motion.

Type of Rocket Propellants

Depending upon the physical state, the propellants can be classified as:

1. Solid propellants,
2. Liquid propellants,
3. Hybrid propellants.

1. Solid propellants : They are the mixtures of solid fuel and solid oxidiser. These are further divided into two classes:

(a) Composite propellants : These propellants use a polymeric binder such as polyurethane or polybutadiene as a fuel and ammonium perchlorate as an oxidiser. The performance of these propellants can be increased by using some additives such as finely divided magnesium or aluminium metal along with the fuel.

(b) Double base propellants : These mainly use nitroglycerine (liquid) and nitrocellulose (solid). The nitrocellulose gels in nitroglycerine sets in as a solid mass.

The main **disadvantage** of solid propellants is that these propellants once ignited will continue burning with a predetermined rate without having a start or stopping capability.

2. Liquid propellants : These consist of an oxidiser such as liquid oxygen, dinitrogen tetraoxide (N_2O_4) or nitric acid and a fuel such as kerosene, alcohol, hydrazine or liquid hydrogen. These are further divided into two types:

(a) Monopropellants : The liquid propellants in which a single chemical substance acts both as a fuel as well as an oxidiser are called monopropellants. For example, hydrazine (H_2NNH_2), nitromethane (CH_3NO_2), methyl nitrate (CH_3ONO_2) and hydrogen peroxide (H_2O_2), etc. Among these, except hydrazine, all other compounds serve both as a fuel as well as an oxidiser.

(b) Bi-liquid propellants : These consist of two liquids in which one of them acts as a fuel, while the other acts as the oxidiser. Most commonly used liquid fuels are kerosene, alcohol, hydrazine, monomethyl hydrazine **(MMH)**, unsymmetrical dimethyl hydrazine **(UDMH)** or liquid hydrogen, etc., while the most commonly used liquid oxidisers are liquid oxygen, liquid dinitrogen tetraoxide (N_2O_4) or nitric acid.

Advantages of Bi-liquid Propellants over Solid Propellants

(i) The bi-liquid propellants give higher thrust than solid propellants.

(ii) The thrust generated by liquid propellants can be controlled by switching on and off the flow of propellants. On the other hand, the thrust cannot be controlled in solid propellants.

3. Hybrid propellants : These consist of a solid fuel and a liquid oxidiser. For example, acrylic rubber (solid fuel) and liquid N_2O_4 (liquid oxidiser).

Examples of propellants used in different rockets

(i) Saturn Booster Rocket of American Space Programme : Used a mixture of kerosene and liquid oxygen as a propellant in the initial stage whereas liquid oxygen and liquid hydrogen were used for the upper stages.

(ii) The Titan Ballistic Missile : Used a mixture of hydrazine (fuel) and N_2O_4 (oxidiser).

(iii) PROTON (a Russian Rocket) : Used kerosene and liquid oxygen as liquid propellant.

(iv) SLV-3 (Space Launch Vehicle-3) and ASLV (Augmented Space Launch Vehicle), the Indian Satellites: Used composite solid propellants.

(v) PSLV (Polar Space Launch Vehicle), the Indian Rocket Recently Launched : Used solid propellants in the first and third stages and bi-liquid propellants such as N_2O_4 + **UDMH** (Unsymmetrical dimethyl hydrazine) in the second stage and $\mathbf{N_2O_4}$ + **MMH** (Mono methyl hydrazine) in the fourth stage.

(vi) Space Shuttle : Used liquid oxygen and liquid hydrogen along with solid boosters in the lower stages.

QUESTIONS

1. [A] Fill in the blanks:

(a) The monomer of natural rubber is ....
(b) The monomers of terylene are terephthalic acid and ....
(c) The starting raw materials for nylon-6,6 are adipic acid and ....
(d) Rubber particles in latex are coagulated by adding .....
(e) The monomer of teflon is ....
(f) Protein is a ...... polymer.
(g) Substances which lower body temperature in high fevers are called ....
(h) The chemical name of aspirin is ....
(i) Indigo is a...... dye while alizarin is a ...... dye.
(j) Phenol is used as an/a ...... and ....
(k) Phenacetin, paracetamol and methacetin are used as ....
(l) The drugs which relieve or decrease pain are called ....
(m) Streptomycin is a ...... spectrum antibiotic.
(n) Chloroquine is an ...... drug.
(o) The melamine-formaldehyde resin is quite ...... polymer. The articles made from this polymer...... even dropped from considerable height.
(p) Salol is used as ....
(q) Bakelite is made by the action of...... and ....
(r) Tincture of iodine is 2-3% solution of .... in alcohol-water.
(s) Equanil is used as ....
(t) A group with multiple bonds in an organic dye molecule is known as ....
(u) The auxochromes ...... the colour of chromogen.
(v) Malachite green is an example of...... dyes.
(w) ...... is used in the manufacture of paints and lacquers.
(x) ...... is used for the treatment of typhoid.
(y) Alizarin is a typical...... dye.
(z) Vinyl chloride on reaction with dimethyl copper gives ....

[B] Fill in the blanks:

	Monomers	Polymers	Other important use
(i)	Formaldehyde, phenol	....	....
(ii)	....	Teflon	....
(iii)	....	PMMA	....
(iv)	Chloroprene	....	....
(v)	....	....	For making crockery
(vi)	....	Orlon	....
(vii)	Adipic acid, hexamethylene diamine	....	....
(viii)	....	Glyptal	....

2. State, whether the following statements are **True** or **False:**

(a) The colour of the dye is due to auxochrome group.
(b) Aspirin is an antibiotic.
(c) Indigo is a mordant dye.
(d) Cellulose nitrate is a natural polymer.
(e) The bakelite is a thermosetting plastic.
(f) 2-Chlorobutadiene is a monomer of synthetic rubber.
(g) Paracetamol is an antipyretic drug.
(h) Calmpose is a tranquillizer.
(i) PVC is a step growth polymer.
(j) Acid dyes are used in basic medium.
(k) Nylon is a polyamide polymer.
(l) Terylene is a polyamide polymer.
(m) Bakelite is an example of thermoplastic.
(n) Thermoplastic polymer is one which softens on heating and becomes hard on cooling.
(o) Tranquillizers affect the central nervous system and induce sleep.
(p) Buna-S is obtained by polymerization of butadiene and styrene.
(q) Glyptal is obtained by polymerization of glycol and terephthalic acid.
(r) Methyl orange is an azo dye.
(s) Chemotherapy means use of chemicals to destroy infectious microorganisms without causing any injury to host.
(t) Phenyl butazone is considered as a safe drug.
(u) Sulphapyridine is used to cure pneumonia.
(v) Streptomycin is administrated orally.
(w) Penicillin is an effective drug for pneumonia, bronchitis and abcesses.
(x) Tetracyclines are effective in the treatment of typhoid fever, diarrhoea and dysentary.
(y) Chloramphenicol is a broad spectrum antibiotic.
(z) In propellant, the burning of a fuel should not leave any ash.

3. [A] Match the following:

(a) Natural rubber	(1) Thermosetting polymer
(b) Buna-S	(2) Homopolymer
(c) Nylon-6,6	(3) Antibiotic
(d) Bakelite	(4) Acid dye
(e) Melamine	(5) Antiseptic
(f) Orlon	(6) Basic dye
(g) Terramycin	(7) Butadiene and styrene
(h) Iodine	(8) Melamine-formaldehyde resin
(i) Malachite green	(9) Isoprene
(j) Martius yellow	(10) Polyamide

[B]

(a) Penicillin	(p) Bacteriostatic
(b) Chloramphenicol	(q) Antibiotic

(c) Aspirin	(r) Bactericidal
(d) Ibuprofen	(s) Analgesic
	(t) Antipyretic

[C]

(a) Cellulose	(p) Natural polymer
(b) Nylon-6,6	(q) Synthetic polymer
(c) Protein	(r) Amide linkage
(d) Sucrose	(s) Glycoside linkage

[IIT 2007]

[D]

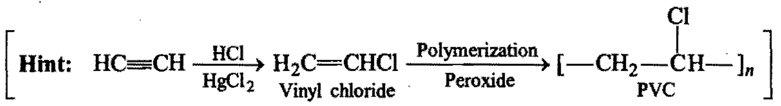
(a) Sodium perbenzoate	(p) Disinfectant
(b) Chlorine	(q) Antiseptic
(c) Bithional	(r) Milk bleaching agent
(d) Potassium stearate	(s) Soap

[DCE 2009]

4. Write the names and structures of the monomers of the following polymers:
(i) Natural rubber, (ii) Synthetic rubber, (iii) Nylon-6,6, (iv) Polythene, (v) PVC, (vi) Teflon, (vii) Terylene, (viii) Bakelite, (ix) Polypropylene, (x) Neoprene, (xi) Plexiglas.

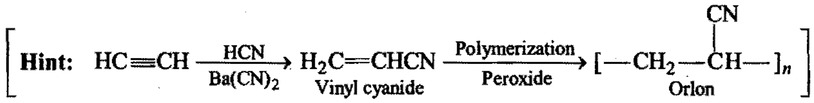
5. How will you synthesise?

(a) Polyvinyl chloride (PVC) from acetylene.



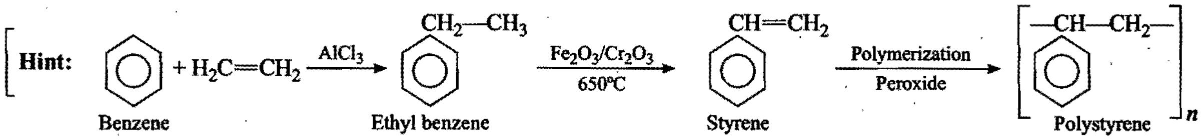
$$\left[\textbf{Hint: } HC{\equiv}CH \xrightarrow[HgCl_2]{HCl} \underset{\text{Vinyl chloride}}{H_2C{=}CHCl} \xrightarrow[\text{Peroxide}]{\text{Polymerization}} \underset{\text{PVC}}{[-CH_2-\overset{\overset{Cl}{|}}{C}H-]_n}\right]$$

(b) Orlon from acetylene.

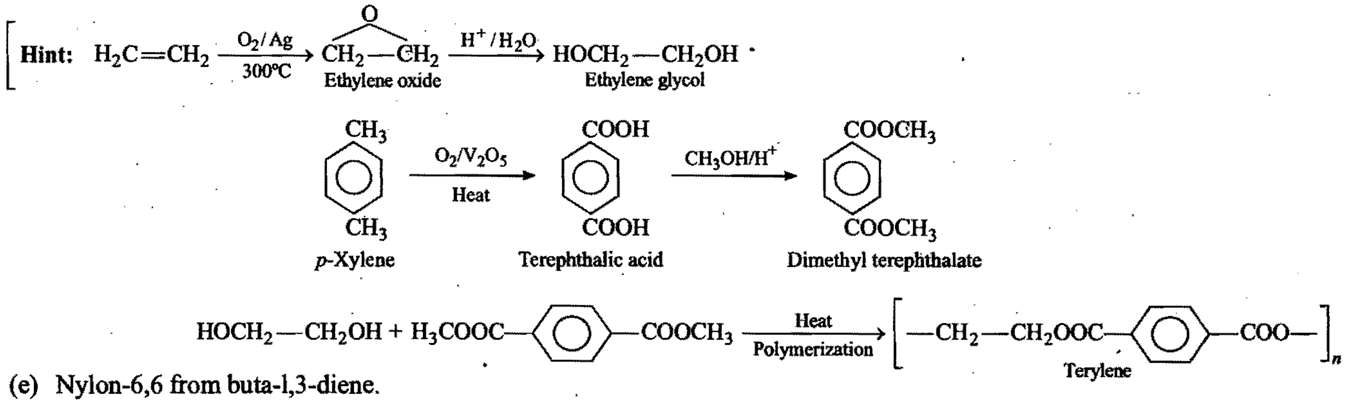


$$\left[\textbf{Hint: } HC{\equiv}CH \xrightarrow[Ba(CN)_2]{HCN} \underset{\text{Vinyl cyanide}}{H_2C{=}CHCN} \xrightarrow[\text{Peroxide}]{\text{Polymerization}} \underset{\text{Orlon}}{[-CH_2-\overset{\overset{CN}{|}}{C}H-]_n}\right]$$

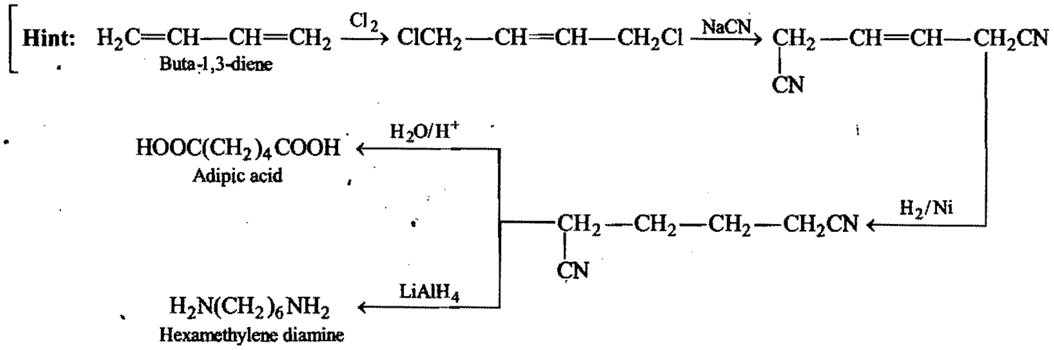
(c) Polystyrene from benzene.



(d) Terylene from ethylene and *p*-xylene.



(e) Nylon-6,6 from buta-1,3-diene.



$$n\text{HOOC(CH}_2)_4\text{COOH} + n\text{NH}_2(\text{CH}_2)_6\text{NH}_2 \xrightarrow[277°\text{C}]{\text{High pressure}} \text{Nylon-6,6} + n\text{H}_2\text{O}\ ]$$

6. Describe how the following polymers are synthesised? (i) Nylon-6,6, (ii) Thiokol, (iii) Buna-S, (iv) Bakelite, (v) Terylene, (vi) Melamine, (vii) Nylon-6.

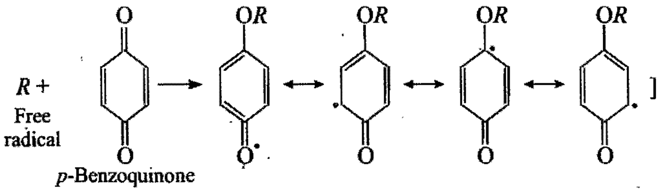
7. Write the short notes on the following: (a) Co-polymer, (b) Synthetic rubber, (c) Thermoplastic, (d) Thermosetting, (e) Elastomer, (f) Vulcanization of rubber.

8. Write the free radical mechanism for the polymerization of ethene.

   [**Hint:** Free radical mechanism for polymerization of ethene is initiated by organic peroxide or other reagents which decompose to give free radicals [Refer to sec. 17.2 (3)] 1037.

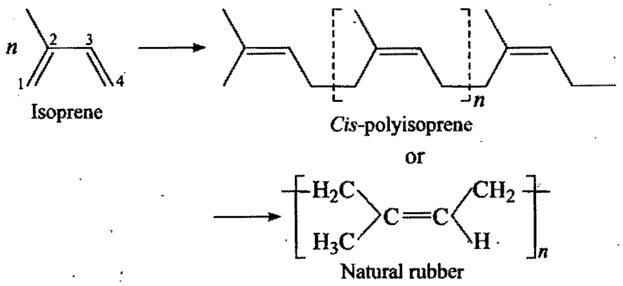
9. How does the presence of benzoquinone inhibit the free radical polymerization of vinyl derivative?

   [**Hint:** Benzoquinone combines with free radical intermediate to form a non-reactive free radical, which is highly stabilized by resonance. Because of the lack of reactivity of this intermediate, it inhibits the further progress of the chain reaction and the reaction stops.



10. How does the presence of double bonds in rubber molecules influence their structure and reactivity?

    [**Hint:** From the structural point of view, the natural rubber is a linear *cis*-1,4-polyisoprene. In this polymer, the double bonds are located between C_2 and C_3 of each isoprene unit. The *cis*-configuration about double bonds do not allow the chain to come closer for effective interactions and hence intermolecular forces are quite weak. Therefore, the natural rubber has a coiled structure and shows elasticity.]



11. Answer the following:
    (i) What does 6,6 indicate in nylon-6,6 ? In what way it is different from nylon-6?
    (ii) What is the effect of heating on (a) thermoplastics and (b) thermosetting plastics?
    (iii) What type of drug phenacetin is?
    (iv) Name the chemical responsible for antiseptic properties of dettol.
    (v) Give the name of first antibiotic.
    (vi) Give the name with structure of a broad spectrum antibiotic.
    (vii) Name the drug which is used to bring down body temperature during fever.
    (viii) What type of drug chloramphenicol is ?
    (ix) What are tranquillizers ?
    (x) What are direct dyes ?

12. Select acid dyes, basic dyes, vat dyes and mordant dyes from the following:
    Alizarin; Malachite green; Martius yellow; Indigo; Orange-1; Aniline yellow.

13. (a) Give four examples of chromophore groups.
    (b) Give two examples of direct dyes.
    (c) Write the one name of each of the following:
        (i) Nitro dye, (ii) Azo dye, (iii) Triphenyl methane dye.
    (d) Give one use of each of the following :
        (i) Morphine, (ii) LSD, (iii) Streptomycin, (iv) Saccharin.

14. Write the short notes on the following:
    (a) Chromogen, (b) Auxochromes, (c) Ingrain dyes, (d) Azo dyes, (e) Disperse dyes, (f) Mordant dyes, (g) Vat dyes, (h) Basic dyes.

15. Answer the following:
    (i) Name a drug in case of mental depression.
    (ii) Write the names of some antacids.
    (iii) Write the name of chemicals used in food.
    (iv) Give four examples of anti-histamines.
    (v) Name the medicines which can act both as an analgesic as well as an antipyretic.
    (vi) Name the main species responsible for malaria.
    (vii) Which alkaloid is used for? **[CBSE (Med.) 2005]**
        (a) Hypertension (b) Malaria fever

16. Distinguish between:
    (i) Antipyretics and antiseptics.
    (ii) Antiseptics and disinfectants.
    (iii) Broad spectrum and narrow spectrum antibiotics.
    (iv) General and local anaesthetics.
    (v) Narcotics and hypnotics.
    (vi) Antioxidant and antimicrobial preservatives.

17. What are bi-liquid propellants? Give their advantages over solid propellants?

18. What are propellants? What type of propellant is used in SLV-3 and ASLV rockets?

19. What is the role of monomethyl and dimethyl hydrazines in rockets?

ANSWERS

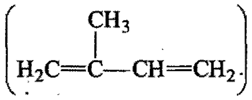
1. [A] (a) isoprene; (b) ethylene glycol; (c) hexamethylene diamine; (d) dilute acetic acid; (e) tetrafluoro ethylene; (f) condensation/natural; (g) antipyretics; (h) acetyl salicylic acid; (i) vat, mordant; (j) antiseptic, disinfectant; (k) antipyretic; (l) analgesics; (m) broad; (n) antimalarial; (o) hard, do not break; (p) antiseptic; (q) phenol, formaldehyde; (r) iodine; (s) tranquillizer; (t) chromophore; (u) deepen; (v) basic; (w) glyptal; (x) chloramphenicol; (y) anthraquinone; (z) polyvinyl chloride.

[B] (i) Bakelite, manufacture of electric goods
(ii) Tetrafluoro ethylene, manufacture of insulators
(iii) Methyl methylacrylate, for making eye lenses
(iv) Neoprene, for making automobiles and refrigerator parts
(v) Melamine, formaldehyde, melamine formaldehyde resin
(vi) Vinyl cyanide, for making carpets and blankets
(vii) Nylon 6,6, for making carpets and textile fibres
(viii) Ethylene glycol, phthalic acid, for manufacture of paints and lacquers.

2. (a) False, (b) False, (c) True, (d) False, (e) True, (f) True, (g) True, (h) True, (i) False, (j) False, (k) True, (l) False, (m) False, (n) True, (o) True, (p) True, (q) False, (r) True, (s) True, (t) False, (u) True, (v) False, (w) True, (x) False, (y) True, (z) True.

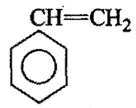
3. [A] (a–9); (b–7); (c–10); (d–1); (e–8); (f–2); (g–3); (h–5); (i–6); (j–4);
[B] (a–q,r); (b–p,q); (c–s,t); (d–s,t);
[C] (a–p,s); (b–q,r); (c–p,r); (d–s);
[D] (a–r); (b–p); (c–q); (d–s)

4. (i) Isoprene



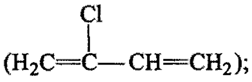
$\left(H_2C{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2\right)$;

(ii) 1,3-Butadiene ($H_2C{=}CH{-}CH{=}CH_2$) and styrene



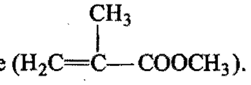
;

(iii) Hexamethylene diamine [$H_2N(CH_2)_6NH_2$] and adipic acid [$HOOC(CH_2)_4COOH$];
(iv) Ethylene ($H_2C{=}CH_2$);
(v) Vinyl chloride ($H_2C{=}CHCl$);
(vi) Tetrafluoro ethylene ($F_2C{=}CF_2$);
(vii) Ethylene glycol ($HOCH_2{-}CH_2OH$) and phthalic acid;
(viii) Phenol and formaldehyde;
(ix) Propylene ($CH_3CH{=}CH_2$);
(x) Chloroprene



($H_2C{=}\overset{Cl}{\overset{|}{C}}{-}CH{=}CH_2$);

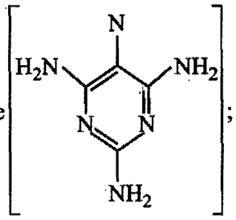
(xi) Methyl methylacrylate



($H_2C{=}\overset{CH_3}{\overset{|}{C}}{-}COOCH_3$).

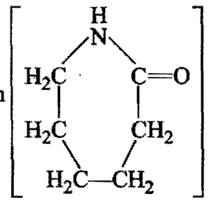
6. (i) Hexamethylene diamine [$H_2N(CH_2)_4NH_2$] and adipic acid [$HOOC(CH_2)_4COOH$]; (ii) Ethylene chloride [$ClCH_2{-}CH_2Cl$] and sodium polysulphide [$Na{-}S{-}S{-}Na$]; (iii) Buta-1,3-diene [$H_2C{=}CH{-}CH{=}CH_2$] and styrene [$C_6H_5CH{=}CH_2$];
(iv) Formaldehyde [HCHO] and phenol [C_6H_5OH];
(v) Ethylene glycol [$HOCH_2{-}CH_2OH$] and dimethyl terephthalate [$H_3COOC(C_6H_4)COOCH_3$];

(vi) Formaldehyde [HCHO] and melamine



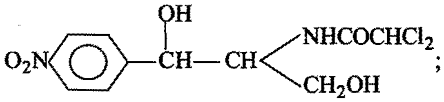
;

(vii) Caprolactum



on heating at 260–270°C.

11. (i) Nylon-6,6 gets its name from its two constituents, adipic acid and hexamethylene diamine, both of which have six carbon atoms each. Nylon-6 is prepared by prolonged heating of caprolactum at 260°–270°C (It has six carbon atoms in repeating units.); (ii) Thermoplastics soften and melt on heating while thermosetting polymers do not soften on heating rather become hard; (iii) Antipyretic; (iv) Chloroxylenol; (v) Penicillin; (vi) Chloramphenicol,



; (vii) Paracetamol or aspirin; (viii) Antibiotic; (ix) The chemical compounds which relieve anxiety and result in a more calm outlook without producing any marked degree of sedation or hypnosis are called tranquillizers; (x) The direct dyes can be directly applied to fibre.

12. Alizarin—Mordant dye
Indigo—Vat dye
Malachite green, Aniline yellow—Basic dyes
Martius yellow, Orange-1—Acidic dyes

15. (i) Equanil or Vitalin;
(ii) Ranitidine, Cimetidine, Omeprazole and Pentaprazole, etc;
(iii) (a) Preservatives (Sodium benzoate) (b) Antioxidants (BHA, BHT); (c) Artificial sweetening agents (saccharin); (d) Edible colours (Chlorophyll, Saffron);
(iv) (a) Diphenhydramine (Benadryl); (b) Pheniramine maleate (Avil and Cough syrups); (c) Promethazine (Phenargan); (d) Chlorotheopyllinate salt (Avomine);
(v) Aspirin, Paracetamol, Ibuprofen, Diclofenac sodium, Combiflam, etc; (vi) Plasmodium vivax, Plasmodium malariae, Plasmodium ovale, Plasmodium falciparum;
(vii) (a) Reserpine (b) Quinine.

