NEW AGE

Second Edition

ORGANIC CHEMISTRY

PROBLEMS AND SOLUTIONS

(FOR I.I.T., AIEEE, ENGINEERING & MEDICAL ENTRANCE EXAMINATIONS)

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NEW AGE INTERNATIONAL PUBLISHERS

Published by New Age International (P) Ltd., Publishers
First Edition : 1999
Second Edition : 2006

ISBN : 81-224-1797-3

Rs. 225.00

C-05-10-430

Printed in Hindustan Offset, Delhi.
Typesetter Goswami Printer, Delhi.

PUBLISHING FOR ONE WORLD

NEW AGE INTERNATIONAL (P) LIMITED, PUBLISHERS
(formerly Wiley Eastern Limited)
4835/24, Ansari Road, Daryaganj, New Delhi - 110002
Visit us at **www.newagepublishers.com**

CONTENTS

CHAPTER

1

Electron and the Chemical Bonding

Problem 1.1:

Describe the following terms:

Polar bond, bond angle, association, electropositive elements, formal charge, bond length, bond dissociation energy, molecular dipole moment, atomic orbital, molecular orbital, bonding and anti-bonding orbitals.

Solution: Polar bond: A covalent bond in which there is an unequal sharing of electrons between the two bonded atoms is called a *polar bond*. A bond with equal sharing of electrons is called a *nonpolar bond*.

Bond angle: The angle subtended by two bonds joined to an atom is called *bond angle*. The bond angle determines the shape of a molecule whether it is bent or linear. A bond exhibiting different types of hybridization also forms different bond angles. Bond angle is a property of a bond similar to bond energy and bond length. A bond angle cannot be predicted by using the simple *s* and *p* orbitals alone.

Association: The intermolecular hydrogen bonding in a liquid results in its huge molecular aggregate. This is referred to as *association*. The association of liquid molecules causes an increase in its boiling points.

Electropositive elements: Those elements which have low electronegativity (or have a tendency to lose an electron) are *electropositive*.