OBJECTIVE QUESTIONS

SET I : This set contains the questions with single correct answer.

1. Which of the following is a natural polymer?
(a) Protein ☐ (b) Polythene ☐
(c) Buna-S ☐ (d) Bakelite ☐

2. The monomers used in the manufacture of nylon-6,6 are:
(a) sebacic acid and hexamethylene diamine ☐
(b) adipic acid and butadiene ☐
(c) sebacic acid and butadiene ☐
(d) adipic acid and hexamethylene diamine ☐

3. PVC polymer can be prepared by which of the monomers? **[JEE (WB) Engg. 2006]**
(a) $CH_3CH{=}CH_2$ ☐ (b) $C_6H_5CH{=}CH_2$ ☐
(c) $H_2C{=}CHCl$ ☐ (d) $H_2C{=}CH_2$ ☐

4. Which of the following sets contains only addition polymers?
(a) Polyethylene, polypropylene, terylene ☐
(b) Polyethylene, PVC, acrilon ☐
(c) Buna-S, nylon, polybutadine ☐
(d) Bakelite, PVC, polyethylene ☐

5. Which of the following fibres is not made up of polyamides? **[MGIMS (Med.) 2008]**
(a) Artificial silk ☐ (b) Natural silk ☐
(c) Wool ☐ (d) Nylon ☐

6. Nylon is:
(a) polyester fibre ☐
(b) polyamide fibre ☐
(c) polythene derivative ☐
(d) polyethylene methyl acrylate fibre ☐

7. Which of the following is an antibiotic?
(a) Terramycin ☐ (b) Aspirin ☐
(c) Paracetamol ☐ (d) Chloroquine ☐

8. Which of the following is used as antipyretic?
(a) Paracetamol ☐ (b) Chloroquine ☐
(c) Chloramphenicol ☐ (d) LSD ☐

9. Point out the wrong statement.
(a) Penicillin was discovered by A. Fleming ☐
(b) Phenacetin is a very important antibiotic ☐
(c) Chloroquine is an antimalarial drug ☐
(d) Ether is an anaesthetic ☐

10. Which of the following groups would you introduce into a dye to make it water soluble?
(a) $—NO_2$ ☐ (b) —Cl ☐
(c) $—SO_3H$ ☐ (d) —OH ☐

11. A dye absorbs the wavelength corresponding to blue colour of light. The observed colour will be:
(a) blue ☐ (b) red ☐
(c) green ☐ (d) orange ☐

12. Which one is an example of vat dye?
(a) Congo red ☐ (b) Alizarin ☐
(c) Malachite green ☐ (d) Indigo ☐

13. With which of the following cations, alizarin will impart a violet colour on the fabrics?
(a) Fe^{3+} ☐ (b) Cr^{3+} ☐
(c) Ba^{2+} ☐ (d) Al^{3+} ☐

14. Aspirin is a/an: **[BHU 2005]**
(a) narcotic ☐ (b) antipyretic ☐
(c) tranquillizer ☐ (d) anaesthetic ☐

15. Which one is a protein fibre?
(a) Cotton ☐ (b) Rayon ☐
(c) Silk ☐ (d) Polyester ☐

16. LSD (Lysergic acid diethylamide) is:
(a) sweetening agent ☐ (b) synthetic fibre ☐
(c) psychedelic drug ☐ (d) antibiotic ☐

17. The antibiotic used for the treatment of typhoid is:
(a) penicillin ☐ (b) chloramphenicol ☐
(c) terramycin ☐ (d) sulphadiazine ☐

18. Reserpine is:
(a) tranquillizer ☐ (b) antibiotic ☐
(c) vitamin ☐ (d) hormone ☐

19. Which one of the following is a chromophore group?
(a) —N=N— ☐ (b) —OH ☐
(c) $—SO_3H$ ☐ (d) $—NH_2$ ☐

20. Which one of the following statements is wrong?
(a) PVC stands for polyvinyl chloride ☐
(b) PTFE stands for teflon ☐
(c) PMMA stands for polymethyl methyl acrylate ☐
(d) Buna-S stands for natural rubber ☐

21. The monomer of polystyrene is: **[PMT (Kerala) 2010]**
(a) $C_2H_5CH{=}CH_2$ ☐ (b) $CH_2{=}CHCl$ ☐
(c) $C_6H_5CH{=}CH_2$ ☐ (d) $CH_2{=}CHCHO$ ☐
(e) $C_6H_5CH{=}CHCHO$ ☐

22. Which of the following statements is not correct? **[DUMET 2010]**
(a) Caprolactum is the monomer of nylon-6 ☐
(b) Terylene is a polyester polymer ☐
(c) Phenol formaldehyde resin is knwon as bakelite ☐
(d) The monomer of natural rubber is butadiene ☐

23. Which one of the following is an example of co-polymer? **[JEE (WB) 2010]**
(a) Teflon ☐ (b) Buna-S ☐
(c) PVC ☐ (d) Polypropylene ☐

24. Natural rubber is a polymer of: **[UGET(Med.) 2004; BCECE (Med.) 2008]**
(a) neoprene ☐ (b) isoprene ☐
(c) chloroprene ☐ (d) butadiene ☐

25. Heating of rubber with sulphur is known as:
(a) galvanisation ☐ (b) bessemerisation ☐
(c) vulcanisation ☐ (d) sulphonation ☐

26. Synthetic polymer which resembles natural rubber is: **[CMC Ludhiana (Med.) 2008]**
(a) chloroprene ☐ (b) neoprene ☐
(c) nylon ☐ (d) glyptal ☐

27. Natural polymer among the following is: **[JEE (Orissa) 2010]**
(a) nylon ☐ (b) cellulose ☐
(c) glyptal ☐ (d) terylene ☐

28. 1,3-Butadine and styrene on polymerisation give: **[EAMCET (Med.) 2010]**
(a) Buna-S ☐ (b) Terylene ☐
(c) Teflon ☐ (d) Bakelite ☐

29. Dacron is an example of: **[PET (MP) 2004]**
(a) polyamide ☐ (b) polypropylene ☐
(c) polyurethane ☐ (d) polyester ☐

30. Orlon has a unit: **[AFMC 2004]**
(a) isoprene ☐ (b) acrolein ☐
(c) glycol ☐ (d) vinylcyanide ☐

31. Teflon is a polymer of the monomer: **[AFMC 2006; JIPMER (Med.) 2008]**
(a) $CHF{=}CH_2$ ☐ (b) $CHF{=}CHCl$ ☐
(c) $CHCl{=}CHCl$ ☐ (d) $F_2C{=}CF_2$ ☐

32. The fibre obtained by the condensation of hexamethylene diamine and adipic acid is:
(a) dacron ☐ (b) nylon-6,6 ☐
(c) rayon ☐ (d) teflon ☐

33. Which one of the following is a thermosetting polymer? **[DCE 2006; AMU (Engg.) 2007]**
(a) Nylon-6 ☐ (b) Nylon-6,6 ☐
(c) Bakelite ☐ (d) SBR ☐

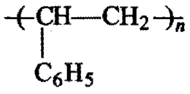
34. The widely used plastic PVC is a polymerization product of:
(a) $H_2C{=}CH_2$ ☐ (b) $H_2C{=}CCl_2$ ☐
(c) $CHCl{=}CHCl$ ☐ (d) $H_2C{=}CHCl$ ☐

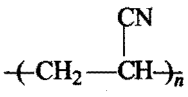
35. Salol can be used as:
(a) antiseptic ☐ (b) antipyretic ☐
(c) both (a) and (b) ☐ (d) none of these ☐

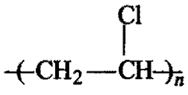
36. Ampicillin is:
(a) an analgesic ☐ (b) an antibiotic ☐
(c) an antimalarial ☐ (d) an antipyretic ☐

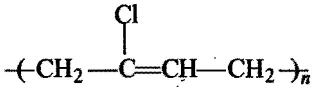
37. Chloroquine is:
(a) an analgesic ☐ (b) an antibiotic ☐
(c) an antimalarial ☐ (d) an antipyretic ☐

38. Which of the following structures represents neoprene polymer? **[CBSE (PMT) Prelims 2010]**

(a)  $\left(\underset{C_6H_5}{\underset{|}{C}}H-CH_2\right)_n$ ☐

(b)  $\left(CH_2-\overset{CN}{\overset{|}{C}}H\right)_n$ ☐

(c)  $\left(CH_2-\overset{Cl}{\overset{|}{C}}H\right)_n$ ☐

(d)  $\left(CH_2-\overset{Cl}{\overset{|}{C}}{=}CH-CH_2\right)_n$ ☐

39. Which of the following is an example of azo dye?
(a) Congo red ☐ (b) Malachite green ☐
(c) Martius yellow ☐ (d) Indigo ☐

40. The basic dye among the following is: **[AFMC 2004]**
(a) alizarin ☐ (b) aniline yellow ☐
(c) congo red ☐ (d) indigo ☐

41. Arsenic drugs are mainly used in the treatment of:
(a) jaundice ☐ (b) typhoid ☐
(c) syphilis ☐ (d) cholera ☐

42. Polypropylene is not used in:
(a) clothes ☐ (b) ropes ☐
(c) heat resistant plastics ☐ (d) parachute ropes ☐

43. To which class of dyes does phenolphthalein belong?
(a) Azo dyes ☐
(b) Nitro dyes ☐
(c) Triphenylmethane dyes ☐
(d) Phthalein dyes ☐

44. Which of the following is not a biopolymer?
(a) Starch ☐ (b) Rubber ☐
(c) Proteins ☐ (d) Nucleic acids ☐

45. Which of the following is a chain growth polymer?
(a) Polypropylene ☐ (b) Glyptal ☐
(c) Nylon-6,6 ☐ (d) Nylon-6 ☐

46. An example of natural biopolymer is:
(a) nylon ☐ (b) rubber ☐
(c) teflon ☐ (d) DNA ☐

47. The product of addition polymerization reaction is:
(a) nylon ☐ (b) glyptal ☐
(c) polythene ☐ (d) terylene ☐

48. Which of the following is an example of condensation polymer?
(a) Buna-S rubber ☐ (b) Bakelite ☐
(c) Nylon-6,6 ☐ (d) All of these ☐

49. Terylene is a condensation polymer of ethylene glycol and:
(a) phthalic acid ☐ (b) terephthalic acid ☐
(c) benzoic acid ☐ (d) salicylic acid ☐

50. Arrange the following in increasing order of their intermolecular forces:
Nylon-6,6 (I), Buna-S (II), Polythene (III) **[AMU (Medical) 2010]**
(a) II, III, I ☐ (b) III, II, I ☐
(c) I, II, III ☐ (d) II, I, III ☐

51. Neoprene is a polymer of:
(a) isoprene ☐ (b) butadiene ☐
(c) styrene ☐ (d) chloroprene ☐

52. A polyamide synthetic polymer prepared by prolonged heating of caprolactum, is:
(a) nylon-6,6 ☐ (b) nylon-6 ☐
(c) nylon-6,10 ☐ (d) glyptal ☐

53. The polymer containing strong intermolecular forces *e.g.*, hydrogen bonding is: **[AIEEE 2010]**
(a) natural rubber ☐ (b) teflon ☐
(c) nylon-6,6 ☐ (d) polystrene ☐

54. Hydrazine as a drug is used in the treatment of:
(a) malaria ☐ (b) typhoid ☐
(c) cholera ☐ (d) tuberculosis ☐

55. Which of the following is an alkaloid?
(a) Nicotine ☐ (b) Atropine ☐
(c) Cocaine ☐ (d) All of these ☐

56. The drug which is effective in curing malaria is:
(a) quinine ☐ (b) aspirin ☐
(c) salol ☐ (d) analgin ☐

57. A substance which can act both as an antiseptic and disinfectant is:
(a) aspirin ☐ (b) phenol ☐
(c) analgin ☐ (d) sodium pentothal ☐

58. The substances which relieve anxiety, reduce mental tension and induce sleep are called:
(a) analgesics ☐ (b) antipyretics ☐
(c) tranquillizer ☐ (d) anaesthetics ☐

59. Which of the following is used as anaesthetic?
(a) N_2 ☐ (b) N_2O ☐
(c) CH_4 ☐ (d) CO_2 ☐

60. Dettol consists of:
(a) cresol + ethanol ☐
(b) xylenol + terpeneol ☐
(c) chloroxylenol + terpeneol ☐
(d) none of the above ☐

61. Heroin is a derivative of:
(a) morphine ☐ (b) nicotine ☐
(c) cocaine ☐ (d) caffeine ☐

62. The pupils of eyes are dilated with a very dilute solution of an alkaloid which is:
(a) adrenaline ☐ (b) atropine ☐
(c) equanil ☐ (d) ephedrine ☐

63. Putrefaction of substances is caused by:
(a) bacteria only ☐
(b) air only ☐
(c) bacteria and air ☐
(d) bacteria and air at temperature above 0°C ☐

64. Penicillin was first discovered by:
(a) A. Fleming ☐ (b) L. Pasteur ☐
(c) G. Thompson ☐ (d) A. Noble ☐

65. The poisonous gas evolved in Bhopal tragedy was: **[EAMCET (Engg.) 2007]**
(a) $COCl_2$ ☐ (b) CH_3NCO ☐
(c) CH_3CN ☐ (d) CO ☐

66. In making lemon pickle:
(a) chillies are used to kill all germs and bacteria ☐
(b) lemon oil acts as preservative ☐
(c) salt plays the same role as sugar in jam ☐
(d) citric acid acts as preservative ☐

67. Refrigeration helps in food preservation by:
(a) killing the germs ☐
(b) reducing the rates of biochemical reactions ☐
(c) destroying enzyme action ☐
(d) sealing the food with a layer of ice ☐

68. A large number of antibiotics have been isolated from:
(a) bacteria actinomycetes ☐
(b) bacteria staphylococcus ☐
(c) bacteria rhizobium ☐
(d) acids ☐

69. An antibiotic, contains nitro group attached to benzene nucleus in its structure, is:
(a) chloramphenicol ☐ (b) penicillin ☐
(c) tetracycline ☐ (d) streptomycin ☐

70. Germinated barley called malt is a source of enzyme:
(a) invertase ☐ (b) diastase ☐
(c) zymase ☐ (d) maltase ☐

71. Which one is a broad spectrum antibiotic?
(a) Procaine ☐ (b) Plasmoquin ☐
(c) Aspirin ☐ (d) Chloramphenicol ☐

72. Sulpha drugs are used for:
(a) removing bacteria ☐
(b) precipitating bacteria ☐
(c) stopping the growth of bacteria ☐
(d) decreasing the size of bacteria ☐

73. Morphine is:
(a) antiseptic ☐ (b) analgesic ☐
(c) antibiotic ☐ (d) anaesthetic ☐

74. Arsenic containing medicine used for the treatment of syphilis is: **[PMT (Kerala) 2010]**
(a) Erythromycin ☐ (b) Ofloxacin ☐
(c) Tetracycline ☐ (d) Salvarsan ☐
(e) Penicillin ☐

75. Phenol is used as:
(a) an antiseptic ☐ (b) an insecticide ☐
(c) a disinfectant ☐ (d) styptic ☐

76. The artificial sweetener containing chlorine that has the appearance and taste as that of sugar and is stable at cooking temperature is: **[PET (Kerala) 2010]**
(a) Aspartame ☐ (b) Saccharin ☐
(c) Sucrolose ☐ (d) Alitame ☐
(e) Bithional ☐

77. The relationship between colour and chemical constitution was put forwarded by:
(a) A. Noble ☐ (b) Otto Witt ☐
(c) P. Ehrlich ☐ (d) A. Fleming ☐

78. Which of the following is an auxochrome?
(a) $—OH$ ☐ (b) $—COOH$ ☐
(c) $—NR_2$ ☐ (d) All of these ☐

79. Which of the following acts as chromophores group?
(a) Carbonyl or thio carbonyl ☐
(b) Azo or azoxy ☐
(c) Nitro or nitroso ☐
(d) All of the above ☐

80. Indigo belongs to:
(a) direct dyes ☐ (b) vat dyes ☐
(c) ingrain dyes ☐ (d) mordant dyes ☐

81. Which of the following is a correct statement for a substance to act as dye?
(a) Presence of chromophore is necessary ☐
(b) Presence of auxochrome group as well as chromophore is necessary ☐
(c) Every coloured substance ☐
(d) All of the above ☐

82. The compounds used to fix a dye to the fabric are known as:
(a) mordant ☐ (b) bleaching agent ☐
(c) azeotrope ☐ (d) leuco base ☐

83. Cetyl trimethyl ammonium bromide is a popular : **[PET (Kerala) 2010]**
(a) non-ionic detergent ☐ (b) anionic detergent ☐
(c) cationic detergent ☐ (d) sweetener ☐
(e) antioxidant ☐

84. Red ink is prepared from:
(a) aniline ☐ (b) eosin ☐
(c) phenol ☐ (d) congo red ☐

85. Alizarin, a mordant dye is not used in:
(a) painting ☐ (b) wool dyeing ☐
(c) printing ☐ (d) cotton dyeing ☐

86. Which one of the following is a mordant?
(a) Tannic acid ☐ (b) Metallic hydroxides ☐
(c) Salts of Al, Cr, Fe, Sn ☐ (d) All of these ☐

87. The number of chromophores in picric acid is:
(a) 1 ☐ (b) 2 ☐
(c) 3 ☐ (d) 4 ☐

88. Which of the following compounds can make clothes fire proof ?
(a) $MgSO_4$ ☐ (b) $Al_2(SO_4)_3$ ☐
(c) $FeSO_4$ ☐ (d) Cu_2Cl_2 ☐

89. Which of the following is a plasticizer?
(a) Coconut oil ☐ (b) Mustard oil ☐
(c) Castor oil ☐ (d) Pine oil ☐

90. Which of the following is used to make non-stick cook-wares?
(a) Polyvinyl chloride ☐
(b) Polytetra fluoro ethylene ☐
(c) Polystyrene ☐
(d) Polyethylene terephthalate ☐

91. Match the List I with List II and select the correct answer using the codes given below the list: **[SCRA 2000]**

List I	List II
I. Iodoform	A. Anaesthetic
II. Methyl salicylate	B. Antiseptic
III. Diethyl ether	C. Insecticide
IV. Hexachlorocyclohexane	D. Detergent
	E. Pain balm.

Codes:
(a) I-B, II-E, III-C, IV-D ☐
(b) I-D, II-B, III-A, IV-C ☐
(c) I-B, II-E, III-A, IV-C ☐
(d) I-C, II-A, III-D, IV-B ☐

92. Which of these is a hypnotic? **[AFMC 2001]**
(a) Metaldehyde ☐ (b) Acetaldehyde ☐
(c) Paraldehyde ☐ (d) None of these ☐

93. Which of the following is used as an antiseptic? **[MGIMS (Wardha) 2001]**
(a) Phenol ☐ (b) Benzaldehyde ☐
(c) Benzalamine ☐ (d) Malic anhydride ☐

94. Which of the following is not an artificial sweetener? **[AMU (Engg.) 2010]**
(a) Aspartame ☐ (b) Sucrolose ☐
(c) Sucrose ☐ (d) Alitame ☐

95. Tranquillizers are the substances used for the treatment of:
(a) cancer ☐ (b) AIDS ☐
(c) mental diseases ☐ (d) physical disorders ☐
(e) blood infection ☐

96. Which of the following is used to make paints and lacquers? **[DPMT 2002]**
(a) Polystyrene ☐ (b) Polyvinyl chloride ☐
(c) Glyptal ☐ (d) Nylon ☐

97. Which of the following is not a biliquid propellant? **[DUMET 2010]**
(a) Nitroglycerine + nitrocellulose ☐
(b) Hydrazine + N_2O_4 ☐
(c) Unsym. dimethyl hydrazine + N_2O_4 ☐
(d) Kerosene oil + liquid oxygen ☐

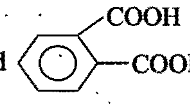
98. Which one of the following is not a tranquillizer? **[PMT (Kerala) 2010]**
(a) Equanil ☐ (b) Salvarsan ☐
(c) Veronal ☐ (d) Serotonin ☐
(e) Luminal ☐

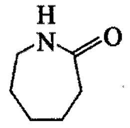
99. Nylon threads are made of: **[AIEEE 2003; JCECE (Med.) 2008]**
(a) polyvinyl polymer ☐ (b) polyester polymer ☐
(c) polyamide polymer ☐ (d) polyethylene polymer ☐

100. SLV-3 rockets are used in:
(a) solid propellants ☐
(b) liquid propellants ☐
(c) composite solid propellants ☐
(d) hybrid propellants ☐

101. Which of the following represents a bi-liquid propellant?
(a) Nitro glycerine + nitro cellulose ☐
(b) N_2O_4 + unsymmetrical dimethyl hydrazine ☐
(c) N_2O_4 + acrylic rubber ☐
(d) Polybutadiene + ammonium perchlorate ☐

102. Which one of the following is a chain growth polymer? **[CBSE (Med.) 2004; BHU (Mains) 2008]**
(a) Starch ☐ (b) Nucleic acid ☐
(c) Polystyrene ☐ (d) Protein ☐

103. The monomer of dacron is/are: **[DPMT 2004]**
(a) $HOCH_2—CH_2OH$ and  ☐

(b)  ☐

(c) $HOCH_2—CH_2OH$ and HOOC——COOH ☐

(d) $F_2C{=}CF_2$ ☐

104. The dyes which are applied to the fabric in the colourless reduced state and then oxidised to coloured state are called: **[DPMT 2004]**

(a) vat dyes ☐

(b) disperse dyes ☐

(c) triphenyl methane dyes ☐

(d) azo dyes ☐

105. Which of the following is a mordant dye? **[JIPMER 2004]**

(a) Aniline black ☐ (b) Congo red ☐

(c) Alizarin ☐ (d) Indigo ☐

106. Which one of the following is employed as a tranquillizer drug? **[CBSE (Med.) Prelims 2010]**

(a) Promethazine ☐ (b) Valium ☐

(c) Naproxen ☐ (d) Mife pristone ☐

107. Which of the following polymers has an ester linkage? **[BVP (Pune) 2004]**

(a) PVC ☐ (b) Nylon-6,6 ☐

(c) SBR ☐ (d) Terylene ☐

108. Nylon is not a: **[PMT (Raj.) 2004; CET (Haryana) 2005]**

(a) condensation polymer ☐

(b) polyamide ☐

(c) copolymer ☐

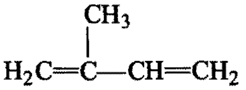
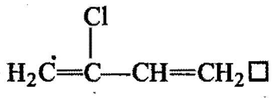
(d) homopolymer ☐

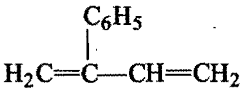
109. Which of the following is used in vulcanization of rubber? **[MH-CET 2004]**

(a) SF_6 ☐ (b) CF_4 ☐

(c) Cl_2F_2 ☐ (d) C_2F_2 ☐

110. Structure of (monomer unit of) natural rubber is: **[BCECE (Engg.) 2004]**

(a)  $H_2C{=}C(CH_3)—CH{=}CH_2$ ☐ (b)  $H_2C{=}C(Cl)—CH{=}CH_2$ ☐

(c)  $H_2C{=}C(C_6H_5)—CH{=}CH_2$ ☐ (d) $(—CH_2—CH_2—)_n$ ☐

111. Paracetamol is an: **[BCECE (Engg.) 2004]**

(a) antibiotic ☐ (b) antipyretic ☐

(c) antimalarial ☐ (d) analgesic ☐

112. A polymer containing nitrogen is : **[UPSEAT 2004; AIIMS 2008]**

(a) bakelite ☐ (b) dacron ☐

(c) rubber ☐ (d) nylon-6,6 ☐

113. In elastomer, intermolecular forces are: **[BHU 2004]**

(a) nil ☐ (b) weak ☐

(c) strong ☐ (d) very strong ☐

114. Which of the following is a biodegradable polymer? **[AIIMS 2004]**

(a) PVC ☐ (b) Nylon-6 ☐

(c) Cellulose ☐ (d) Polythene ☐

115. 2-Acetoxy benzoic acid is used as an: **[KCET 2004; CET (Haryana) 2005]**

(a) antimalarial ☐ (b) antidepressant ☐

(c) antiseptic ☐ (d) antipyretic ☐

116. Which of the following is a polyamide? **[AIEEE 2005; UPSEAT 2006]**

(a) Teflon ☐ (b) Nylon-6,6 ☐

(c) Terylene ☐ (d) Bakelite ☐

117. Which one of the following types of drugs reduces fever? **[AIEEE 2005]**

(a) Antipyretic ☐ (b) Analgesic ☐

(c) Antibiotic ☐ (d) Tranquillizer ☐

118. Buna-S is a polymer of: **[CET (Karnataka) 2008; CBSE (Med.) 2009]**

(a) butadiene only ☐ (b) butadiene and nitryl ☐

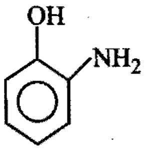
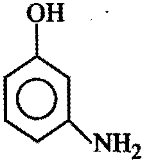
(c) styrene only ☐ (d) butadiene and styrene ☐

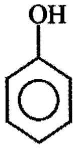
119. Which one of the following is not a broad spectrum antibiotic? **[DPMT 2005]**

(a) Tetracycline ☐ (b) Chloromycetin ☐

(c) Penicillin ☐ (d) None of these ☐

120. Which of the following gives paracetamol on acetylation? **[EAMCET (Med.) 2005]**

(a)  ☐ (b)  ☐

(c)  ☐ (d)  ☐

121. Antiseptic, chloroxylenol is: **[KCET 2005]**

(a) 4-chloro-3,5-dimethyl phenol ☐

(b) 3-chloro-4,5-dimethyl phenol ☐

(c) 4-chloro-2,5-dimethyl phenol ☐

(d) 5-chloro-3,4-dimethyl phenol ☐

122. Condensation product of caprolactum is: **[BCECE (Med.) 2005]**

(a) nylon-6 ☐ (b) nylon-6,6 ☐

(c) nylon-60 ☐ (d) nylon-6,10 ☐

123. A drug that is antipyretic as well as analgesic is: **[AMU (Med.) 2005]**

(a) chloroquin ☐

(b) penicillin ☐

(c) paracetamol ☐

(d) chloropromazine hydrochloride ☐

124. Which of the following rubbers is not a polydiene? **[JIPMER 2005]**

(a) Nitrile ☐ (b) Polyisoprene ☐

(c) Polychloroprene ☐ (d) Thiokol ☐

125. Which of the following is a cross-linked polymer? **[UPSEAT 2005]**
(a) Teflon ☐ (b) Orlon ☐
(c) Nylon ☐ (d) Bakelite ☐

126. $\left[-NH(CH_2)_6NHCO(CH_2)_4CO-\right]_n$ is a: **[CBSE (Med.) 2006]**
(a) thermosetting polymer ☐
(b) homopolymer ☐
(c) copolymer ☐
(d) addition polymer ☐

127. Which is not a polymer? **[MGIMS (Wardha) 2006]**
(a) Sucrose ☐ (b) Enzyme ☐
(c) Starch ☐ (d) Teflon ☐

128. Phenacetin is used as an: **[JEE (WB) Engg. 2006]**
(a) antipyretic ☐ (b) antiseptic ☐
(c) analgesic ☐ (d) antimalarial ☐

129. Which of the following compounds is used as a body deodorant? **[PMT (Kerala) 2006]**
(a) Aspirin ☐ (b) Omeprazole ☐
(c) Indigosol-O ☐ (d) *p*-Chlorometaxylenol ☐
(e) Bithional ☐

130. Which of the following is a bacteriostatic? **[PET (Kerala) 2006]**
(a) Penicillin ☐ (b) Erythromycin ☐
(c) Aminoglycodine ☐ (d) Ofloxacin ☐
(e) Bithional ☐

131. The hybrid rocket propellant consists of : **[PET (Kerala) 2006]**
(a) acrylic rubber and liquid nitrogen tetroxide ☐
(b) polyurethane and ammonium perchlorate ☐
(c) nitroglycerine and nitrocellulose ☐
(d) liquid hydrogen and liquid oxygen ☐
(e) hydrogen peroxide ☐

132. The pair whose both species are used in antiacid medicinal preparation is: **[AIIMS 2006]**
(a) $NaHCO_3$ and $Mg(OH)_2$ ☐
(b) Na_2CO_3 and $Ca(HCO_3)_2$ ☐
(c) $Ca(HCO_3)_2$ and $Mg(OH)_2$ ☐
(d) $Ca(OH)_2$ and $NaHCO_3$ ☐

133. Which of the following colours is imparted by alizarin dye in presence of Cr^{3+} ion? **[CET (Gujarat) 2006]**
(a) Violet ☐ (b) Brown-red ☐
(c) Pink ☐ (d) Red ☐

134. Which of the following polymers can be used for lubrication and as an insulator? **[CET (Gujarat) 2006]**
(a) SBR ☐ (b) PVC ☐
(c) PTFE ☐ (d) PAN ☐

135. A hybrid rocket propellant uses: **[DCE 2006]**
(a) a liquid oxidiser and a solid fuel ☐
(b) a composite solid propellant ☐
(c) a biliquid propellant ☐
(d) a solid, liquid and gas as a propellant ☐

136. Which one of the following polymers is prepared by condensation polymerization? **[CBSE (Med.) 2007]**
(a) Rubber ☐ (b) Styrene ☐
(c) Nylon-6,6 ☐ (d) Teflon ☐

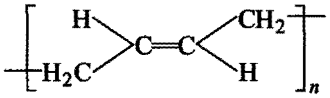
137. Which of the following is a biodegradable polymer? **[EAMCET(Engg.) 2007]**
(a) Polythene ☐ (b) PVC ☐
(c) Bakelite ☐ (d) PHBV ☐

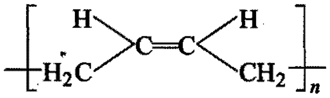
138. The raw material used in nylon-6 is: **[EAMCET (Med.) 2007; PMET (Med.) 2008]**
(a) adipic acid ☐ (b) phthalic acid ☐
(c) ethylene glycol ☐ (d) caprolactum ☐

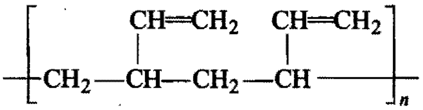
139. Which one is a chain growth polymer? **[DCE (Engg.) 2007]**
(a) Teflon ☐ (b) Nylon-6 ☐
(c) Nylon-6,6 ☐ (d) Bakelite ☐

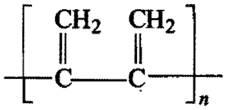
140. Which of the following is true for polypropylene? **[DPMT (Med.) 2007]**
(a) Propylene, condensation polymer ☐
(b) Propylene, addition polymer ☐
(c) Propylene, ammonic polymer ☐
(d) Propylene, cationic ammonic polymerase ☐

141. Mark out the most unlike form of polymerization of $H_2C{=}CH{-}CH{=}CH_2$: **[AMU (Engg.) 2007]**

(a)  ☐

(b)  ☐

(c) 
$\left[-CH_2-\overset{CH=CH_2}{\overset{|}{CH}}-CH_2-\overset{CH=CH_2}{\overset{|}{CH}}-\right]_n$ ☐

(d) 
$\left[-\overset{CH_2}{\overset{\|}{C}}-\overset{CH_2}{\overset{\|}{C}}-\right]_n$ ☐

142. Terylene is the polyester of: **[MH-CET 2007]**
(a) hexamethylene diamine and adipic acid ☐
(b) vinyl chloride and formaldehyde ☐
(c) melamine and formaldehyde ☐
(d) ethylene glycol and terephthalic acid ☐

143. The basic dye among the following is: **[DCE (Engg.) 2007]**
(a) orange-1 ☐ (b) aniline yellow ☐
(c) anthraquinone ☐ (d) phenolphthalein ☐

144. An insoluble dye is reduced to a soluble colourless leuco form by an alkaline reducing agent. The fibre is soaked in the dye solution and then exposed to air to develop the colour. The dye is: **[PMT (Kerala) 2007]**
(a) mordant dye ☐ (b) vat dye ☐
(c) azo dye ☐ (d) direct dye ☐
(e) disperse dye ☐

145. Chloramphenicol is: **[DCE (Engg.) 2007]**
(a) narrow spectrum antibiotic ☐
(b) broad spectrum analgesic ☐
(c) broad spectrum antibiotic ☐
(d) broad spectrum antibacterial ☐

146. Bithional is an example of: **[AMU (Engg.) 2007]**
(a) disinfectant ☐ (b) antiseptic ☐
(c) antibiotic ☐ (d) analgesic ☐

147. Which of the following is used as a "morning after pill"? **[PMT (Kerala) 2007; AIIMS 2010]**
(a) Norethindrone ☐ (b) Ethynylestradiol ☐
(c) Mifepristone ☐ (d) Bithional ☐
(e) Promethazine ☐

148. Tincture of iodine is: **[BCECE (Med.) 2007]**
(a) aqueous solution of I_2 ☐
(b) alcoholic solution of I_2 ☐
(c) solution of I_2 in aqueous KI ☐
(d) aqueous solution of KI ☐

149. Which of the following alkenes is most reactive towards cationic polymerization? **[UGET (Med.) 2008]**
(a) $H_2C{=}CHCH_3$ ☐ (b) $H_2C{=}CHCl$ ☐
(c) $H_2C{=}CHC_6H_5$ ☐ (d) $H_2C{=}CHCO_2CH_3$ ☐

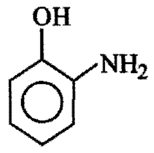
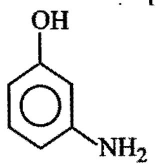
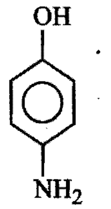
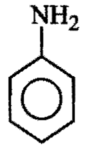
150. Which one of the following is not a correct match? **[Punjab CET (Engg.) 2008]**

	Polymer	**Monomer/s**	
(a)	Teflon	Tetrafluoroethylene	☐
(b)	Plexiglas	Methyl methacrylate	☐
(c)	Orlon	Glycerol, phthalic anhydride	☐
(d)	Buna-S	Styrene-1,3-butadine	☐

151. Which one of the following statements is not true? **[CBSE (Med.) 2008]**
(a) Buna-S is a co-polymer of butadiene and styrene ☐
(b) Natural rubber is a 1,4-polymer of isoprene ☐
(c) In vulcanization, the formation of sulphur bridges between different chains make rubber harder and stronger ☐
(d) Natural rubber has the *trans*-configuration at every double bond ☐

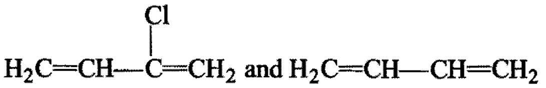
152. Aspirin is chemically: **[CMC Ludhiana (Med.) 2008; JEE (WB) 2010]**
(a) methyl benzoate ☐ (b) ethyl salicylate ☐
(c) acetyl salicylic acid ☐ (d) *o*-hydroxy benzoic acid ☐

153. Which of the following is not true for antibiotics? **[BHU (Screening) 2008]**
(a) Tetracycline is one of the broad spectrum antibiotics which is effective against a large number of harmful microorganism ☐
(b) Streptomycin is highly effective against microorganisms which cause tuberculosis ☐
(c) Penicillin has a narrow spectrum and certain persons are sensitive to it ☐
(d) Penicillin may be administered without testing the patients for sensitivity to it ☐

154. Which of the following gives paracetamol on acetylation? **[DCE 2008]**
(a)  ☐ (b)  ☐
(c)  ☐ (d)  ☐

155. Chloramine-T is a: **[CMC Ludhiana (Med.) 2008]**
(a) disinfectant ☐ (b) antiseptic ☐
(c) analgesic ☐ (d) antipyretic ☐

156. Which of the following statements is not true? **[PMT (Kerala) 2008]**
(a) Some disinfectants can be used as antiseptic at low concentration ☐
(b) Sulphadiazine is a synthetic antibacterial ☐
(c) Pheromones provide chemical means of establishing communication ☐
(d) Aspirin is analgesic and antipyretic ☐
(e) Norethindrone is a pheromone ☐

157. Buna-N synthetic rubber is a co-polymer of: **[AIEEE 2009]**
(a)  $H_2C{=}CH{-}\overset{Cl}{\overset{|}{C}}{=}CH_2$ and $H_2C{=}CH{-}CH{=}CH_2$ ☐
(b) $H_2C{=}CH{-}CH{=}CH_2$ and $H_5C_6{-}CH{=}CH_2$ ☐
(c) $H_2C{=}CH{-}CN$ and $H_2C{=}CH{-}CH{=}CH_2$ ☐
(d)  $H_2C{=}CH{-}CN$ and $H_2C{=}CH{-}\overset{Cl}{\overset{|}{C}}{=}CH_2$ ☐

158. Given the polymers,
A = Nylon-6,6 ; B = Buna-S ; C = Polythene
Arrange these in decreasing order of their intermolecular forces: **[DCE 2009]**
(a) $C < B < A$ ☐ (b) $B > C > A$ ☐
(c) $B < C < A$ ☐ (d) $C < A < B$ ☐

159. The polymer of natural rubber is: **[AFMC 2009]**
(a) all *trans* isoprene ☐ (b) Buna-N ☐
(c) all *cis* isoprene ☐ (d) none of these ☐

160. The condensation polymer among the following is: **[Karnataka CET 2009]**
(a) protein ☐ (b) PVC ☐
(c) polythene ☐ (d) rubber ☐

161. The catalyst used for olefin polymerization is: **[JEE (WB) 2009]**
(a) Ziegler-Natta catalyst ☐
(b) Wilkinson catalyst ☐
(c) Raney nickel catalyst ☐
(d) Merrifield resin ☐

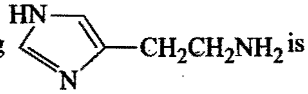
162. Among cellulose, polyvinyl chloride, nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest, is: **[IIT 2009]**
(a) nylon ☐ (b) polyvinyl chloride ☐
(c) cellulose ☐ (d) natural rubber ☐

163. The oxidant which is used as an antiseptic is: **[JEE (WB) 2009]**
(a) $KBrO_3$ ☐ (b) $KMnO_4$ ☐
(c) CrO_3 ☐ (d) KNO_3 ☐

164. Which one of the following is employed as a tranquilizer? **[CBSE (Med.) 2009]**

(a) Naproxen ☐ (b) Tetracycline ☐
(c) Chlorpheninamine ☐ (d) Equanil ☐

165. The drug

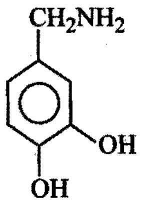


is used as: **[DCE 2009]**

(a) antacid ☐ (b) analgesic ☐
(c) antimicrobial ☐ (d) antiseptic ☐
(e) none of these ☐

166. Parkinson's disease is linked to abnormalities in the levels of dopamine in the body. The structure of dopamine is: **[EAMCET 2009]**

(a)



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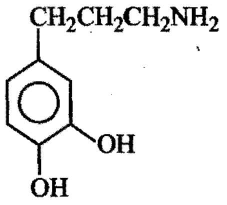

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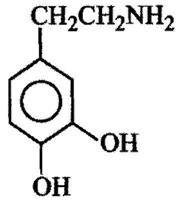
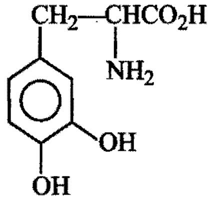
(c)



☐ (d)



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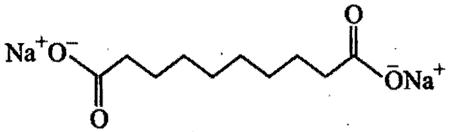
167. Which of the following molecules is most suitable to disperse benzene in water? **[AFMC 2009]**

(a)

☐

(b)



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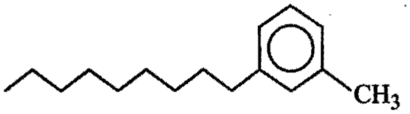
(c)



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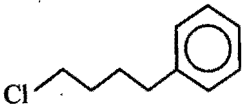
(d)



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168. Match the chemicals in column I with their uses in column II.

Column I	Column II
(A) Sodium perbenzoate	1. Disinfectant
(B) Chlorine	2. Antiseptic
(C) Bithional	3. Milk bleaching agent
(D) Potassium stearate	4. Soap

[DCE 2009]

(a) A = 1, B = 2, C = 3, D = 4 ☐
(b) A = 2, B = 3, C = 4, D = 1 ☐
(c) A = 3, B = 1, C = 2, D = 4 ☐
(d) A = 4, B = 1, C = 2, D = 3 ☐

SET II: This set contains questions with two or more correct answers.

169. Which of the following polymers involves cross-linkages?

(a) Polythene ☐ (b) Bakelite ☐
(c) Melamine ☐ (d) Vulcanized rubber ☐

170. Glyptal polymer is obtained from phthalic acid by treating it with:

(a) malonic acid ☐ (b) glycerol ☐
(c) maleic acid ☐ (d) ethylene glycol ☐

171. Terylene (Dacron) is prepared by condensing ethylene glycol with :

(a) phthalic acid ☐
(b) isophthalic acid ☐
(c) terephthalic acid ☐
(d) dimethyl terephthalate ☐

172. Synthetic fibres manufactured from cellulose are termed as:

(a) rayon ☐ (b) nylon ☐
(c) dacron ☐ (d) artificial silk ☐

173. Which of the following are homopolymers?

(a) Polyvinyl chloride ☐ (b) Polyacrylonitrile ☐
(c) Buna rubber ☐ (d) Nylon-6,6 ☐

174. Which of the following are co-polymers?

(a) Bakelite ☐ (b) Melamine ☐
(c) Buna-S ☐ (d) Nylon-6,6 ☐

175. Polymers can be classified on the basis of:

(a) origin ☐ (b) structure ☐
(c) mechanism ☐ (d) synthesis ☐

176. Natural polymers are:

(a) bakelite ☐ (b) polyisoprene ☐
(c) proteins ☐ (d) polyethylene ☐

177. Synthetic polymers are:

(a) bakelite ☐ (b) polyvinyl chloride ☐
(c) polystyrene ☐ (d) natural rubber ☐

178. Chain growth addition polymerization is an important reaction of :

(a) alkenes ☐ (b) conjugated dienes ☐
(c) polyamides ☐ (d) polyesters ☐

179. The reagent(s) used for softening the temporary hardness of water is(are): **[IIT 2010]**

(a) $Ca_3(PO_4)_2$ ☐ (b) $Ca(OH)_2$ ☐
(c) Na_2CO_3 ☐ (d) NaOCl ☐

ASSERTION-REASON TYPE QUESTIONS

These questions given below consist of an **Assertion (A)** and **Reason (R).** Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) Polypropylene is an addition polymer.
(R) Polypropylene is polythene.
2. (A) Bakelite is co-polymer.
(R) Bakelite is a thermosetting material.
3. (A) Polybutadiene is an example of chain growth polymer.
(R) In chain growth polymers, the reactive particles may be free radicals or ions (cations or anions) to which monomers get added by a chain reaction.
4. (A) Teflon has high thermal stability and chemical inertness.
(R) Teflon is a thermoplastic.
5. (A) Glyptal is obtained by the condensation polymerization of ethylene glycol and terephthalic acid.
(R) Glyptal is used in the manufacture of paints and lacquers.
6. (A) Analgesics bring down body temperature during high fever.
(R) Tetracyclin is a tranquillizer.
7. (A) Aspirin can cause ulcer in the stomach.
(R) The ester group in aspirin gets hydrolysed to acid group in the stomach where the pH is 2.
8. (A) Saccharin is an artificial sweetner.
(R) It has a high calorific value.
9. (A) Disinfectants kill microorganisms but are harmful to the human tissues.
(R) Thymol is a powerful disinfectant.
10. (A) Sulphanilamide is an antimalarial.
(R) Malaria is a highly widespread infectious disease.
11. (A) Detergents are preferred to soaps for washing purposes.
(R) Detergents having branched hydrocarbon chains are non-biodegradable.
12. (A) Soaps are obtained by the hydrolysis of oils and fats with aqueous alkali.
(R) Sodium salts of higher fatty acids are known as soft soaps.
13. (A) A micelle formed by sodium stearate in water has $-COO^-$ groups at the surface.
(R) Surface tension of water is reduced by the addition of stearate. [AIIMS 2003]

ANSWERS

OBJECTIVE QUESTIONS

1. (a) 2. (d) 3. (c) 4. (b) 5. (a) 6. (b) 7. (a) 8. (a) 9. (b) 10. (c)
11. (d) 12. (d) 13. (a) 14. (b) 15. (c) 16. (c) 17. (b) 18. (a) 19. (a) 20. (d)
21. (c) 22. (d) 23. (b) 24. (b) 25. (c) 26. (b) 27. (b) 28. (a) 29. (d) 30. (d)
31. (d) 32. (b) 33. (c) 34. (d) 35. (a) 36. (b) 37. (c) 38. (d) 39. (a) 40. (b)
41. (c) 42. (c) 43. (d) 44. (b) 45. (a) 46. (d) 47. (c) 48. (d) 49. (b) 50. (a)
51. (d) 52. (b) 53. (c) 54. (d) 55. (d) 56. (a) 57. (b) 58. (c) 59. (b) 60. (c)
61. (a) 62. (b) 63. (d) 64. (a) 65. (b) 66. (c) 67. (b) 68. (a) 69. (a) 70. (b)
71. (d) 72. (c) 73. (b) 74. (d) 75. (a) 76. (c) 77. (b) 78. (d) 79. (d) 80. (b)
81. (b) 82. (a) 83. (c) 84. (b) 85. (a) 86. (d) 87. (c) 88. (b) 89. (c) 90. (b)
91. (c) 92. (c) 93. (a) 94. (c) 95. (c) 96. (c) 97. (a) 98. (b) 99. (c) 100. (c)
101. (b) 102. (c) 103. (c) 104. (a) 105. (c) 106. (b) 107. (d) 108. (d) 109. (a) 110. (a)
111. (b) 112. (d) 113. (b) 114. (c) 115. (d) 116. (b) 117. (a) 118. (d) 119. (c) 120. (d)
121. (a) 122. (a) 123. (c) 124. (d) 125. (d) 126. (c) 127. (a) 128. (a) 129. (d) 130. (b)
131. (a) 132. (a) 133. (b) 134. (c) 135. (a) 136. (c) 137. (d) 138. (d) 139. (a) 140. (b)
141. (d) 142. (d) 143. (b) 144. (b) 145. (c) 146. (a) 147. (c) 148. (b) 149. (c) 150. (c)
151. (d) 152. (c) 153. (d) 154. (c) 155. (b) 156. (c) 157. (c) 158. (a) 159. (c) 160. (a)
161. (a) 162. (d) 163. (b) 164. (d) 165. (e) 166. (c) 167. (c) 168. (c) 169. (a,b,c) 170. (b,d)
171. (c,d) 172. (a,d) 173. (a,b,c) 174. (a,b,c,d) 175. (a,b,c,d) 176. (b,c) 177. (a,b,c) 178. (a,b) 179. (b,c)

ASSERTION-REASON TYPE QUESTIONS

1. (c) 2. (b) 3. (a) 4. (b) 5. (d) 6. (c) 7. (a) 8. (c) 9. (a) 10. (d)
11. (b) 12. (c) 13. (a)

BRAIN STORMING PROBLEMS

1. DDT is an example of :
(a) fungicide ☐ (b) herbicide ☐
(c) insecticide ☐ (d) rodenticide ☐

2. Which one of the following can be used as anaesthetic ?
(a) N_2O ☐ (b) NO ☐
(c) NCl_3 ☐ (d) NO_2 ☐

3. Amoxicillin is semi-synthetic modification of :
(a) penicillin ☐ (b) streptomycin ☐
(c) tetracycline ☐ (d) chloramphenicol ☐

4. 2,4-dichlorophenoxy acetic acid is used as :
(a) fungicide ☐ (b) insecticide ☐
(c) herbicide ☐ (d) moth repellent ☐

5. Dettol consists of :
(a) xylenol + terpeneol ☐
(b) chloroxylenol + terpeneol ☐
(c) cresol + ethanol ☐
(d) none of the above ☐

6. Which of the following chemicals is used as pain killer ?
(a) Phenyl acetate ☐ (b) Methyl acetate ☐
(c) Acetyl salicylic acid ☐ (d) Salicylic acid ☐

7. A substance, which can be used both as analgesic and antipyretic, is :
(a) analgin ☐ (b) aspirin ☐
(c) paracetamol ☐ (d) all of these ☐

8. Which of the following compounds can be used as analgesic without causing addiction and mood elevator ?
(a) *N*-acetyl *p*-amino phenol ☐
(b) Morphine ☐
(c) Diazepam ☐
(d) Heroine ☐

9. Select the incorrect statement among the following.
(a) Aspirin is analgesic and antipyretic both.
(b) Ampicillin is a natural antibiotic.
(c) Sulphadiazine is a synthetic antibacterial.
(d) Some disinfectants can be used as antiseptics in lower concentrations.

10. Which of the following substances is not a organophosphorus insecticide ?
(a) Malathion ☐ (b) Parathion ☐
(c) Phosdrin ☐ (d) Rotenone ☐

11. Hypnotic chloretone is obtained by :
(a) condensation of acetone with chloroform
(b) condensation of acetaldehyde with chloroform
(c) condensation of acetone with bleaching powder
(d) condensation of acetaldehyde with bleaching powder

12. Tick mark the wrong match.
(a) morphine — narcotic ☐
(b) charas — hallucinogenic ☐
(c) cocaine — sedative ☐
(d) morphine — analgesic ☐

13. Polyethylene is a/an :
(a) random co-polymer ☐
(b) homopolymer ☐
(c) alternate co-polymer ☐
(d) cross-linked co-polymer ☐

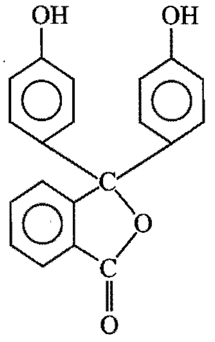
14. Gammexane is :
(a) DDT ☐
(b) hexachlorobenzene (HCB) ☐
(c) benzene hexachloride (BHC) ☐
(d) chloral ☐

15. What substance is formed when $F_2C{=}CF_2$ is polymerized ?
(a) Polyethylene ☐ (b) Polyurethane ☐
(c) PVC ☐ (d) Teflon ☐

16. The abbreviation PDI refers to :
(a) name of the polymer ☐
(b) polydispersity index ☐
(c) Planck's disposal index ☐
(d) polydiagonal index ☐

17. A drug which is structurally related to adrenaline is :
(a) salbutamol ☐ (b) salvarsan ☐
(c) diazepam ☐ (d) LSD ☐

18. Phenolphthalein is formed by condensation of phthalic anhydride and C_6H_5OH (phenol). Which of the following structures shows colour in basic medium ?

(a)


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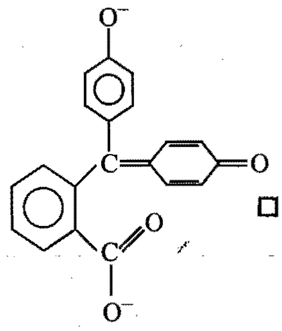
(b)


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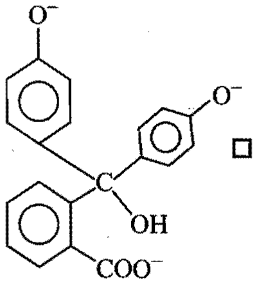


☐ (d) All of these ☐

19. Eye lenses are manufactured by :
(a) PMMA ☐ (b) teflon ☐
(c) PVC ☐ (d) buna-N ☐

20. Which polymer is obtained in the following sequence of reactions ?

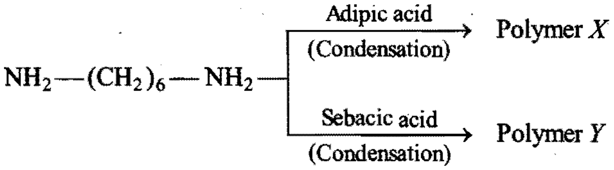
$$CHCl_3 \xrightarrow[SbF_3]{HF} X \xrightarrow{800°C} Y \xrightarrow{\text{Polymerization}} \underset{\text{(Polymer)}}{\text{Plastic}}$$

(a) Bakelite ☐ (b) Teflon ☐
(c) Polythene ☐ (d) Nylon-6,6 ☐

21. For synthetic polymers :
(a) PDI = 1 ☐ (b) PDI < 1 ☐
(c) PDI ≥ 1 ☐ (d) PDI ≤ 1 ☐

22. A polyamide polymer is :
(a) neoprene ☐ (b) PVC ☐
(c) acrilon ☐ (d) nylon-6,6 ☐

23.



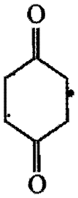
Polymers '*X*' and '*Y*' respectively are :
(a) nylon-6; nylon-6,6 ☐
(b) nylon-6,6; nylon-6 ☐
(c) nylon-6; nylon-6,10 ☐
(d) nylon-6,6; nylon-6,10 ☐

24. The most suitable method for determination of the molecular mass of polymer is :
(a) osmotic pressure ☐
(b) Victor-Meyer's method ☐
(c) elevation in boiling point ☐
(d) depression in freezing point ☐

25. Teflon, polystyrene and neoprene are all :
(a) co-polymers ☐ (b) condensation polymers ☐
(c) homopolymers ☐ (d) monomers ☐

26. Rubber is a :
(a) conducting polymer ☐
(b) oriented polymer ☐
(c) elastomer ☐
(d) strong commercial fabric ☐

27. Caprolactum is monomer for the manufacture of nylon-6 and is obtained by Beckmann's rearrangement of :

(a)


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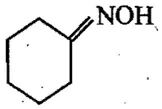
(b)


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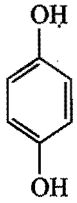
(c)


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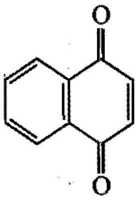
(d)


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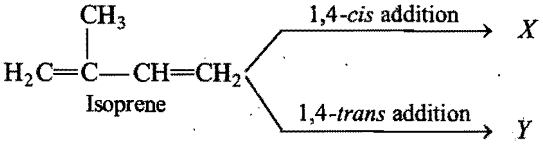
28. Chain-growth polymerization may proceed by the following mechanism:
(a) free radical polymerization ☐
(b) cationic polymerization ☐
(c) anionic polymerization ☐
(d) all of the above ☐

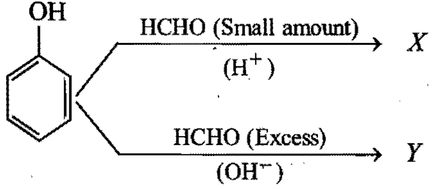
29.



X and *Y* are :

	X	*Y*	
(a)	natural rubber	gutta percha	☐
(b)	gutta percha	natural rubber	☐
(c)	natural rubber	natural rubber	☐
(d)	gutta percha	gutta percha	☐

30. Phenol gives two polymers on condensation with formaldehyde :



X and *Y* are :

	X	*Y*	
(a)	bakelite	novolak	☐
(b)	novolak	bakelite	☐
(c)	bakelite	bakelite	☐
(d)	novolak	novolak	☐

ANSWERS : BRAIN STORMING PROBLEMS

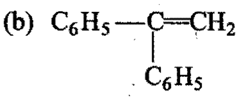
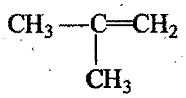
1. (c)	**2.** (a)	**3.** (a)	**4.** (c)	**5.** (b)	**6.** (c)	**7.** (d)	**8.** (a)	**9.** (b)	**10.** (d)
11. (a)	**12.** (c)	**13.** (b)	**14.** (c)	**15.** (d)	**16.** (b)	**17.** (a)	**18.** (b)	**19.** (a)	**20.** (b)
21. (c)	**22.** (d)	**23.** (d)	**24.** (a)	**25.** (c)	**26.** (c)	**27.** (b)	**28.** (d)	**29.** (a)	**30.** (b)

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Polymers are made up of small molecules called monomers. Polymer which are formed by one type of monomer is called homopolymer and which are formed by more than one type of monomers are called co-polymers. Natural polymers are biodegradable whereas synthetic polymers may or may not be. Addition or chain growth polymerization involves the repeated addition of monomers to the polymer chain. The monomers are unsaturated compounds and this type of polymerization takes place by ionic (cationic or anionic) as well as free radical mechanism. Condensation or step growth polymerization involves a series of condensation reactions between two monomers. Each monomer normally contains two functional groups. Branch chain polymers may be condensation or addition but cross linked polymers are always condensation polymers.

Answer the following questions :

1. Which of the these are natural polymers ?
   (a) Proteins (b) Starch
   (c) Nucleic acid (d) All of these
2. Which one of the following polymer is prepared by condensation polymerization ?
   (a) Dacron (b) Teflon
   (c) Styrene (d) Rubber
3. Which one of the following is biodegradable polymer ?
   (a) Nylon-66 (b) Glyptal
   (c) Cellulose (d) PVC
4. Which of the following is a chain growth polymer ?
   (a) Polystyrene (b) PTFE
   (c) Polybutadiene (d) All of these
5. Which one of the following monomer is most reactive for anionic polymerization ?
   (a) $C_6H_5-CH=CH_2$
   (b) 
   $C_6H_5-C(C_6H_5)=CH_2$
   (c) 
   $CH_3-C(CH_3)=CH_2$
   (d) $H_2C=CH_2$

Passage 2

Antibiotics are the chemical substances which are produced by microorganisms like bacteria, fungi and moulds. Antibiotics can inhibit the growth or even destroy other microorganisms. Now-a-days, synthetic antibiotics are also available. The first successful antibiotic produced was penicillin. The antibiotics may be either bacteriocidal (kills the organism in the body) or bacteriostatic (inhibits the growth of organism). Ampicillin and amoxycillin are modified antibiotics. Broad spectrum antibiotics are effective against several types of harmful microorganisms.

Answer the following questions :

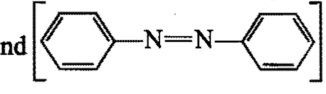
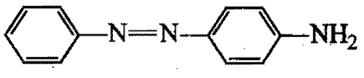
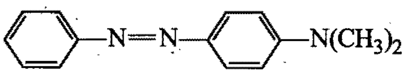
1. Chloramphenicol is :
   (a) antipyretic (b) broad spectrum antibiotic
   (c) azo dye (d) tranquillizer
2. Which of the following is not an antibiotic ?
   (a) Chloramphenicol (b) Sulphadiazine
   (c) Penicillin (d) Bithional
3. Which among the following antibiotics is bacteriostatic?
   (a) Penicillin (b) Ofloxacin
   (c) Aminoglycosiders (d) Erythromycin
4. Which of the following antibiotics is/are the modification of penicillins ?
   (a) Ofloxacin (b) Ampicillin
   (c) Amoxycillin (d) Tetracycline
5. Which of the following antibiotics is effective against tuberculosis?
   (a) Chloromycetin (b) Tetracycline
   (c) Penicillin (d) Streptomycin

Passage 3

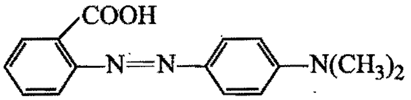
Dyes are the coloured substances that can be applied in solution or dispersion to a substance giving it a colour. Earliest known dyes were indigo and alizarin. These were generally obtained from plants. Dyes generally absorb the electromagnetic radiation of visible region. The dye appears in the complementary colour to that which is absorbed.

Azo dyes have $(-N=N-)$ azo group as chromophore. There are several azo dyes, *e.g.*, congo red, methyl orange, methyl red, aniline yellow, butter yellow, etc. Those azo dyes which contain salts of amino or substituted amino groups ($-NH_2$, $-NR_2$) are basic dyes, which in acid medium form water soluble cation. These dyes attack anionic sites present on the fabrics. Those azo dyes which are usually salt of carboxylic or sulphonic group are acid dyes. Acid dyes can be applied to wool, silk, nylon which have basic group ($-NH_2$).

Answer the following questions :

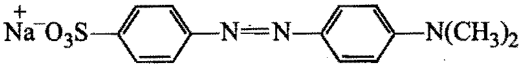
1. A dye absorbs green coloured radiation then it will appear :
   (a) red (b) violet
   (c) orange (d) yellow
2. Which of the following is an example of azo dye ?
   (a) Martius yellow (b) Triphenyl methane
   (c) Indigo (d) Orange-I
3. The compound  azo benzene having a chromophore $(-N=N)$ is known as:
   (a) vat dye (b) chromogen
   (c) mordant dye (d) auxochrome
4. Which of the following is/are not basic dye ?
   (a) 
   Aniline yellow
   (b) 
   Butter yellow

(c)



Methyl red

(d)



Methyl orange

5. Select the correct statement(s) among the following :

(a) Azo dyes do not impart fast colours

(b) Azo dyes are adsorbed only on the surface of fabrics

(c) —NH_2 group acts as auxochrome in aniline yellow

(d) All azo dyes are acid dyes

ANSWERS : LINKED COMPREHENSION TYPE QUESTIONS

Passage 1	**1.** (d)	**2.** (a)	**3.** (c)	**4.** (d)	**5.** (b)
Passage 1	**1.** (b)	**2.** (b,d)	**3.** (d)	**4.** (b,c)	**5.** (d)
Passage 2	**1.** (b)	**2.** (d)	**3.** (b)	**4.** (c,d)	**5.** (a,b,c)

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PROBLEMS BASED UPON STRUCTURES AND REACTIONS OF ORGANIC COMPOUNDS

It has already been discussed in chapter 2, the determination of empirical and molecular formulae of an organic compound. For the sake of revision, the various points are again given below:

Percentage composition : Percentage composition of a compound is the relative mass of each of its constituent elements in 100 parts of it.

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{\text{Mass of CO}_2\text{ formed}}{\text{Mass of organic compound}} \times 100$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{\text{Mass of H}_2\text{O formed}}{\text{Mass of organic compound}} \times 100$$

$$\text{Percentage of nitrogen} = \frac{28}{22400} \times \frac{\text{Volume of nitrogen evolved at NTP}}{\text{Mass of the organic compound}} \times 100 \qquad \text{(Duma's method)}$$

or

$$= \frac{1.4 \times \text{Volume of acid} \times \text{Normality of the acid}}{\text{Mass of organic compound}} \qquad \text{(Kjeldahl's method)}$$

$$\text{Percentage of chlorine} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of organic compound}} \times 100$$

$$\text{Percentage of bromine} = \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of organic compound}} \times 100$$

$$\text{Percentage of iodine} = \frac{127}{235} \times \frac{\text{Mass of AgI formed}}{\text{Mass of organic compound}} \times 100$$

$$\text{Percentage of sulphur} = \frac{32}{233} \times \frac{\text{Mass of BaSO}_4\text{ formed}}{\text{Mass of organic compound}} \times 100$$

$$\text{Percentage of phosphorous} = \frac{62}{222} \times \frac{\text{Mass of Ammonium phosphomolybdate}}{\text{Mass of compound}} \times 100$$

Percentage of oxygen = 100 – (Sum of percentage of all other elements present in the compound)

Determination of empirical formula : It represents the simplest relative whole number ratio of the atoms of each element present in a molecule of the substance.

The following steps are followed to determine the empirical formula:

(i) The percentage of each element is divided by its atomic mass to obtain the atomic ratio of the element present in the compound.

(ii) The atomic ratio of each element is divided by the minimum value of atomic ratio as to get the simplest ratio of the elements in the compound.

(iii) The simplest ratio thus obtained is made whole number ratio by multiplying all ratios by a suitable integer, if need be.

(iv) Symbols of various elements present are written side by side with their whole number ratio as a subscript to the lower right hand corner of the symbol in order to get empirical formula.

Determination of molecular formula : Molecular formula represents the actual number of atoms of elements present in one molecule of the compound.

$$\text{Molecular formula} = n \times \text{Empirical formula}$$

where

$$n = \frac{\text{Molecular mass}}{\text{Empirical mass}}$$

Thus, for the determination of molecular formula, molecular mass of the compound should be known.

$$\text{Molecular mass of the substance (volatile)} = 2 \times \text{vapour density}$$

or

$$= \frac{\text{Mass of the compound}}{\text{Volume of the vapour given by the compound at NTP}} \times 22400$$

$$\text{Molecular mass of the substance (non-volatile)} = \frac{100 \times K \times \text{mass of the compound}}{\Delta T \times \text{mass of the solvent}}$$

where K = Molecular elevation constant or molecular depression constant

ΔT = Elevation in boiling point or depression in freezing point

$$\text{Molecular mass of the acid} = \text{Equivalent mass} \times \text{Basicity}$$

$$= \left(\frac{\text{Mass of silver salt} \times 108}{\text{Mass of silver}} - 107\right)\text{Basicity}$$

$$\text{Molecular mass of the base} = \text{Equivalent mass} \times \text{Acidity}$$

$$= \frac{1}{2}\left(\frac{\text{Mass of platinum salt} \times 195}{\text{Mass of platinum}} - 410\right)\text{Acidity}$$

Molecular formula does not provide the correct picture of the compound as two or more compounds having different properties may have the same molecular formula. Acetone, propionaldehyde and allyl alcohol have the same molecular formula, C_3H_6O, but differ in properties.

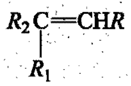
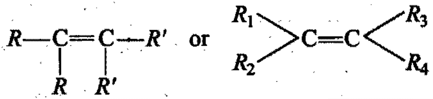
Structural formula : The structural formula represents the arrangement by which the various atoms and groups are linked within the molecule of a compound. Having known the molecular formula, the structural formula can be worked out by the study of the nature of compound and its reactions which confirm the presence of typical group or groups in the compound. Taking into account the valencies of various atoms or groups present, the structural formula can be written down.

In the following tables some characteristic reactions of various homologous series and the inference drawn from them have been listed.

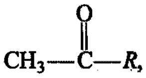
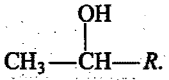
ALIPHATIC COMPOUNDS

(i) Compounds Containing C and H

	Reactions	Inference
1.	Compound decolourises bromine water or dilute alkaline potassium permanganate solution (Baeyer's reagent).	It is an unsaturated compound. It may be alkene ($>C{=}C<$) or alkyne ($-C{\equiv}C-$).
2.	Compound gives precipitate with ammoniacal solution of cuprous chloride or silver nitrate.	The compound is alkyne having acidic hydrogen, *i.e.*, 1-Alkyne ($R-C{\equiv}C-H$).

Reactions	Inference
3. (i) Compound undergoes ozonolysis to give carbonyl compounds.	It is an alkene.
(ii) Ozonolysis products are :	
(a) Only HCHO (2 molecules).	$H_2C{=}CH_2$
(b) One molecule of HCHO and one molecule of higher aldehyde.	$RCH{=}CH_2$
(c) Two different aldehydes other than formaldehyde.	$R_1CH{=}CHR_2$
(d) Two molecules of same aldehyde other than formaldehyde.	$RCH{=}CHR$
(e) One molecule of ketone and one molecule of aldehyde.	 $R_2\underset{R_1}{\underset{\vert}{C}}{=}CHR$
(f) Two different ketones.	 $R{-}\underset{R}{\underset{\vert}{C}}{=}\underset{R'}{\underset{\vert}{C}}{-}R'$ or $R_1R_2C{=}CR_3R_4$

(ii) Compounds containing C, H and O

Reactions	Inference
1. The compound liberates hydrogen with sodium.	The compound may be alcohol or acid.
2. It gives red colouration with ceric ammonium nitrate solution.	The compound is alcohol.
3. (i) It gives aldehyde on oxidation.	The compound is primary alcohol, *i.e.*, $—CH_2OH$ group.
(ii) It gives ketone on oxidation.	The compound is secondary alcohol, *i.e.*, $>$CHOH group.
(iii) It gives ketone with lesser number of carbon atoms on oxidation.	The compound is tertiary alcohol, *i.e.*, $\geq$COH group.
4. With Lucas reagent (conc. HCl + $ZnCl_2$):	
(i) The compound gives turbidity immediately.	The compound is tertiary alcohol.
(ii) The compound gives turbidity within five minutes.	The compound is secondary alcohol.
(iii) The compound does not give turbidity at room temperature.	The compound is primary alcohol.
5. The compound gives pink colour with Schiff's reagent.	The compound is an aldehyde.
6. The compound forms a crystalline precipitate with 2 : 4 dinitrophenyl hydrazine.	The compound may be either aldehyde or ketone.
7. The compound gives silver mirror with Tollens' reagent and red precipitate with Fehling's solution.	The compound is an aldehyde.
8. The compound on reduction gives a primary alcohol.	The compound is an aldehyde.
9. The compound on oxidation gives an acid containing same number of carbon atoms.	The compound is an aldehyde.
10. The compound gives reactions with $NaHSO_3$, H_2NOH, $C_6H_5NHNH_2$, etc., but does not reduce Fehling's solution and Tollens' reagent.	The compound is ketone.
11. The compound on reduction gives secondary alcohol.	The compound is ketone.
12. The compound undergoes iodoform test.	The compound is  $CH_3{-}\overset{O}{\overset{\Vert}{C}}{-}R$, where *R* may be H also, or the compound is  $CH_3{-}\overset{OH}{\overset{\vert}{CH}}{-}R$. (Ethyl alcohol also gives iodoform test.)
13. The compound gives effervescence with $NaHCO_3$.	The compound is an acid.
14. The compound forms ester with alcohol (pleasant smelling liquid).	The compound is an acid.

	Reactions	Inference
15.	On heating, the compound gives CO_2.	The compound is dibasic acid. The two —COOH groups are attached with the same carbon atom.
16.	On heating, the compound loses water.	The compound may be dibasic acid in which both the —COOH groups are present on the adjacent carbon atoms.
17.	The compound on heating loses water and a lactide is formed.	The compound is α-hydroxy acid.
18.	The compound on heating loses water and an unsaturated acid is formed.	The compound is β-hydroxy acid.
19.	The compound on heating loses water and an inner ester (Lactone) is formed.	The compound is γ-hydroxy acid.
20.	The compound is sweet smelling liquid and on hydrolysis produces acid and alcohol.	The compound is an ester.
21.	The compound is boiled with NaOH and phenolphthalein. The pink colour is discharged.	The compound is an ester.

(iii) Compound Containing C, H, N and O

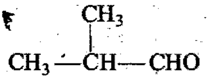
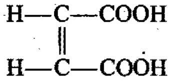
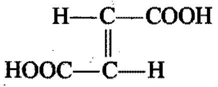
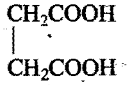
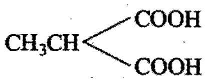
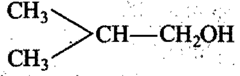
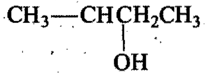
	Reactions	Inference
1.	The compound on heating loses ammonia or the compound on heating with NaOH evolves NH_3.	The compound may be amide or ammonium salt or urea.
2.	The compound on heating with dehydrating agent (P_2O_5) forms a cyanide (nitrile).	The compound is an amide.
3.	The compound yields a primary amine with Br_2 and KOH (Hofmann's bromamide reaction).	The compound is an amide.
4.	The compound gives an amine on reduction with tin and HCl.	The compound is nitro compound.
5.	The compound on reduction gives an alcohol and ammonia.	The compound is alkyl nitrite.

(iv) Compounds Containing C, H and N

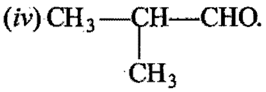
	Reactions	Inference
1.	The compound is soluble in HCl.	The compound may be an amine.
2.	The compound gives offensive smell with chloroform and alcoholic KOH (Carbylamine reaction).	The compound is primary amine.
3.	The compound reacts with nitrous acid ($NaNO_2 + HCl$) to give alcohol and nitrogen.	The compound is primary amine.
4.	The compound on reduction gives primary amine.	The compound is alkyl cyanide (nitrile).
5.	The compound on hydrolysis with dilute mineral acids gives an acid and ammonia.	The compound is alkyl cyanide.
6.	The compound on reduction gives secondary amine.	The compound is alkyl isocyanide.
7.	The compound on hydrolysis gives primary amine and formic acid.	The compound is alkyl isocyanide.

(v) The compound is optically active. The compound contains at least one asymmetric carbon atom.

Isomeric compounds : A molecular formula might represent various isomers. On the basis of molecular formula, the possible isomers are written first and then one of the isomers is selected corresponding to various properties and reactions of the compound given in the problem. Some molecular formulae with possible isomers are given ahead:

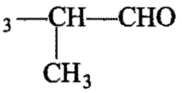
Molecular formula	Possible isomers		
1. C_2H_6O	CH_3CH_2OH Ethanol	CH_3OCH_3 Dimethyl ether	
2. C_3H_6O	CH_3COCH_3 Acetone	CH_3CH_2CHO Propionaldehyde	$H_2C{=}CHCH_2OH$ Allyl alcohol
3. $C_3H_6O_2$	CH_3CH_2COOH Propionic acid	$HCOOC_2H_5$ Ethyl formate	CH_3COOCH_3 Methyl acetate
4. $C_3H_6O_3$	$CH_3CHOHCOOH$ α-Hydroxy propionic acid (Lactic acid)	CH_2OHCH_2COOH β-Hydroxy propionic acid	$(HCHO)_3$ Metaformaldehyde
5. C_4H_8O	$CH_3CH_2CH_2CHO$ *n*-butyraldehyde	$CH_3COC_2H_5$ Ethyl methyl ketone	 $CH_3-\underset{}{\overset{CH_3}{\overset{\vert}{CH}}}-CHO$ Isobutyraldehyde
6. $C_4H_4O_4$	 $\begin{matrix}H-C-COOH\\ \Vert\\ H-C-COOH\end{matrix}$ Maleic acid	 $\begin{matrix}H-C-COOH\\ \Vert\\ HOOC-C-H\end{matrix}$ Fumaric acid	
7. $C_4H_6O_4$	 $\begin{matrix}CH_2COOH\\ \vert\\ CH_2COOH\end{matrix}$ Succinic acid	 $CH_3CH\begin{matrix}COOH\\ COOH\end{matrix}$ Methyl malonic acid	
8. $C_4H_8O_2$	$CH_3CH_2CH_2COOH$ *n*-Butyric acid $CH_3COOC_2H_5$ Ethyl acetate	$(CH_3)_2CHCOOH$ Isobutyric acid $C_2H_5COOCH_3$ Methyl propionate	$HCOOC_3H_7$, *n*- and iso-propyl formate $CH_3CHOHCH_2CHO$ Aldol (β-Hydroxy butyraldehyde)
9. $C_4H_{10}O$	$C_2H_5OC_2H_5$ Diethyl ether  $(CH_3)_2CH-CH_2OH$ 2-Methyl propan-I-ol (iso-butyl alcohol)	$CH_3-O-C_3H_7$ Methyl propyl ether (*n*- or iso-)  $CH_3-\underset{\underset{OH}{\vert}}{CH}CH_2CH_3$ 2-Butanol (Sec. butyl alcohol)	$CH_3CH_2CH_2CH_2OH$ (*n*-Butyl alcohol) 1-Butanol $(CH_3)_3C-OH$ (*Tert.* butyl alcohol) 2-Methyl propan-2-ol
10. C_2H_7N	$CH_3CH_2NH_2$ Ethyl amine	$CH_3-NH-CH_3$ Dimethyl amine	
11. C_3H_5N	CH_3CH_2CN Ethyl cyanide	CH_3CH_2NC Ethyl isocyanide	

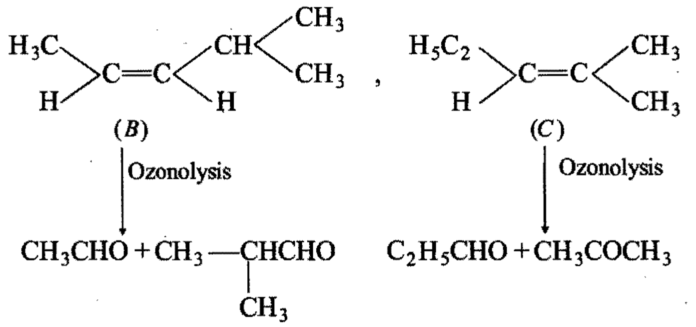
SOME SOLVED PROBLEMS

Problem 1. *A white precipitate was formed slowly when silver nitrate was added to compound (A) with molecular formula* $C_6H_{13}Cl$. *Compound (A) on treatment with alcoholic KOH gave a mixture of two isomeric alkenes (B) and (C), having formula* C_6H_{12}. *The mixture of (B) and (C) on ozonolysis furnished four compounds (i)* CH_3CHO, *(ii)* C_2H_5CHO, *(iii)* CH_3COCH_3 *and (iv)*  $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CHO$.

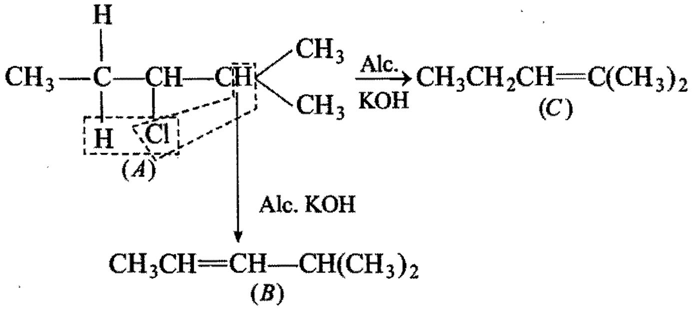
What are the structures of (A), (B) and (C)?

Solution : (*A*) forms slowly a white precipitate with silver nitrate, hence, it should be a secondary alkyl halide.

Since, each alkene has six carbon atoms (C_6H_{12}), so CH_3CHO and  $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CHO$ must result from one alkene and C_2H_5CHO and CH_3COCH_3 from other alkene. Thus, the structure of two alkenes are:



The structure of secondary alkyl halide which yields (*B*) and (*C*) alkenes on treatment with alc. KOH is:



Problem 2. *A chloro compound (A) showed the following properties:*

(*i*) *decolourised bromine in* CCl_4,

(*ii*) *absorbed hydrogen catalytically,*

(*iii*) *gave a precipitate with ammonical* Cu_2Cl_2,

(*iv*) *when vaporised* 1.49 *g of* (*A*) *gave* 448 *mL of vapour at STP.*

Identify (*A*) *and write down the equation of reaction at step* (*iii*).

Solution : The (i) and (ii) properties show that the chloro compound (*A*) is an unsaturated compound having double or triple bond.

The compound gives a precipitate with ammoniacal Cu_2Cl_2. It is, therefore, an alkyne having acidic hydrogen, *i.e.*, $—C{\equiv}CH$.

Determination of molecular mass:

448 mL of the compound weights at STP = 1.49 g

22400 mL of the compound will weigh at STP

$$= \frac{1.49}{448} \times 22400$$

Mol. mass = 74.5

Let the formula of the compound be $RClC{\equiv}CH$

The formula mass $= R + Cl + (—C{\equiv}CH) = 74.5$

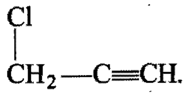
$$R + 35.5 + 25 = 74.5$$

$$R + 60.5 = 74.5$$

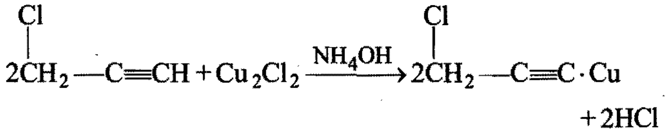
So, $R = 14$

i.e., CH_2

The structure of compound (*A*) is $\overset{Cl}{\overset{|}{CH_2}}—C{\equiv}CH$.



Equation of step (iii).



$$2\overset{Cl}{\overset{|}{CH_2}}—C{\equiv}CH + Cu_2Cl_2 \xrightarrow{NH_4OH} 2\overset{Cl}{\overset{|}{CH_2}}—C{\equiv}C\cdot Cu + 2HCl$$

Problem 3. *From analysis and molecular weight determination the molecular formula of a compound (A) is* C_3H_7NO. *The compound gives the following information.*

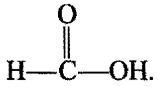
(*i*) *On hydrolysis it gives an amine* (*B*) *and a carboxylic acid* (*C*).

(*ii*) *Amine* (*B*) *reacts with benzene sulphonyl chloride and gives a product which is insoluble in aqueous sodium hydroxide solution.*

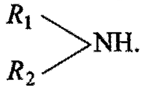
(*iii*) *Acid* (*C*) *on reaction with Tollens' reagent gives a silver mirror.*

What are (*A*), (*B*) *and* (*C*)? *Explain the reactions with the help of equations.*

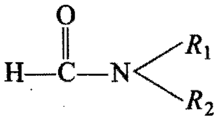
Solution : Acid (*C*) gives silver mirror with Tollens' reagent, thus, the acid (*C*) is formic acid (The acid which possesses aldehydic group), *i.e.*, $H—\overset{O}{\overset{\|}{C}}—OH$.



Compound (*B*) gives a product with benzene sulphonyl chloride which is insoluble in aqueous NaOH. Hence, (*B*) is a secondary amine, *i.e.*, R_1R_2NH.

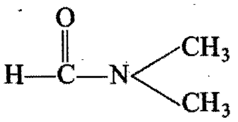


(*B*) and (*C*) are obtained from compound (*A*) on hydrolysis. Thus, the compound (*A*) is amide, *i.e.*, amide of formic acid (C_3H_7NO).



The compound (*A*) contains only 3 carbon atoms, thus, R_1 and R_2 contain one carbon atom each.

The structure of (*A*) is,



N,*N*'-Dimethyl formamide

Reactions :

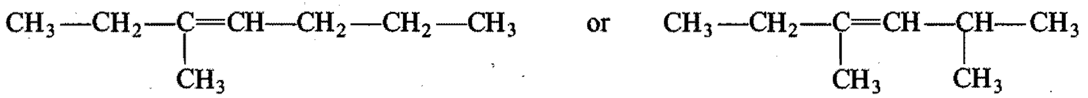
$$\underset{(A)}{HCON(CH_3)_2} + H_2O \longrightarrow \underset{(C)}{HCOOH} + \underset{\substack{Sec.\ amine \\ (B) \\ Dimethyl\ amine}}{(CH_3)_2NH}$$

$$\underset{(B)}{(CH_3)_2NH} + C_6H_5SO_2Cl \longrightarrow \underset{\text{(Insoluble in NaOH)}}{(CH_3)_2NSO_2C_6H_5} + HCl$$

$$\underset{(C)}{HCOOH} + Ag_2O \longrightarrow H_2O + CO_2 + \underset{\text{Silver mirror}}{2Ag}$$

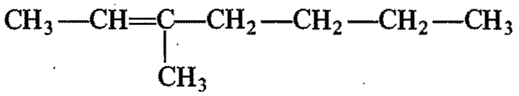
Problem 4. *Alkenes (A) and (B) yield the same alcohol (C) on hydration. On vigorous oxidation with $KMnO_4$, (A) gives a carbonyl compound (D) and an acid (E), each containing four carbon atoms. On the other hand (B) gives an acid (F) and a carbonyl compound (G). In (G), no two identical groups are attached to the same carbon atom. Give structures of (A) to (G) with proper reasoning.*

Solution : Alkene (A) on oxidation gives a carbonyl compound (D) and an acid (E), each having four carbon atoms. Thus, the probable structure of (A) may be,



$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-CH_3 \quad \text{or} \quad CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

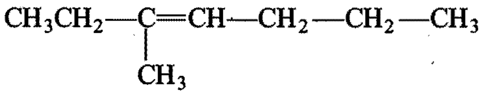
Alkene (B) gives an acid (F) and a carbonyl compound (G). Alkene (B) gives same alcohol on hydration and is isomeric to (A). The carbonyl compound (G) has no carbon atom having two identical groups. Thus, the structure of (B) should be,



$$CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH_2-CH_3$$

(B)

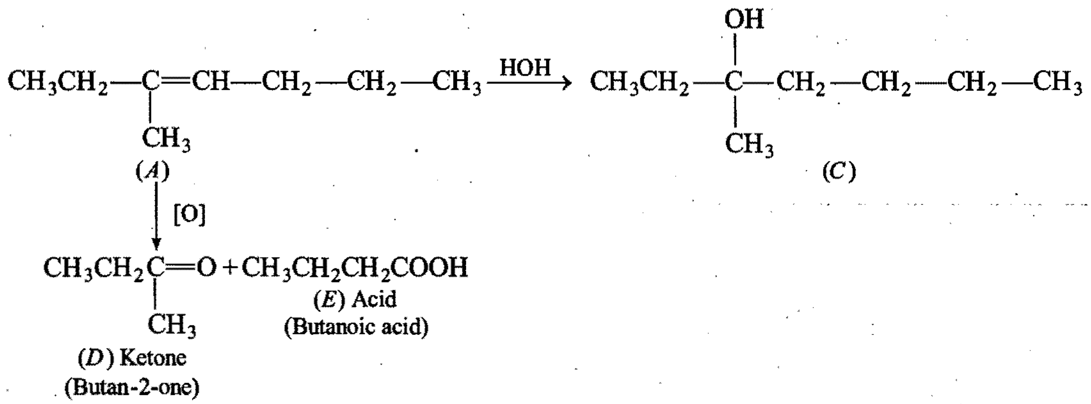
The alkene (A) should also possess the corresponding structure, thus, structure of (A) is,



$$CH_3CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-CH_3$$

(A)

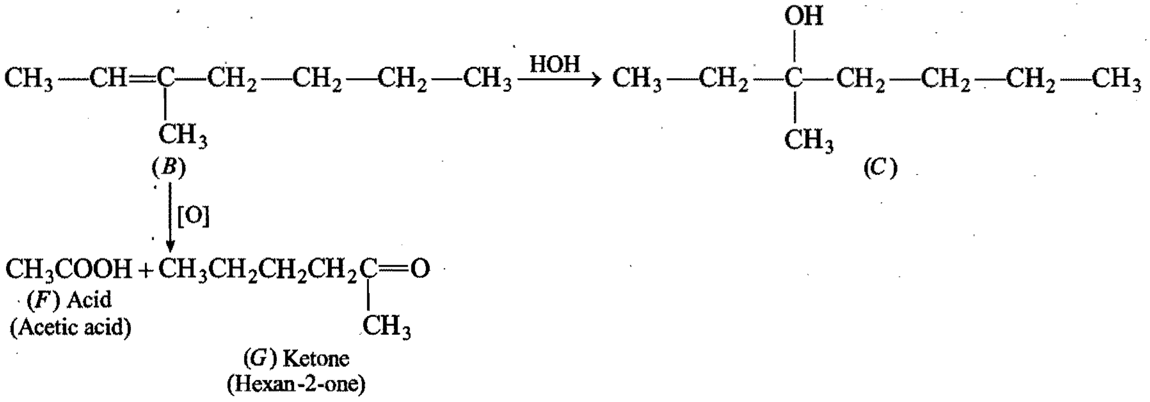
Reactions :



$$\underset{(A)}{CH_3CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-CH_3} \xrightarrow{HOH} \underset{(C)}{CH_3CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2-CH_2-CH_3}$$

$$\downarrow [O]$$

$$\underset{\substack{(D)\text{ Ketone}\\ \text{(Butan-2-one)}}}{CH_3CH_2\underset{\underset{CH_3}{|}}{C}=O} + \underset{\substack{(E)\text{ Acid}\\ \text{(Butanoic acid)}}}{CH_3CH_2CH_2COOH}$$



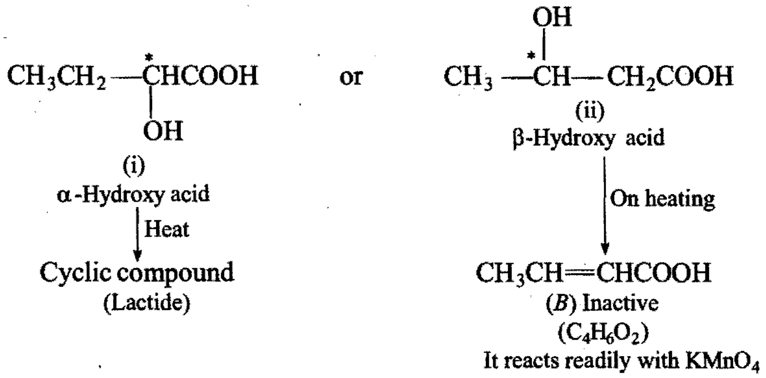
$$\underset{(B)}{CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH_2-CH_3} \xrightarrow{HOH} \underset{(C)}{CH_3-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2-CH_2-CH_3}$$

$$\downarrow [O]$$

$$\underset{\substack{(F)\text{ Acid}\\ \text{(Acetic acid)}}}{CH_3COOH} + \underset{\substack{(G)\text{ Ketone}\\ \text{(Hexan-2-one)}}}{CH_3CH_2CH_2CH_2\underset{\underset{CH_3}{|}}{C}=O}$$

Problem 5. *An acidic compound (A), $C_4H_8O_3$, loses its optical activity on strong heating yielding (B), $C_4H_6O_2$, which reacts readily with $KMnO_4$. (B) forms a derivative (C) with $SOCl_2$, which on reaction with $(CH_3)_2NH$ gives (D). The compound (A) on oxidation with dilute chromic acid gives an unstable compound (E) which decarboxylates readily to give (F), C_3H_6O. The compound (F) gives a hydrocarbon (G) on treatment with amalgamated Zn and HCl. Give structures of (A) to (G) with proper reasoning.*

Solution : The compound (*A*) is an acid and optical active. It possesses an asymmetric carbon and a carboxylic group. The structure of (*A*) may be,



$$\mathrm{CH_3CH_2-\underset{OH}{\underset{|}{\overset{*}{C}}}HCOOH} \quad \text{or} \quad \mathrm{CH_3-\overset{OH}{\overset{|}{\overset{*}{C}}}H-CH_2COOH}$$

(i)
α-Hydroxy acid
Heat
Cyclic compound
(Lactide)

(ii)
β-Hydroxy acid
On heating
$CH_3CH{=}CHCOOH$
(*B*) Inactive
($C_4H_6O_2$)
It reacts readily with $KMnO_4$

Thus, (*A*) is $CH_3CHOHCH_2COOH$.

$$\underset{\substack{(A)\\ \beta\text{-Hydroxy butyric acid}}}{CH_3CHOHCH_2COOH} \xrightarrow[\text{acid}]{\text{Dil. chromic}} \underset{(E)}{CH_3COCH_2COOH} \xrightarrow{-CO_2} \underset{\substack{(F)\\ (C_3H_6O)}}{CH_3COCH_3}$$

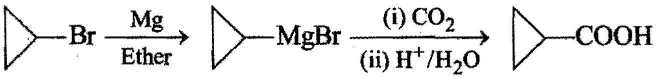
$$\Big\downarrow \text{Zn(Hg)/HCl}$$

$$\underset{(G)}{CH_3CH_2CH_3}$$

$$\underset{(B)}{CH_3CH{=}CHCOOH} \xrightarrow{SOCl_2} \underset{(C)}{CH_3CH{=}CHCOCl} \xrightarrow{(CH_3)_2NH} \underset{(D)}{CH_3CH{=}CHCON(CH_3)_2}$$

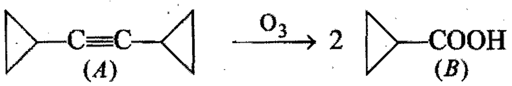
Problem 6. *A hydrocarbon A, of C_8H_{10}, on ozonolysis gives compound (B), $C_4H_6O_2$ only. The compound (B) can also be obtained from alkyl bromide (C), C_3H_5Br, upon treatment with magnesium in dry ether, followed by CO_2 and acidification. Identify (A), (B) and (C) and also give equations for the reactions.*

Solution : The compound (*B*) is formed *via* the formation of Grignard reagent followed by reaction with CO_2 and acidification. It shows that C_3H_5Br behaves like saturated compound. It is only possible if C_3H_5Br is bromocyclopropane (Cyclo propyl bromide).



C_3H_5Br (*C*) (*B*) $C_4H_6O_2$

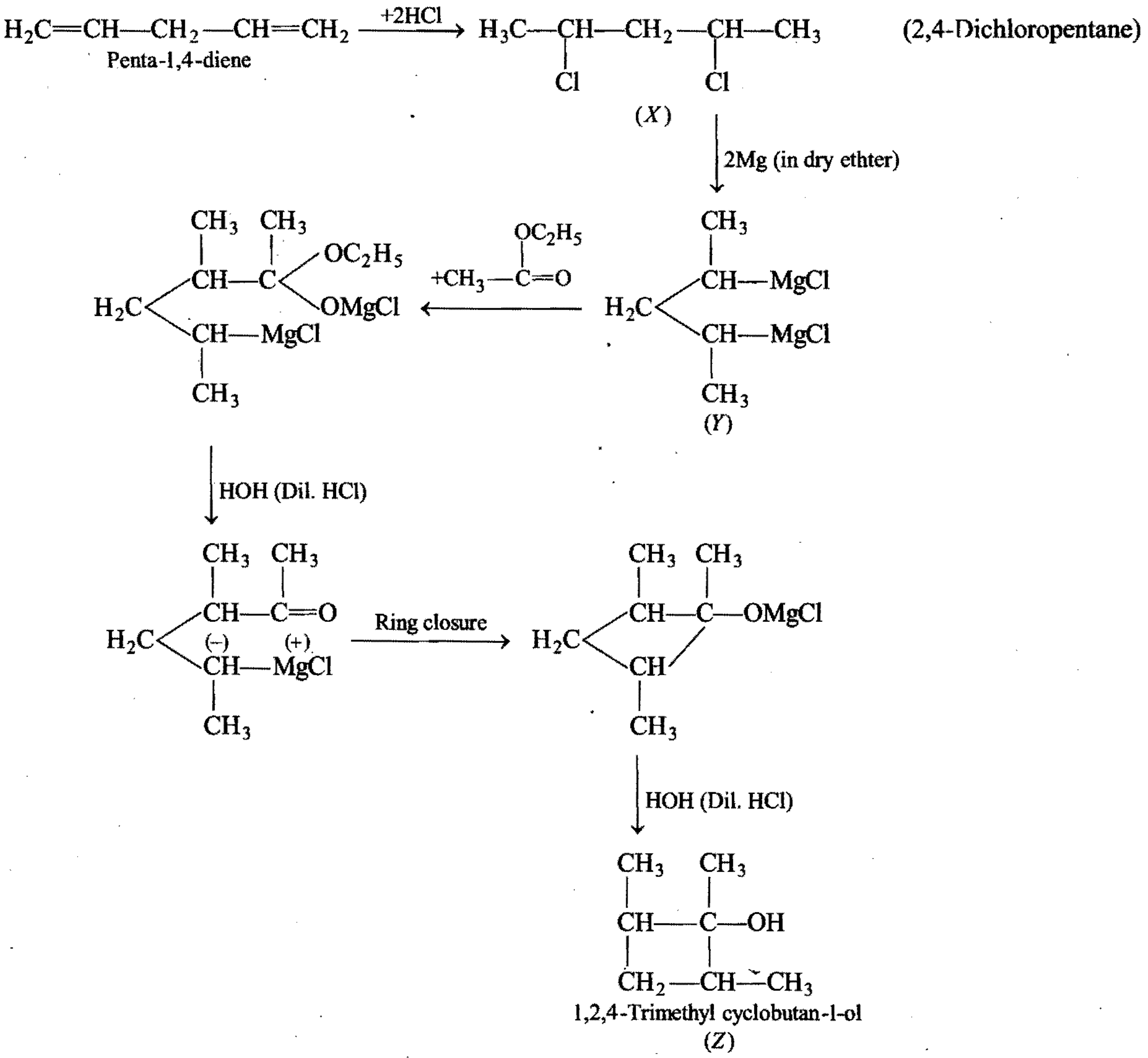
(*A*) on ozonolysis gives only (*B*), hence it should be symmetrical unsaturated hydrocarbon.



(*A*)
C_8H_{10}
(*B*)

Problem 7. *1,4-pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound X which upon reaction with excess of Mg in dry ether forms Y. Compound Y on treatment with ethyl acetate followed by dilute acid yields Z. Identify the structures of compounds X, Y and Z.*

Solution : 1,4-pentadiene on addition with excess of HCl in the presence of benzoyl peroxide, forms 2,4-dichloro pentane (*X*) because HCl does not show peroxide effect.



Problem 8. *A mixture of an acid anhydride (A) and a mono basic acid (B) on heating produces another mono basic acid (C) of equivalent weight 74 and an anhydride (D). The acids and anhydrides remain in equilibrium. The anhydride (D) contains two identical fluoro alkyl groups. The acid (B) contains a trifluoro methyl group and has an equivalent weight of 128. Give structures of (A) to (D) with proper reasoning (Atomic weight of fluorine = 19).*

Solution :

$$\underset{(A)}{(RCO)_2O} + \underset{(B)}{2R'\text{—}COOH} \longrightarrow \underset{\substack{(C)\\ \text{(Mol. wt. 74)}}}{2RCOOH} + \underset{(D)}{(R'CO)_2O}$$

Mol. wt. of R—COOH = 74, $R + 12 + 32 + 1 = 74$, $R = 74 - 45 = 29$ (C_2H_5)

Thus, (C) is CH_3CH_2COOH and on the basis of above reaction, acid anhydride (A) is $(C_2H_5CO)_2O$.

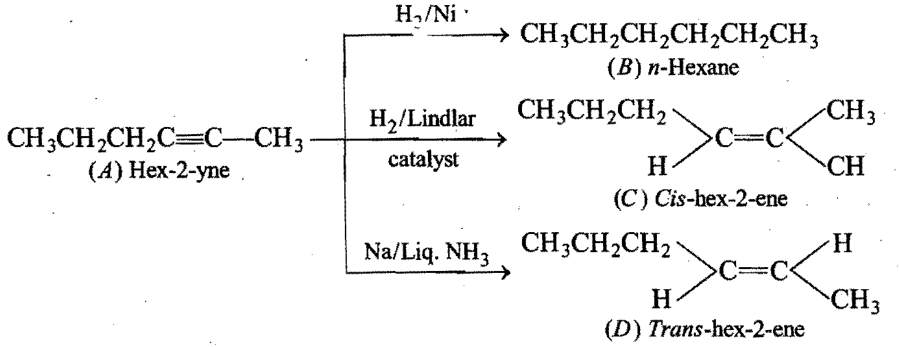
The acid anhydride (D) contains two identical fluoro alkyl groups. The acid (B) contains a trifluoro methyl group and has an equivalent weight of 128. Hence, mono basic acid (B) is CF_3CH_2COOH and so, acid anhydride (D) is $(CF_3CH_2CO)_2O$.

Reactions:

$$\underset{(A)}{(CH_3CH_2CO)_2O} + \underset{\substack{(B)\\ \text{Eq. wt.} = 128}}{CF_3CH_2COOH} \longrightarrow \underset{\substack{(C)\\ \text{Eq. wt.} = 74}}{CH_3CH_2COOH} + \underset{(D)}{(CF_3CH_2CO)_2O}$$

Problem 9. *Hydrocarbon (A), C_6H_{10} on treatment with H_2/Ni, H_2/Lindlar catalyst and Na/liquid ammonia forms three different reduction products (B), (C) and (D) respectively. (A) does not form any salt with ammoniacal* $AgNO_3$ *solution, but forms a salt (E) on heating with* $NaNH_2$ *in an inert solvent. Compound (E) reacts with* CH_3I *to give (F). Compound (D) on oxidative ozonolysis gives n-butanoic acid along with other product. Give structures of (A) to (F) with proper reasoning.*

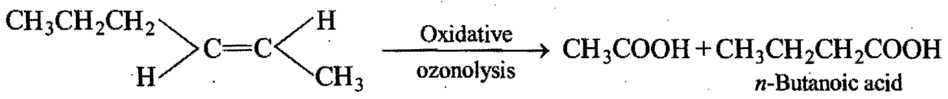
Solution : (i) The given compound (*A*) is confirmed by the following reactions.



(ii) *A* does not form any salt with ammoniacal $AgNO_3$ solution, but forms a salt (*E*) on heating with $NaNH_2$ in an inert solvent.

$$\underset{(A)\ \text{Hex-2-yne}}{CH_3CH_2CH_2C{\equiv}C{-}CH_3} \xrightarrow{NaNH_2} \underset{(E)}{CH_3CH_2CH_2CH_2C{\equiv}CNa} \xrightarrow{CH_3I} \underset{(F)}{CH_3CH_2CH_2CH_2C{\equiv}CCH_3}$$

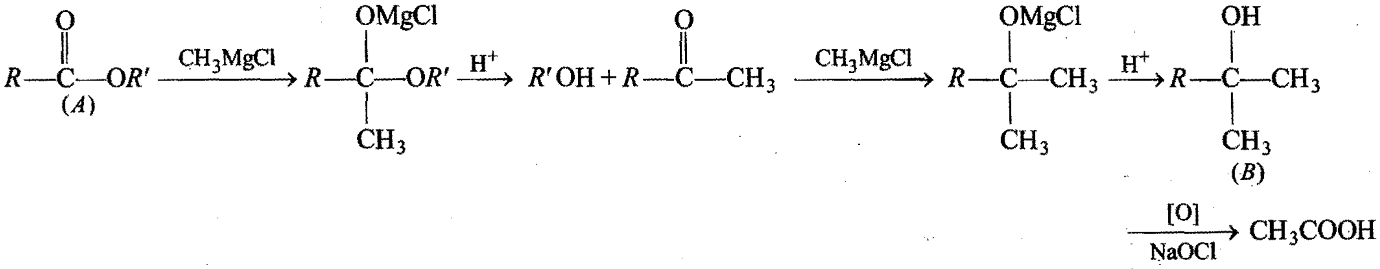
(iii) Oxidative ozonolysis of (D) gives $CH_3CH_2CH_2COOH$ along with CH_3COOH



Problem 10. *An ester* (*A*) ($C_4H_8O_2$), *on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol* (*B*) *as the sole organic product. Alcohol* (*B*), *on oxidation with* NaOCl *followed by acidification gives acetic acid. Deduce the structures of* (*A*) *and* (*B*). *Show the reactions involved.*

Solution : Let the ester be $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR'$, *i.e.*, $C_4H_8O_2$.

The reactions of an ester with methyl magnesium chloride are as follows:



$$\underset{(A)}{R{-}\overset{\overset{O}{\|}}{C}{-}OR'} \xrightarrow{CH_3MgCl} R{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OMgCl}{|}}{C}}{-}OR' \xrightarrow{H^+} R'OH + R{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow{CH_3MgCl} R{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OMgCl}{|}}{C}}{-}CH_3 \xrightarrow{H^+} \underset{(B)}{R{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH_3} \xrightarrow[NaOCl]{[O]} CH_3COOH$$

Thus, *R*, should be H, because only secondary alcohol can be oxidised by NaOCl and not tertiary.

Hence, the ester is $H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_3H_7$ ($C_4H_8O_2$) and *R*'OH on oxidation gives CH_3COOH. Thus, *R*'OH must be secondary alcohol of three carbon atoms, $(CH_3)_2CH{-}OH$, *i.e.*, *R*' is isopropyl $(CH_3)_2CH{-}$. Therefore, the ester (*A*) is $H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}CH_3$ (isopropyl formate) and alcohol (*B*) is a secondary alcohol, $CH_3{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}CH_3$ (isopropyl alcohol).

AROMATIC COMPOUNDS

The following characteristic properties are greatly helpful in deciding the structure of an aromatic compound.

Compounds containing C and H

Reactions	Inference
1. On oxidation a new compound having —COOH group is formed.	The compound contains a side chain attached to the benzene nucleus.
2. Compound obtained on oxidation is phthalic acid.	The compound has two side chains, *ortho* to each other.
3. The compound decolourises bromine water or forms addition product with bromine.	The compound has unsaturated side chain, *i.e.*, presence of —C═C— or —C≡C— bond in the side chain.

Compounds containing C, H and O

Reactions	Inference
1. It liberates hydrogen by the action of Na.	The compound has either alcoholic or carboxylic group.
2. It gives red colouration with ceric ammonium nitrate.	The compound has alcoholic group.
3. The compound turns blue litmus red.	The compound is either phenol or acid.
4. The compound gives blue, red, green or violet colouration or ppt. with $FeCl_3$.	Phenolic group, *i.e.*, —OH is present in benzene nucleus.
5. The compound gives pink colour with Schiff's reagent.	—CHO group is present.
6. The compound reduces Tollens' reagent, *i.e.*, produces silver mirror or greyish black precipitate.	—CHO group is present.
7. The compound forms an oxime with hydroxyl amine and hydrazone with hydrazine.	Carbonyl group ($>C{=}O$), *i.e.*, aldehydic or ketonic group is present.
8. The compound undergoes Cannizzaro's reaction, *i.e.*, it reacts with conc. soln. of KOH to produce a molecule of alcohol and a molecule of potassium salt of an acid.	—CHO (aldehydic group) is linked to benzene nucleus as in benzaldehyde.
9. The compound gives effervescence with $NaHCO_3$ solution.	The compound contains a carboxylic group.
10. Aromatic dibasic acid loses a water molecule.	The compound is phthalic acid.
11. The compound on distillation with zinc dust gives benzene or its homologue.	The compound has phenolic group, *i.e.*, —OH in the nucleus.
12. The compound undergoes Reimer-Tiemann reaction.	The compound is a phenol.

Compounds containing C, H, N and O

Reactions	Inference
1. The compound evolves ammonia when heated with NaOH.	The compound has amide, —$CONH_2$ group.
2. With Br_2 and KOH, the compound gives primary amine.	The compound is an amide.
3. On hydrolysis, it forms an amine.	The compound is an anilide or benzanilide.
4. The compound forms a primary amine on reduction with Sn and HCl or $SnCl_2$ and HCl.	—NO_2 group is present.

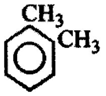
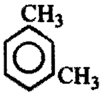
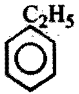
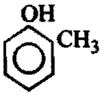
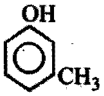
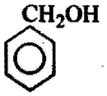
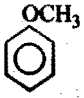
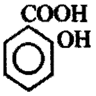
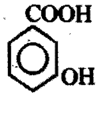
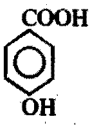
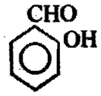
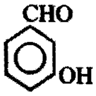
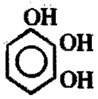
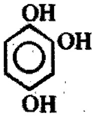
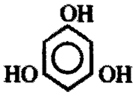
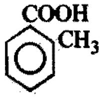
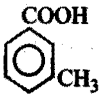
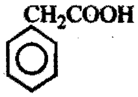
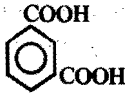
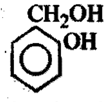
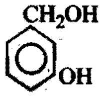
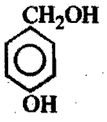
Compounds containing C, H and N

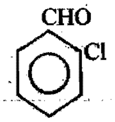
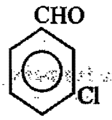
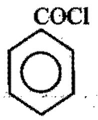
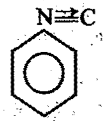
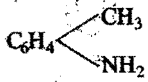
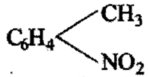
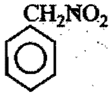
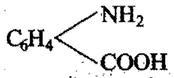
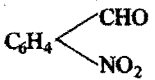
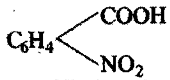
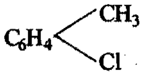
Reactions	Inference
1. Compound is soluble in water and turns red litmus blue.	It has —NH_2 group in the side chain.
2. The compound is soluble in dilute HCl.	The compound is an amine.
3. The compound undergoes diazotisation.	The compound has an (—NH_2) amino group in the benzene nucleus.
4. The compound forms an acid on hydrolysis and a primary amine on reduction.	The compound is a nitrile, *i.e.*, it has —CN group.
5. The compound on partial hydrolysis with H_2O_2 and NaOH gives an amide.	The compound has —CN group.

Compounds containing C, H and Halogens

Reactions	Inference
1. On oxidation, the compound gives an acid in which halogen is absent.	The halogen is present in the side chain.
2. On oxidation, the compound gives an acid which contains halogen.	Compound contains a side chain but halogen atom is present in the benzene nucleus.
3. The halogen is easily replaced by —OH, —CN, —NH_2 groups.	The halogen is present in the side chain.
4. The halogen is not easily replaced by —OH, —CN, —NH_2 groups.	The halogen is present in the nucleus.

Molecular Formula and Possible Isomers

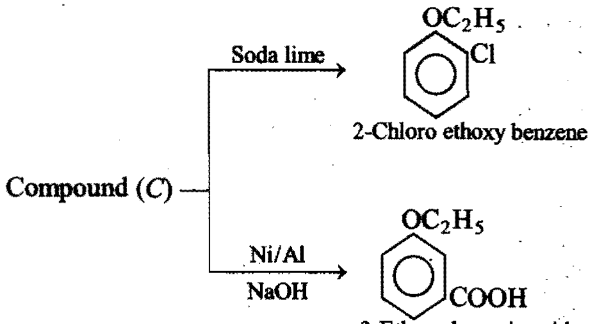
Molecular formula	**Possible Isomers**
(i) C_8H_{10}	, *o*-Xylene , *m*-Xylene , *p*-Xylene  Ethyl benzene
(ii) C_7H_8O	, *o*-Cresol , *m*-Cresol , *p*-Cresol , Benzyl alcohol  Anisole
(iii) $C_7H_6O_3$	, *o*-Hydroxy benzoic acid , *m*-Hydroxy benzoic acid  *p*-Hydroxy benzoic acid
(iv) $C_7H_6O_2$	, *o*-Hydroxy benzaldehyde , *m*-Hydroxy benzaldehyde , *p*-Hydroxy benzaldehyde  Benzoic acid
(v) $C_6H_6O_3$	, 1,2,3-Trihydroxy benzene (Pyrogallol) , 1,2,4-Trihydroxy benzene (Hydroxyquinol)  1,3,5-Trihydroxy benzene (Phloroglucinol)
(vi) $C_8H_8O_2$	, *o*-Toluic acid , *m*-Toluic acid , *p*-Toluic acid , Phenyl acetic acid  Methyl benzoate
(vii) $C_8H_6O_4$	, Phthalic acid , Isophthalic acid  Terephthalic acid
(viii) $C_7H_8O_2$	, *o*-Hydroxy benzyl alcohol , *m*-Hydroxy benzyl alcohol  *p*-Hydroxy benzyl alcohol

(ix) C_7H_5ClO	 *o*-Chloro benzaldehyde ,  *m*-Chloro benzaldehyde ,  *p*-Chloro benzaldehyde ,  Benzoyl chloride
(x) C_7H_5N	 Phenyl cyanide ,  Phenyl isocyanide
(xi) C_7H_9N	 $C_6H_4<^{CH_3}_{NH_2}$ *o*-, *m*-, *p*-Toluidine , $C_6H_5NHCH_3$ Methyl aniline ,  Benzylamine ,
(xii) $C_7H_7NO_2$	 $C_6H_4<^{CH_3}_{NO_2}$ *o*-, *m*-, *p*-Nitrotoluene ,  Phenyl nitromethane , $C_6H_5CH_2—O—N{=}O$ Benzyl nitrite ,  $C_6H_4<^{NH_2}_{COOH}$ *o*-,*m*-, *p*-Amino benzoic acid
(xiii) $C_7H_5NO_3$	 $C_6H_4<^{CHO}_{NO_2}$ *o*-, *m*-, *p*-Nitrobenzaldehyde
(xiv) $C_7H_5NO_4$	 $C_6H_4<^{COOH}_{NO_2}$ *o*-, *m*-, *p*-Nitrobenzoic acid
(xv) C_7H_7Cl	 $C_6H_4<^{CH_3}_{Cl}$ *o*-,*m*-, *p*-Chlorotoluene , $C_6H_5CH_2Cl$ Benzyl chloride

SOME SOLVED PROBLEMS

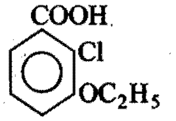
Problem 11. *Two isomeric forms of an organic compound (A),* $C_{11}H_{13}OCl$ *readily decolourise bromine water and give same compound (B) on catalytic hydrogenation. Both the isomeric forms on vigorous oxidation give (C) which on treatment with soda lime gives 2-chloro ethoxy benzene. However, (C) on treatment with Ni/Al alloy in alkaline medium gives 3-ethoxy benzoic acid. Only one of the isomers of (A) gives geometrical isomers (D) and (E). Identify (A) to (E) with proper reasoning.*

Solution :



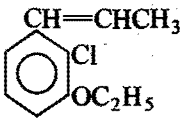
Hence, the structure of compound (*C*) can be,

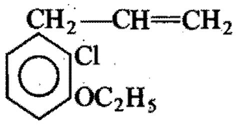
or



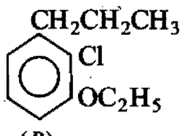
The compound (*A*) is unsaturated which possesses —Cl and —OC_2H_5 groups also.

The two isomers of (*A*) are

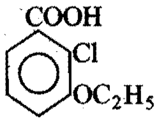

(i)


(ii)

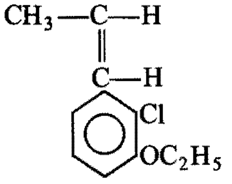
Both the isomers decolourise bromine water and on hydrogenation give the compound (*B*)


(*B*)

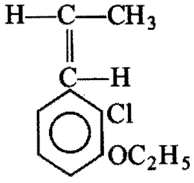
(*B*) on oxidation forms (*C*)


(*C*)

(i) isomer of (*A*) shows geometrical isomerism, (*D*) and (*E*).



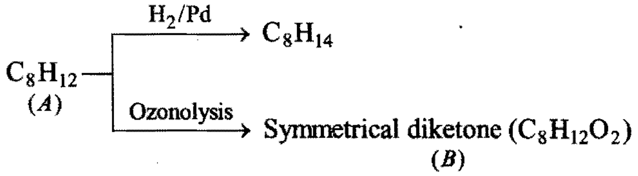
(*Cis*)



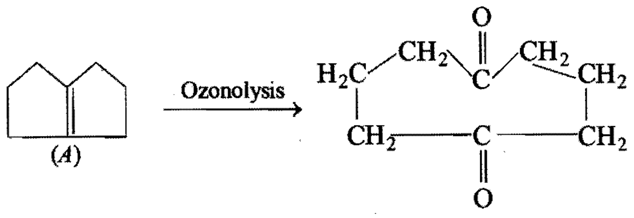
(*Trans*)

Problem 12. *One mole of the compound* (*A*), C_8H_{12} *incapable of showing stereoisomerism, reacts with only one mole of* H_2 *on hydrogenation over Pd.* (*A*) *undergoes ozonolysis to give a symmetrical diketone* (*B*), $C_8H_{12}O_2$. *What are the structures of* (*A*) *and* (*B*)?

Solution :



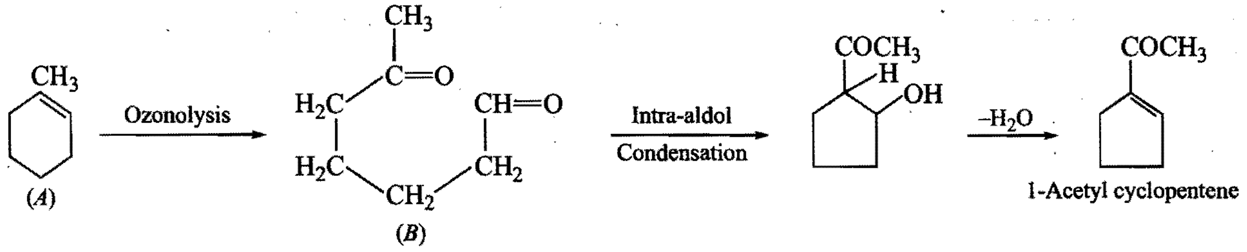
The structures of *A* and *B* are as follows:



(*B*)

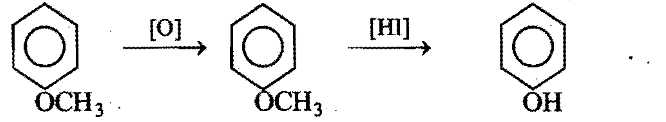
Problem 13. *A hydrocarbon* (*A*) *of the formula,* C_7H_{12} *on ozonolysis gives a compound* (*B*) *which undergoes aldol condensation giving* 1-*acetyl cyclopentene. Identify* (*A*) *and* (*B*).

Solution : Since, the ozonolysis of hydrocarbon, (*A*), C_7H_{12} gives only one compound (*B*), it is clear that the compound (*A*), is cyclo alkene. The ozonolysis product, (*B*) (with no loss of carbon atom) must have undergone intra-aldol condensation and gives 1-acetyl cyclopentene, *i.e.*,



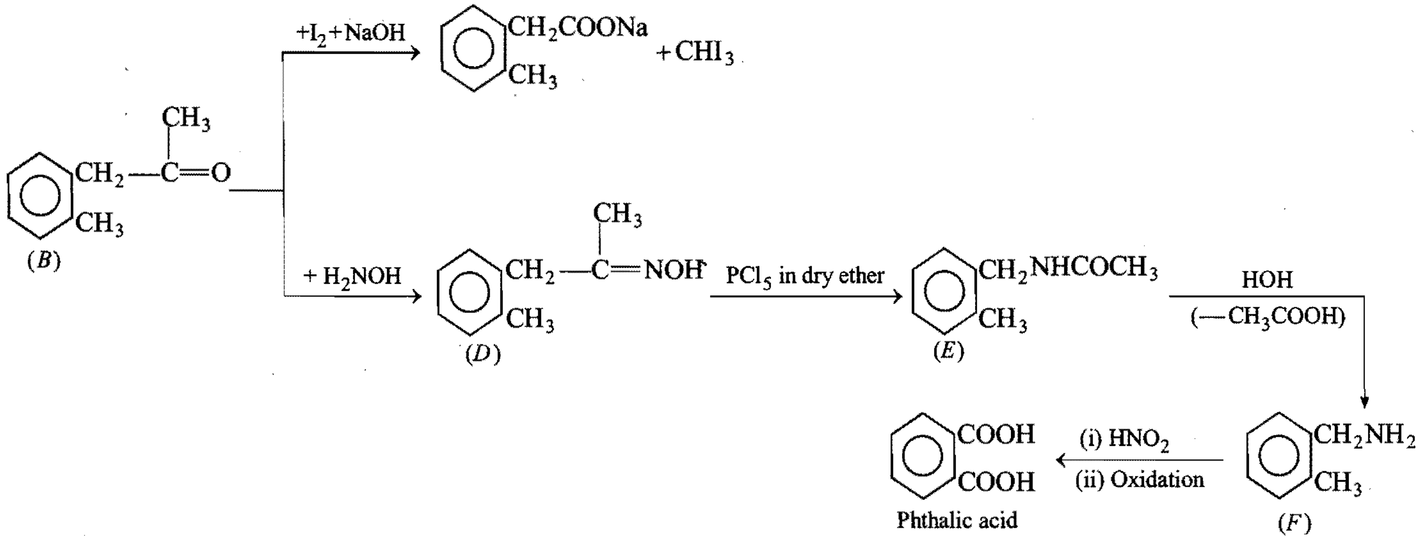
Problem 14. *An organic compound* (*A*), $C_{18}H_{20}O$ *on ozonolysis gives* (*B*), $C_{10}H_{12}O$ *and* (*C*) $C_8H_8O_2$. *Compound* (*B*) *gives iodoform reaction and produces an oxime* (*D*), $C_{10}H_{13}ON$ *on treatment with* NH_2OH. *Compound* (*D*) *reacts with* PCl_5 *in dry ether to give* (*E*) *which on hydrolysis gives* (*F*), $C_8H_{11}N$ *and acetic acid.* (*F*) *on treatment with* HNO_2 *followed by oxidation gives phthalic acid. Compound* (*C*) *on mild oxidation gives* (*G*) *which gives effervescence with* $NaHCO_3$. (*G*) *on treatment with HI produces p-hydroxy benzoic acid and* CH_3I. *Give structures of* (*A*) *to* (*G*) *with proper reasoning.*

Solution :

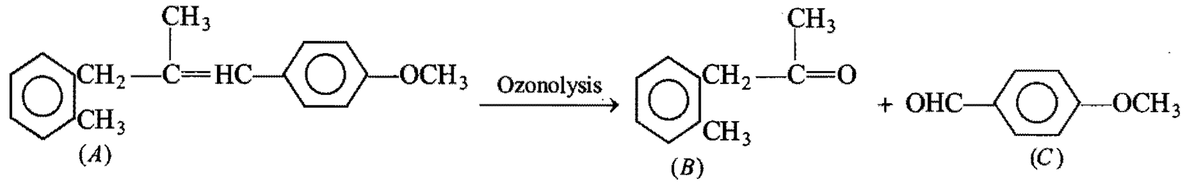


(*C*) (*G*) *p*-Hydroxy benzoic acid

The compound (*B*) gives iodoform test as it has $-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ group and produces oxime with NH_2OH.

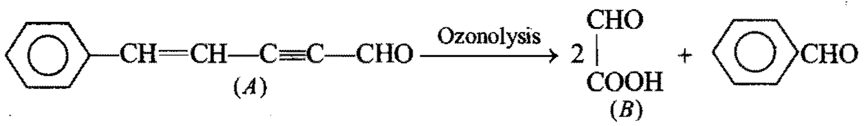


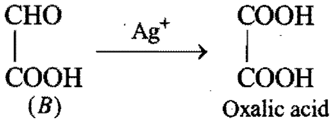
Hence (*A*) is



Problem 15. *An aldehyde (A)* ($C_{11}H_8O$), *which does not undergo self aldol condensation, gives benzaldehyde and two moles of (B) on ozonolysis. Compound (B), on oxidation with silver ion, gives oxalic acid. Identify the compounds (A) and (B).*

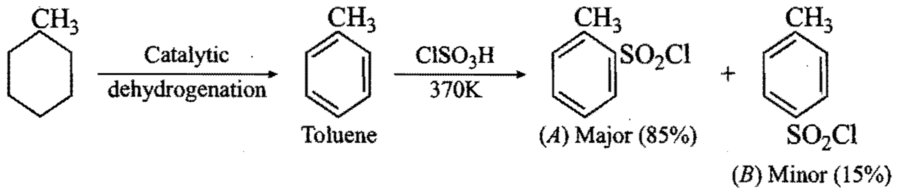
Solution : Since, the given aldehyde does not undergo self aldol condensation, it will not contain α-hydrogen atom. Further it undergoes ozonolysis indicating the presence of unsaturation probably at two places as the products are benzaldehyde and two moles of (*B*). So, the structure of given aldehyde ($C_{11}H_8O$) is

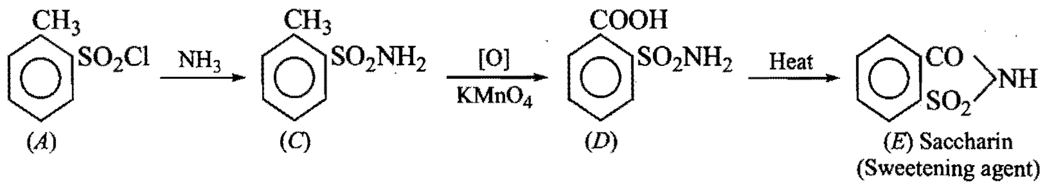


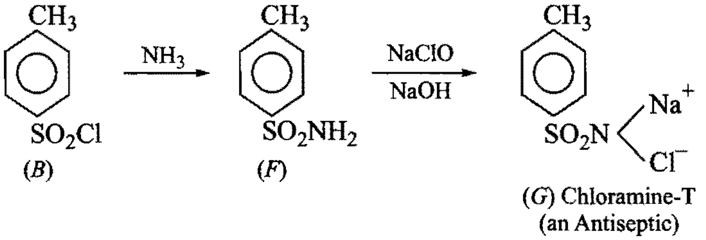


Problem 16. *Catalytic dehydrogenation of methyl cyclohexane, obtained from petroleum gives a liquid which on treatment with chloro sulphonic acid at* 370*K yields a mixture of two isomers (A) and (B),* $C_7H_7SO_2Cl$*. The major isomer (A) reacts with ammonia to form (C), which on oxidation with permanganate gives compound (D). On heating, compound (D) gives a well known sweetening agent (E). The minor isomer (B) also reacts with ammonia to give a compound (F) which on treatment with* NaClO/NaOH *gives an antiseptic (G). Identify (A) to (G) with proper reasoning.*

Solution :

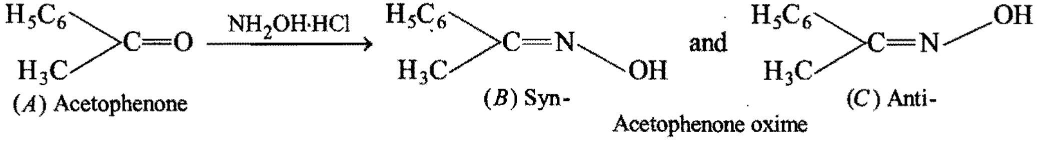


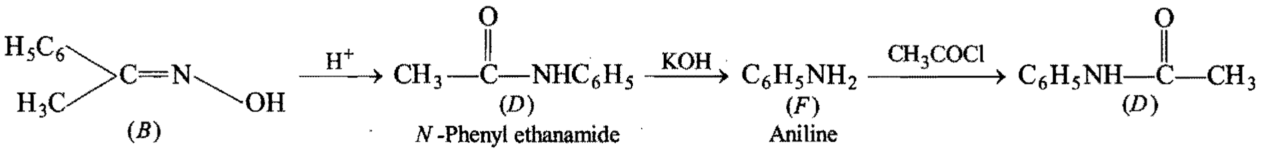


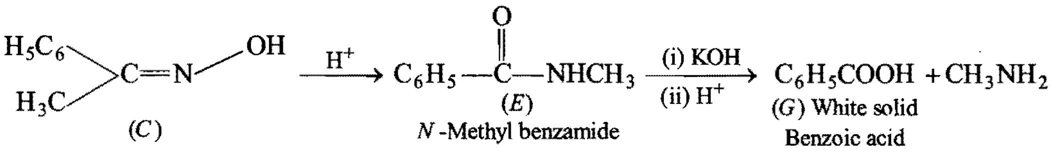


Problem 17. *Compound (A)* (C_8H_8O) *on treatment with* $NH_2OH.HCl$ *gives (B) and (C). (B) and (C) rearrange to give (D) and (E), respectively, on treatment with acid. (B), (C), (D) and (E) are all isomers of molecular formula* (C_8H_9NO)*. When (D) is boiled with alcoholic* KOH, *an oil (F)* (C_6H_7N) *separates out. (F) reacts rapidly with* CH_3COCl *to give back (D). On the other hand, (E) on boiling with alkali followed by acidification gives a white solid (G)* ($C_7H_6O_2$)*. Identify (A) to (G).*

Solution :

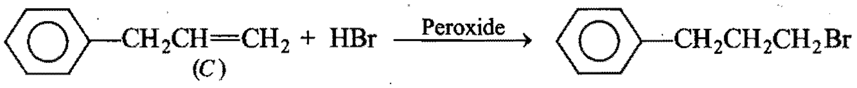






Problem 18. *A Grignard reagent (A) and a haloalkene (B) react together to give (C). Compound (C) on heating with KOH yields a mixture of two geometrical isomers, (D) and (E), of which (D) predominates. (C) and (E) have the same molecular formula and (C) gives 1-bromo-3-phenyl propane on reaction with HBr in the presence of a peroxide. Give structures of (A), (B) and (C) and configurations of (D) and (E) with reasons.* **[Roorkee 2001]**

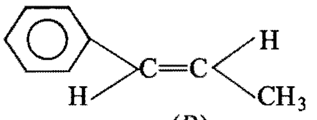
Solution : Since, (C) gives 1-bromo-3-phenyl propane on reaction with HBr in the presence of a peroxide; therefore, (C) is 3-phenyl prop-1-ene.



1-Bromo-3-phenyl propane

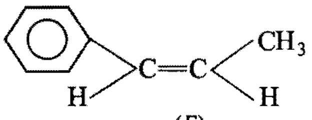
Because (C) and (E) have same molecular formula, therefore, they are isomers and the reaction is:

$(C) \xrightarrow{KOH} (D) + (E)$, it is an isomerisation reaction. So, (D) and (E) are 3-phenyl prop-2-ene.



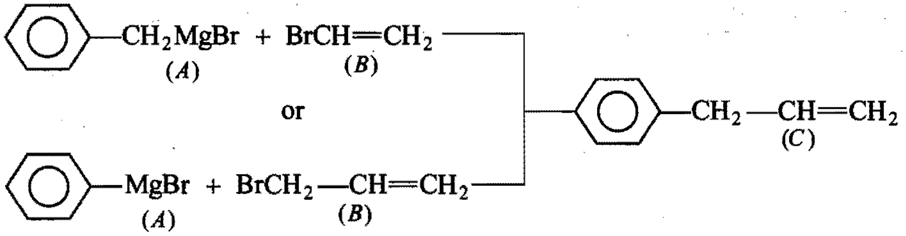
(D)

and



(E)

Since, (*C*) is obtained by the reaction of a Grignard reagent (*A*) with haloalkene (*B*), therefore, (*A*) and (*B*) are:



Problem 19. *Five isomeric para disubstituted aromatic compounds (A) to (E) with molecular formula* $C_8H_8O_2$ *were given for identification. Based on the following observation give structures of the compounds:*

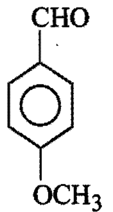
(*i*) *Both (A) and (B) form a silver mirror with Tollens' reagent; also (B) gives a positive test with* $FeCl_3$ *solution.*

(*ii*) *(C) gives a positive iodoform test.*

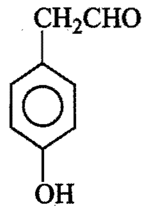
(*iii*) *(D) is readily extracted in aqueous* $NaHCO_3$ *solution.*

(*iv*) *(E) on hydrolysis gives* 1,4-*dihydroxy benzene.* **[IIT 2002]**

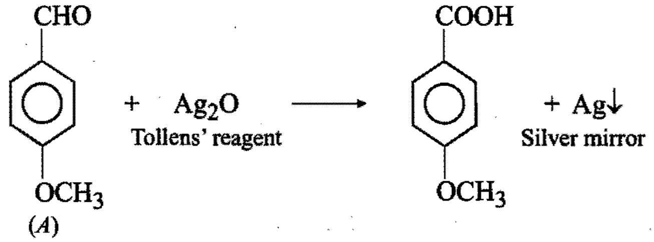
Solution : (i) Compounds (*A*) and (*B*) must contain aldehydic group because both form silver mirror with Tollens' reagent. (*B*) must contain phenolic group because it gives positive $FeCl_3$ test. Hence, compounds (*A*) and (*B*) must be:

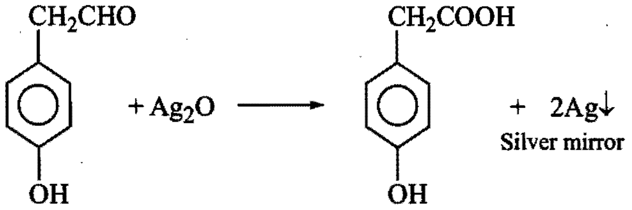


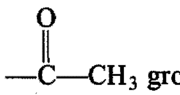
(*A*)
p-Methoxybenzaldehyde

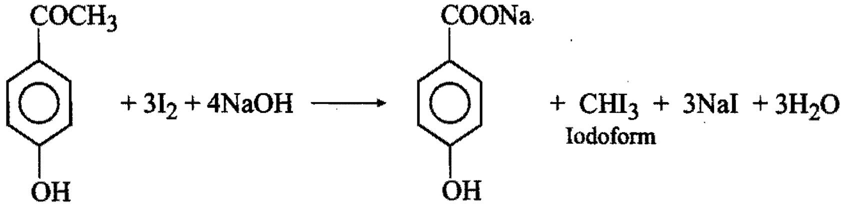


(*B*)
p-Methoxybenzaldehyde



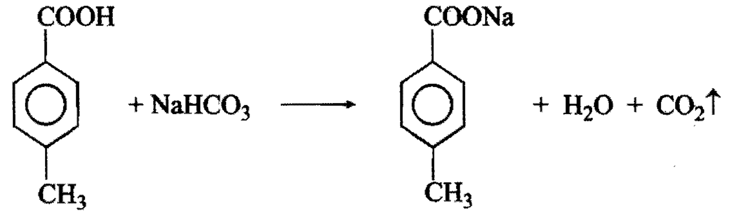


(ii) Compound (*C*) gives positive iodoform test, so it must have  $-\overset{\overset{\large O}{\|}}{C}-CH_3$ group in its structure, *i.e.*, (*C*) is:



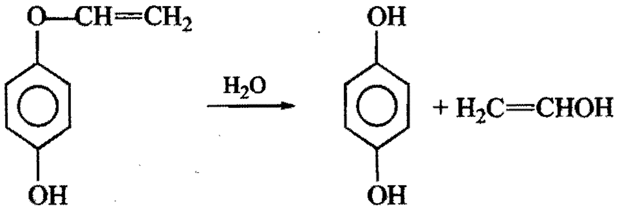
p-Hydroxy-
acetophenone

(iii) Compound (*D*) is readily extracted in aqueous $NaHCO_3$, so it must have —COOH group in its structure, *i.e.*, (*D*) is:



p-Methyl-
benzoic acid

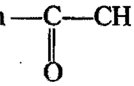
(iv) Compound (*E*) on hydrolysis gives 1,4-dihydroxy benzene; so (*E*) can be.



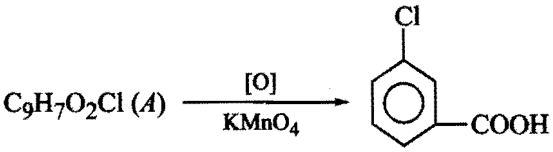
(*E*)
p-Hydroxy phenol
vinyl ether

1,4-Dihydroxy benzene

Problem 20. *Compound* (*A*) *of molecular formula* $C_9H_7O_2Cl$ *exists in keto form and predominantly in enolic form* (*B*). *On oxidation with* $KMnO_4$, (*A*) *gives m-chlorobenzoic acid. Identify* (*A*) *and* (*B*). [IIT 2003]

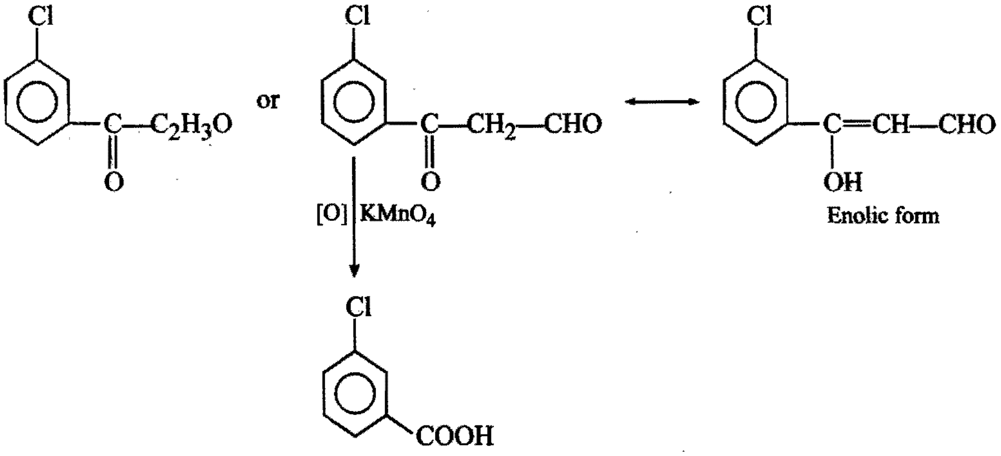
Solution : Formula $C_9H_7O_2Cl$ exist in keto form and predominantly in enolic form so, it must contain  $-\underset{\underset{O}{\|}}{C}-CH_2-$ group.

Oxidation of (*A*) gives *m*-chlorobenzoic acid.



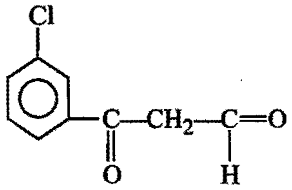
m-Chlorobenzoic acid

Hence, the compound should have a skeleton structure as,



Enolic form

Thus, *A* is:



SECTION OF MATCHING APTITUDE

ESSENTIAL FEATURES

- All questions have been arranged chapterwise in a systematic way.
- The collection of some excellent questions asked in IIT.
- Multiple matching questions.
- Matching in Multiple columns.

MULTIPLE MATCHING PROBLEMS FOR IIT ASPIRANTS

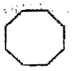
1. Match the List I with List II:

	List I (Tests)		List II (Elements to be detected)
(a)	Lassaigne's test	(p)	Nitrogen
(b)	Beilstein test	(q)	Chlorine
(c)	Sodium nitroprusside test	(r)	Sulphur
(d)	Layer test	(s)	Bromine

2. Match the List I with List II:

	List I (Methods of estimation)		List II (Elements to be estimated)
(a)	Kjeldahl's method	(p)	Halogen
(b)	Duma's method	(q)	Sulphur
(c)	Carius method	(r)	Carbon
(d)	Liebig's method	(s)	Estimation of nitrogen

3. Match the List I with List II:

	List I		List II
(a)	C_nH_{2n}	(p)	Alkene
(b)		(q)	Mono cycloalkane
(c)	C_3H_4	(r)	Non-aromatic
(d)	Decolourise bromine water	(s)	Alkyne or allene

4. Match the List I with List II:

	List I		List II
(a)	Aromatic	(p)	Planar
(b)	Anti-aromatic	(q)	$(4n+2)\pi$ delocalized electrons
~~(c)~~	~~Cyclo-octatetraene~~	~~(r)~~	~~$4n\pi$ localized electrons~~
(d)	Huckel rule	(s)	Non-planar

5. Match the groups in List I with their characteristics in List II:

	List I (Groups)		List II (Characteristics)
(a)	$-R$	(p)	+ Inductive
(b)	$-Cl$	(q)	– Mesomeric
(c)	$-NH_2$	(r)	Deactivating
(d)	$-NO_2$	(s)	Activating

6. Match the List I with List II:

	List I		List II
(a)	Singlet carbene	(p)	Diamagnetic
(b)	Triplet carbene	(q)	Paramagnetic
(c)	Free radical	(r)	Formed by homolytic fission
(d)	Carbonium ion	(s)	Formed by heterolytic fission

7. Match the List I with List II:

	List I		List II
(a)	Benzene	(p)	Form only one mono chloro derivative
(b)	Neopentane	(q)	Aromatic
(c)	Buta-1,3-diene	(r)	Only sp^2 hybridised carbon
(d)	2,2,3,3-Tetramethyl butane	(s)	Undergo 1,2 and 1,4-addition

8. Match the compounds of List I with their functional groups in List II:

	List I		List II
(a)	Glycine	(p)	$-NH_2$
(b)	Salicylic acid	(q)	$-COOH$
(c)	Aniline	(r)	$-OH$
(d)	Toluidine	(s)	$-CH_3$

9. Match the List I with List II:

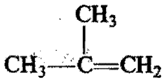
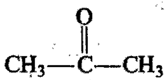
	List I (Reactions)		List II (Intermediates)
(a)	Dickmann's condensation	(p)	Nitrene
(b)	Claisen condensation	(q)	Free radical
(c)	Hofmann's rearrangement	(r)	Carbocation
(d)	Allylic bromination	(s)	Carbanion
(e)	Friedel-Crafts reaction		

10. Match the compounds of List I with the test of their functional groups in List II:

	List I		List II
(a)	Formic acid	(p)	Ammoniacal $AgNO_3$
(b)	Glycol	(q)	$NaHCO_3$
(c)	Benzaldehyde	(r)	HIO_4
(d)	Primary amine	(s)	Chloroform in NaOH

Hydrocarbons
(Aliphatic and Aromatic Hydrocarbons)

11. Match the List I with List II:

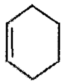
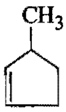
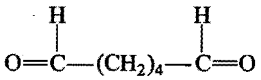
	List I Compounds (Process)		List II (Products)
(a)	 $CH_3-\overset{\overset{CH_3}{\vert}}{C}=CH_2$ (Ozonolysis)	(p)	 $CH_3-\overset{\overset{O}{\Vert}}{C}-CH_3$
(b)	$CH_3-C\equiv CH$ (Hydration)	(q)	HCHO

(c)	$CH_3-C\equiv C-CH_3$ (Ozonolysis)	(r)	CH_3COOH
(d)	$CH_3-C\equiv C-C_2H_5$ (Ozonolysis)	(s)	C_2H_5COOH

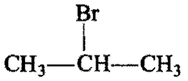
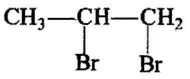
12. Match the List I with List II:

	List I		List II
(a)	C_8H_{18} (*n*-octane)	(p)	Require 25/2 moles of oxygen for combustion of a mole
(b)	C_8H_{18} (iso-octane)	(q)	Highest boiling point
(c)	C_8H_{18} (2,2,3,3-tetra methyl butane)	(r)	Lowest boiling point
(d)	Hexa decane (cetane)	(s)	Grading in diesel oils

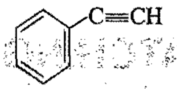
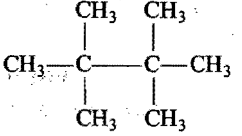
13. Match the List I with List II:

	List I (Isomeric hydrocarbons)		List II (Products)
(a)		(p)	Three products on ozonolysis
(b)	$C_4H_9-C\equiv C-H$	(q)	Absorb 1 mole H_2 in presence of Ni catalyst
(c)	$C_2H_5CH=CHCH=CHCH_3$	(r)	Absorb 2 moles H_2 in presence of Ni catalyst
(d)		(s)	 $O=\overset{H}{C}-(CH_2)_4-\overset{H}{C}=O$ (On ozonolysis)

14. Match the List I with List II:

	List I (Reactions)		List II (Reagents)
(a)	$CH_3-CH=CH_2 \rightarrow$  $CH_3-\overset{Br}{CH}-CH_3$	(p)	Br_2 water
(b)	$CH_3-CH=CH_2 \rightarrow CH_3CH_2CH_2Br$	(q)	*N*-bromosuccinimide
(c)	$CH_3-CH=CH_2 \rightarrow Br-CH_2-CH=CH_2$	(r)	HBr (Peroxide)
(d)	$CH_3-CH=CH_2 \rightarrow$  $CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}$	(s)	HBr(aq.)

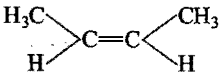
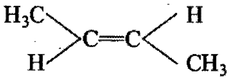
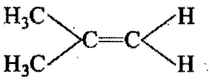
15. Match the compounds in List I with their detecting reagents in List II:

	List I (Compounds)		List II (Reagents)
(a)	$CH_3-CH=CH_2$	(p)	No suitable analytical reagent
(b)	$CH_3-C\equiv C-H$	(q)	Ammoniacal $AgNO_3$
(c)		(r)	Br_2/CCl_4
(d)	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	(s)	Ozonolysis

16. Match the List I with List II:

	List I		List II
(a)	Cyclopropane	(p)	Non-planar
(b)	Cyclobutane	(q)	Planar
(c)	Cyclopentane	(r)	Least stable cycloalkane
(d)	Cyclohexane	(s)	Shows conformations

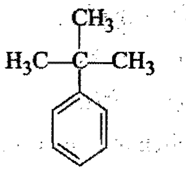
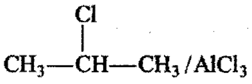
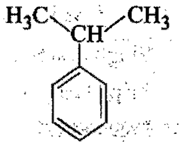
17. Match the List I with List II:

	List I (Compounds)		List II (Properties)
(a)	$H_2C=CH_2$	(p)	Do not show geometrical isomerism
(b)		(q)	Reacts with HBr according to Markownikoff's rule
(c)		(r)	Symmetrical molecule
(d)		(s)	Decolourise Baeyer's reagent

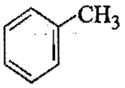
18. Match the List I with List II:

	List I		List II
(a)	Toluene	(p)	On oxidation by $KMnO_4$ in acid medium gives benzoic acid
~~(b)~~	~~Cumene~~	~~(q)~~	~~Used in the manufacture of phenol~~
(c)	Benzene	(r)	Symmetrical trimethyl benzene
(d)	Mesitylene	(s)	On oxidation (V_2O_5/O_2) at 250-450°C gives maleic anhydride

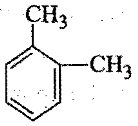
19. Match the List I with List II:

	List I (Reagents for benzene)		List II (Products)
(a)	$CH_3-Cl/AlCl_3$	(p)	
(b)	 $CH_3-\overset{Cl}{CH}-CH_3/AlCl_3$	(q)	

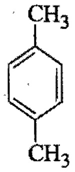
(c) $CH_3CH_2CH_2Cl/AlCl_3$ (r)



(d) $CH_3CH_2CH_2CH_2Cl/AlCl_3$ (s)



and



20. Match the compounds of List I with their properties in List II:

	List I (Compounds)		**List II** (Uses)
(a)	Acetylene	(p)	Moth repellent
(b)	Naphthalene	(q)	Light oil
(c)	Benzene	(r)	Gas welding
(d)	Toluene	(s)	Artificial ripening of fruits

Halogen Containing Compounds

21. Match the List I with List II:

	List I		**List II**
(a)	Carbon tetrachloride	(p)	Solvent
(b)	DDT	(q)	Insecticide
(c)	Chloropicrin	(r)	Antiseptic
(d)	Iodoform	(s)	Fire extinguisher

22. Match the List I with List II and List III:

	List I		**List II**		**List III**
(a)	Pyrene	(p)	2,2'-dichloro diethyl sulphide	(u)	Fire extinguisher
(b)	Mustard gas	(q)	CCl_4	(v)	Warfare gas
(c)	Freon	(r)	CF_2Cl_2	(w)	Insecticide
(d)	Lindane	(s)	Benzene hexachloride	(x)	Refrigerant

23. Match the reactions of List I and metals used in List II:

	List I		**List II**
(a)	Wurtz reaction	(p)	Cu
(b)	Wurtz-Fittig reaction	(q)	Zn
(c)	Frankland's reaction	(r)	Fe
(d)	Ulmann reaction	(s)	Na

24. Match the List I with List II:

	List I		**List II**
(a)	Compounds which give three dichloro derivatives	(p)	Chlorocyclohexane
(b)	Ethanol	(q)	Give chloroform with bleaching powder
(c)	Acetone	(r)	2-chloropropane
(d)	Give propene on treatment with alcoholic KOH	(s)	1-chloropropane

25. Match the List I with List II:

	List I		**List II**
(a)	Monomer of natural rubber	(p)	R—I
(b)	Most reactive alkyl halide for S_{N2} reactions	(q)	$CHCl_3$
(c)	Gives alcohol with NaOH(aq.)	(r)	Isoprene
(d)	Give carboxylic acid with aq. NaOH	(s)	2-methyl buta-1,3-diene

26. Match the compounds of List I with reactions in List II:

	List I		**List II**
(a)	$CHCl_3$	(p)	Carbylamine reaction
(b)	CCl_4	(q)	Hunsdiecker reaction
(c)	R—COOAg + Br_2	(r)	Sandmeyer reaction
(d)	$C_6H_5—\overset{+}{N_2}\overset{-}{Cl}$	(s)	Reimer-Tiemann reaction

27. Match the List I with List II:

	List I (Compounds)		**List II** (Number of halogenated derivatives)
(a)	Benzene $\xrightarrow[\text{Light}]{Cl_2}$	(p)	Three compounds
(b)	Toluene $\xrightarrow[\text{Light}]{Cl_2}$	(q)	Four compounds
(c)	$CH_4 \xrightarrow[\text{Light}]{Cl_2}$	(r)	Single mono chloro derivative
(d)	Benzene $\xrightarrow[AlCl_3]{Cl_3}$	(s)	6-isomeric compounds

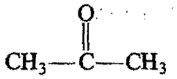
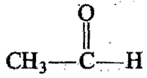
28. Match the List I with List II:

	List I (Reagents)		**List II** (Nature)
(a)	$(\bar{C}N)$	(p)	Neutral nucleophile
(b)	$(\bar{O}NO)$	(q)	Results cyanide
(c)	NH_3	(r)	Ambident nucleophile
(d)	H_2O	(s)	Results isocyanide

29. Match the reactions of List I with the products in List II:

	List I		**List II**
(a)	Chlorination of boiling toluene in presence of light followed by treatment of aq. NaOH	(p)	Benzotrichloride as intermediate
(b)	Oxidation of toluene by acidic $KMnO_4$	(q)	Free radical substitution product followed by nucleophilic substitution
(c)	Oxidation of toluene by $CrO_2Cl_2/AcOH$	(r)	Benzaldehyde
(d)	By treatment of benzal chloride with aq. KOH	(s)	Benzoic acid

30. Match the List I with List II:

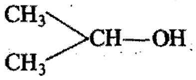
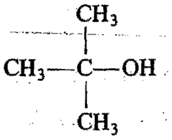
	List I		List II
(a)	CCl_3-CHO	(p)	React with water
(b)	 $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	(q)	Reducing agent for dyes
(c)	 $CH_3-\overset{O}{\overset{\|}{C}}-H$	(r)	Give chloroform with bleaching powder
(d)	CCl_4	(s)	Do not hydrolyse

Alcohol, Phenol, Ether

31. Match the List I with List II:

	List I (Compounds)		List II (Reagents and reactions of response)
(a)	Phenol	(p)	Bakelite formation
(b)	Ethanol	(q)	Ceric ammonium nitrate
(c)	Benzyl alcohol	(r)	Haloform test
(d)	Formaldehyde	(s)	$FeCl_3$

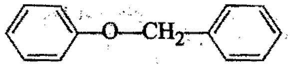
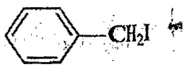
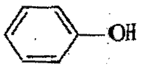
32. Match the compounds of List I and their distinguishing reagents in List II:

	List I (Compounds)		List II (Reagents)
(a)		(p)	Ammoniacal silver nitrate
(b)	HCHO	(q)	Victor Meyer's reagent
(c)	C_6H_5-OH	(r)	Lucas reagent
(d)	 $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{\|}{\overset{\|}{C}}}}-OH$	(s)	$FeCl_3$

33. Match the compounds in List I with their uses in List II:

	List I (Compounds)		List II (Uses)
(a)	Aspirin	(p)	Analgesic
(b)	Wintergreen oil	(q)	Antiseptic
(c)	Salol	(r)	Intestinal antiseptic
(d)	Phenol	(s)	Antipyretic

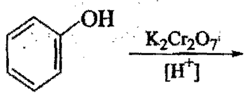
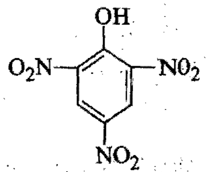
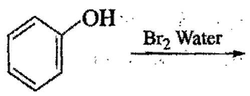
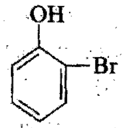
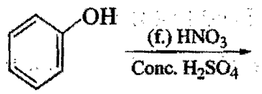
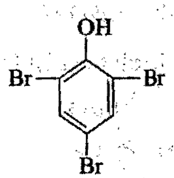
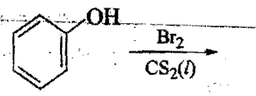
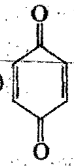
34. Match the List I with List II:

	List I		List II
(a)	Methylated spirit is poisonous due to	(p)	Vinyl ether
(b)	Anaesthetic	(q)	CH_3OH
(c)		(r)	
(d)	Antiseptic with the name of carbolic acid	(s)	

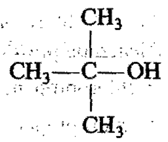
35. Match the compounds in List I with their uses in List II:

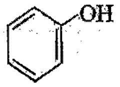
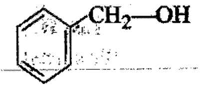
	List I		List II
(a)	Glycol	(p)	Aspirin
(b)	Glycerol	(q)	Chloroform
(c)	Phenol	(r)	Dynamite
(d)	Ethanol	(s)	Antifreeze

36. Match the reactions of List I with List II:

	List I		List II
(a)		(p)	 Picric acid
(b)		(q)	 *Ortho*-bromophenol
(c)		(r)	 *Tri*-bromophenol
(d)		(s)	 *Para*-benzoquinone
		(t)	 *Para*-bromophenol

37. Match the List I with List II:

	List I (Compounds)		List II (Response)
(a)	CH_3-CH_2-OH	(p)	No response to Victor Meyer's reagent
(b)	 $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{\|}{\overset{\|}{C}}}}-OH$	(q)	Turbidity immediately when treated with Lucas reagent

(c)		(r)	No response to Lucas reagent
(d)		(s)	Red colour in Victor Meyer's test

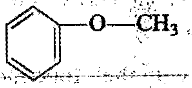
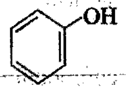
38. Match the List I with List II:

	List I		List II
(a)	Wood alcohol	(p)	CH_3OH
(b)	Grain alcohol	(q)	C_2H_5OH
(c)	Rectified spirit contains	(r)	Petrol
(d)	Power alcohol contains	(s)	4.13% water

39. Match the List I with List II:

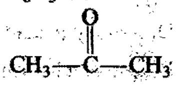
	List I (Compounds/Reactions)		List II (Products)
(a)	Glycerol on reaction with oxalic acid gives	(p)	Acrolein
(b)	Dehydration of glycerol	(q)	2-iodo propane
(c)	Glycerol on treatment of HIO_4	(r)	Allyl alcohol
(d)	Glycerol on treatment with HI	(s)	Formic acid

40. Match the compounds in List I and the products obtained treatment with HI in List II:

	List I (Compounds)		List II (Products when treated with HI in small amount)
(a)	$C_6H_5-O-C_6H_5$	(p)	No product
(b)	$C_2H_5-O-C_2H_5$	(q)	C_2H_5-I
(c)	$C_2H_5-O-CH_3$	(r)	CH_3-I
(d)		(s)	

Aldehydes and Ketones

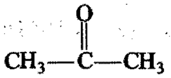
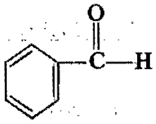
1. Match the compounds in List I with their products when treated with Grignard reagent followed by hydrolysis:

	List I (Compounds)		List II (Products)
(a)	HCHO	(p)	3° alcohol
(b)	CH_3CHO	(q)	Aromatic alcohol
(c)	C_6H_5-CHO	(r)	2° alcohol
(d)	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	(s)	1° alcohol

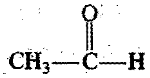
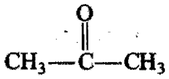
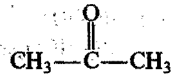
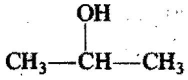
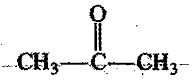
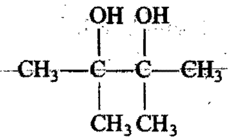
42. Match the List I with List II:

List I (Compounds)	List II (Reaction to give benzaldehyde)
(a) Benzene	(p) Gattermann-Koch aldehyde synthesis
(b) Toluene	(q) Stephen's reaction
(c) Benzoyl chloride	(r) Rosenmund's reaction
(d) Phenyl cyanide	(s) Etard's reaction
	(t) Gattermann aldehyde synthesis

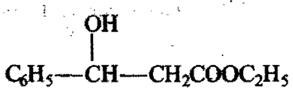
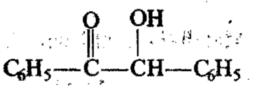
43. Match the List I with List II:

	List I (Compounds)		List II (Reactions)
(a)	CH_3CHO	(p)	Haloform reaction
(b)	HCHO	(q)	Aldol condensation
(c)	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	(r)	Cannizzaro reaction
(d)		(s)	Benzoin condensation

44. Match the List I with List II and List III:

	List I		List II		List III
(a)	 $CH_3-\overset{\overset{O}{\|}}{C}-H$ $\xrightarrow[\text{Conc.HCl}]{\text{Zn/Hg}}$	(p)	$CH_3-CH_2-CH_3$	(u)	Clemmensen reduction
(b)	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ $\xrightarrow{\text{(H)}}$	(q)	CH_3-CH_3	(v)	Pinacol reduction
(c)	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ $\xrightarrow[\text{NaOH}]{NH_2-NH_2}$	(r)	 $CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$	(w)	$LiAlH_4$ reduction
(d)	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ $\xrightarrow{\text{Mg/HCl}}$	(s)	 $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$	(x)	Wolf-Kishner reduction

45. Match the List I with List II:

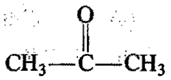
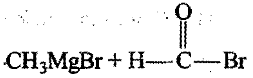
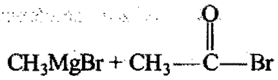
	List I (Reactions)		List II (Products)
(a)	Benzoin condensation	(p)	 $C_6H_5-\overset{\overset{OH}{|}}{CH}-CH_2COOC_2H_5$
(b)	Reformatsky reaction	(q)	$C_6H_5-NH_2$
(c)	Hofmann's reaction	(r)	 $C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH}-C_6H_5$
(d)	Wittig reaction	(s)	$CH_3-CH=CH-CH_3$

46. Match the List I with List II:

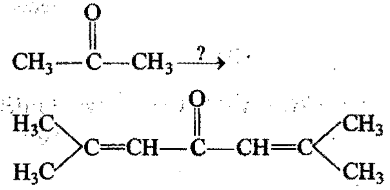
	List I		List II
(a)	HCHO + Water 60%	(p)	Urotropin
(b)	$HCHO + NH_3$	(q)	Bakelite

(c) HCHO + Phenol	(r) CH_3OH
(d) HCHO + NaOH	(s) Formalin
	(t) HCOONa

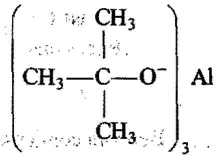
47. Match the reactions List I with List II:

List I (Reactions)	List II (Products)
(a) $CH_3MgBr + HCN \xrightarrow{HOH/H^+}$	(p)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$
(b) $CH_3MgBr + HCOOC_2H_5 \longrightarrow$	(q) CH_3CHO
(c)  $CH_3MgBr + H-\overset{O}{\overset{\|}{C}}-Br$	(r) $MgBr_2$
(d)  $CH_3MgBr + CH_3-\overset{O}{\overset{\|}{C}}-Br$	(s) NH_3

48. Match the List I with List II:

List I (Reactions)	List II (Reagents)
(a) $C_6H_5-CH=CH-CHO \xrightarrow{?} C_6H_5-CH=CH-CH_2OH$	(p) Ammoniacal $AgNO_3$
(b) $C_6H_5-CHO \xrightarrow{?} C_6H_5-CH_2OH$	(q) $NaBH_4$
(c) $CH_3-CH=CH-CHO \xrightarrow{?} CH_3-CH=CH-COOH$	(r) $LiAlH_4$
(d)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{?} (H_3C)_2C=CH-\overset{O}{\overset{\|}{C}}-CH=C(CH_3)_2$	(s) $Ba(OH)_2$ or Dry HCl gas

49. Match the List I with List II:

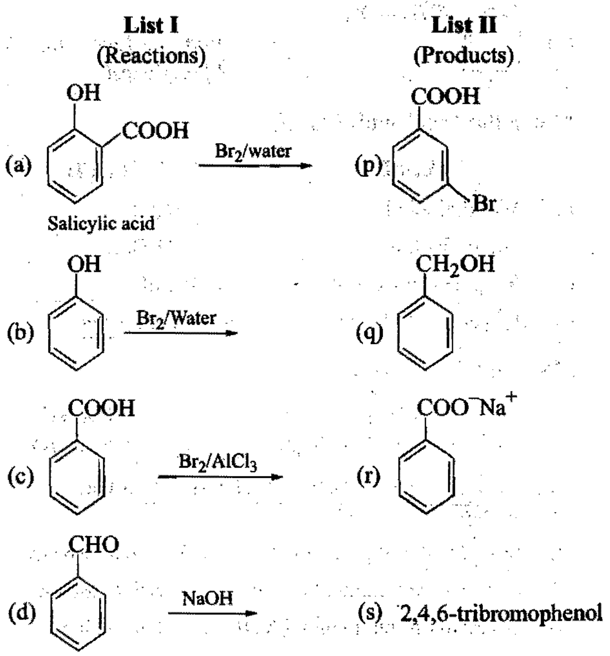
List I (Reactions)	List II (Reagents)
(a) Cannizzaro reaction	(p) $PdCl_2$
(b) Aldol condensation	(q) $CuCl_2$
(c) Benzoin condensation	(r) KCN
(d) Oppenauer oxidation	(s)  $\left(CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O^-\right)_3 Al$
(e) Wacker process	(t) NaOH

50. Match the List I with List II:

List I (Reactions/Reagents)	List II (Metals involved)
(a) Fehling's solution	(p) Zn
(b) Benedict's reaction	(q) Hg
(c) Tollen's reagent	(r) Cu
(d) Clemmensen reduction	(s) Ag
(e) Frankland reaction	

Carboxylic Acids and Their Derivatives

51. Match the List I with List II:



52. Match the compounds of List I with the distinction reagents of List II:

List I (Compounds)	List II (Reagents)
(a) HCOOH	(p) Effervescence of CO_2 with $NaHCO_3$
(b) CH_3COOH	(q) Colour with $FeCl_3$
(c) Benzoic acid	(r) Decolourise Br_2 water
(d) Cinnamic acid	(s) Give silver mirror with Tollens' reagent

53. Match the compounds of List I with their functional groups in List II:

List I	List II
(a) Picric acid	(p) Do not contain carboxylic group
(b) Ascorbic acid	(q) Phenolic group
(c) Salicylic acid	(r) Carboxylic group
(d) Formic acid	(s) Aldehydic group

54. Match the items of List I to those of List II:

List I	List II
(a) Red ants	(p) Dicarboxylic acid
(b) Oxalic acid	(q) Ethene on electrolysis
(c) Potassium succinate	(r) Ethane with red P/HI
(d) CH_3-COOH	(s) Formic acid

55. Match the List I with List II:

List I	List II
(a) Petroleum wax	(p) Esters of glycerol and higher fatty aci
(b) Fats	(q) Amphoteric in nature

(c) Amides	(r) Found in fruits
(d) Esters	(s) Mixture of hydrocarbons

Nitrogen Containing Compounds

56. Match the List I with List II:

List I (Reaction with)	List II (Compounds)
(a) Acetyl chloride	(p) Primary amine
(b) Methyl iodide	(q) Secondary amine
(c) Ethyl alcohol	(r) Tertiary amine
(d) Carbon disulphide	(s) Quaternary ammonium

57. Match the compounds formed of List I from the compounds of List II:

List I	List II
(a) Aniline	(p) Benzamide
(b) Benzylamine	(q) Nitrobenzene
(c) *m*-Dinitrobenzene	(r) Phenylcyanide
(d) Benzaldehyde	(s) Toluene

58. Match the reactions in List I with compounds in List II:

List I	List II
(a) Sandmeyer reactions	(p) Chlorobenzene
(b) Gattermann reaction	(q) Bromobenzene
(c) Raschig method	(r) *p*-Aminophenol
(d) Oxidation of aniline	(s) *p*-Benzoquinone

Biomolecules and Biological Processes

59. Match the vitamins of List I with the deficiency diseases in List II:

List I	List II
(a) Ascorbic acid	(p) Scurvy
(b) Vitamin B	(q) Dental bleeding
(c) Retinol	(r) Beri-beri
(d) Vitamin D	(s) Night blindness
	(t) Rickets

60. Match the diseases of List I with their causes in List II:

List I	List II
(a) Malaria	(p) Protozoal
(b) Dysentery	(q) Amoebic
(c) Typhoid	(r) Viral
(d) AIDS	(s) Bacterial

61. Match the compounds of List I with their hydrolysis products in List II:

List I (Compounds)	List II (Hydrolysis products)
(a) Starch	(p) Fructose
(b) Sucrose	(q) Galactose
(c) Cellulose	(r) β-(*D*) glucose
(d) Lactose	(s) α-(*D*) glucose

62. Match the reactions of List I with their products in List II:

List I	List II
(a) Glucose on reduction with $NaBH_4$	(p) Sorbitol
(b) Fructose on reduction with $NaBH_4$	(q) Gluconic acid
(c) Glucose with Br_2 water	(r) Glucaric acid
(d) Glucose with HNO_3	(s) Mannitol

63. Match the items of List I with the items of List II:

List I	List II
(a) Epimers	(p) α-(*D*) glucose
(b) Anomers	(q) *D*-mannose
(c) Reducing ketose	(r) Fructose
(d) Functional isomer of glucose	(s) β-(*D*) glucose

Polymers

64. Match the polymers of List I with their properties in List II:

List I	List II
(a) PHBV	(p) Elastomer
(b) LDPE	(q) Prepared by coordination polymerization
(c) Natural rubber	(r) Free radical polymerization
(d) HDPE	(s) Biodegradable

Codes :

(a) (a—p); (b—r); (c—q); (d—s)
(b) (a—s); (b—r); (c—p); (d—q)
(c) (a—r); (b—s); (c—p); (d—q)
(d) (a—q); (b—r); (c—s); (d—p)

65. Match the polymers of List I with their units in List II:

List I	List II
(a) Buna-S	(p) Isoprene
(b) Bakelite	(q) Caprolactum
(c) Nylon-6	(r) Butadiene and styrene
(d) Natural rubber	(s) Phenol and formaldehyde

Codes :

(a) (a—r); (b—s); (c—q); (d—p)
(b) (a—r); (b—s); (c—p); (d—q)
(c) (a—s); (b—r); (c—p); (d—q)
(d) (a—q); (b—s); (c—r); (d—p)

66. Match the polymers of List I with their products in List II:

List I	List II
(a) Nylon-6,6	(p) Phthalic acid and ethylene glycol
(b) Buna-N	(q) Terephthalic acid and ethylene glycol
(c) Dacron	(r) Hexamethylenediamine and adipic acid
(d) Glyptal plastic	(s) Acrylonitrile and butadiene

Codes :

(a) (a—s); (b—q); (c—p); (d—r)
(b) (a—r); (b—p); (c—s); (d—q)
(c) (a—p); (b—r); (c—q); (d—s)
(d) (a—r); (b—s); (c—q); (d—p)

ANSWERS

1.	(a—p, q, r, s)	(b—q, s)	(c—r)	(d—s)	
2.	(a—s)	(b—s)	(c—p, q)	(d—r)	
3.	(a—p, q, r)	(b—q, r)	(c—r, s)	(d—p, s)	
4.	(a—p, q)	(b—p, r)	(c—r, s)	(d—q)	
5.	(a—p, s)	(b—r)	(c—s)	(d—q, r)	
6.	(a—q)	(b—p)	(c—p, r)	(d—p, s)	
7.	(a—p, q, r)	(b—p)	(c—r, s)	(d—p)	
8.	(a—p, q)	(b—q, r)	(c—p)	(d—p, s)	
9.	(a—s)	(b—s)	(c—p)	(d—q)	(e—r)
10.	(a—p, q)	(b—r)	(c—p)	(d—s)	
11.	(a—p, q)	(b—p)	(c—r)	(d—r, s)	
12.	(a—p, q)	(b—p)	(c—p, r)	(d—s)	
13.	(a—q, s)	(b—r)	(c—p, r)	(d—q)	
14.	(a—s)	(b—r)	(c—q)	(d—p)	
15.	(a—r, s)	(b—q, r, s)	(c—q, r, s)	(d—p)	
16.	(a—q, r)	(b—q)	(c—q)	(d—p, s)	
17.	(a—p, r, s)	(b—r, s)	(c—s)	(d—p, q, s)	
18.	(a—p)	(b—p, q)	(c—s)	(d—r)	
19.	(a—r, s)	(b—q)	(c—q)	(d—p)	
20.	(a—r, s)	(b—p)	(c—q)	(d—q)	
21.	(a—p, s)	(b—q)	(c—q)	(d—r)	
22.	(a—q—u)	(b—p—v)	(c—r—x)	(d—s—w)	
23.	(a—s)	(b—s)	(c—q)	(d—p)	
24.	(a—p, r, s)	(b—q)	(c—q)	(d—r, s)	
25.	(a—r, s)	(b—p)	(c—p)	(d—q)	
26.	(a—p, s)	(b—s)	(c—q)	(d—r)	
27.	(a—s)	(b—p, r)	(c—q, r)	(d—r)	
28.	(a—q, r, s)	(b—r)	(c—p)	(d—p)	
29.	(a—p, q, s)	(b—s)	(c—r)	(d—r)	
30.	(a—p, q, r)	(b—r)	(c—r)	(d—s)	
31.	(a—p, s)	(b—q, r)	(c—q)	(d—p)	
32.	(a—q, r)	(b—p)	(c—s)	(d—r)	
33.	(a—p, s)	(b—p)	(c—r)	(d—q)	
34.	(a—q)	(b—p)	(c—r, s)	(d—s)	
35.	(a—s)	(b—r, s)	(c—p)	(d—q)	
36.	(a—s)	(b—r)	(c—p)	(d—q, t)	
37.	(a—r, s)	(b—p, q)	(c—p, r)	(d—r, s)	
38.	(a—p)	(b—q)	(c—q, s)	(d—q, s)	
39.	(a—r, s)	(b—p)	(c—s)	(d—q)	
40.	(a—p)	(b—q)	(c—r)	(d—r, s)	
41.	(a—s)	(b—r)	(c—q, r)	(d—p)	
42.	(a—p, t)	(b—s)	(c—r)	(d—q)	
43.	(a—p, q)	(b—r)	(c—p)	(d—r, s)	
44.	(a—q—u)	(b—r—w)	(c—p—x)	(d—s—v)	
45.	(a—r)	(b—p)	(c—q)	(d—s)	
46.	(a—s)	(b—p)	(c—q)	(d—r, t)	
47.	(a—q, s)	(b—q)	(c—q, r)	(d—p, r)	
48.	(a—q, r)	(b—q, r)	(c—p)	(d—s)	
49.	(a—t)	(b—t)	(c—r)	(d—s)	(e—p, q)
50.	(a—r)	(b—r)	(c—s)	(d—p, q)	(e—p)
51.	(a—s)	(b—s)	(c—p)	(d—q, r)	
52.	(a—p, s)	(b—p, q)	(c—p, q)	(d—p, r)	
53.	(a—p, q)	(b—p)	(c—q, r)	(d—r, s)	
54.	(a—s)	(b—p, r)	(c—q)	(d—r)	
55.	(a—s)	(b—p)	(c—q)	(d—r)	
56.	(a—p, q)	(b—p, q, r)	(c—p, q, r)	(d—p, q)	
57.	(a—p, q)	(b—p, r)	(c—q)	(d—r, s)	
58.	(a—p, q)	(b—p, q)	(c—p)	(d—r, s)	
59.	(a—p, q)	(b—r)	(c—s)	(d—t)	
60.	(a—p)	(b—p, q)	(c—s)	(d—r)	
61.	(a—s)	(b—p, s)	(c—r)	(d—q, r)	
62.	(a—p)	(b—p, s)	(c—q)	(d—r)	
63.	(a—p, q)	(b—p, s)	(c—r)	(d—r)	
64.	(a—s)	(b—r)	(c—p)	(d—q)	
65.	(a—r)	(b—s)	(c—q)	(d—p)	
66.	(a—r)	(b—s)	(c—q)	(d—p)	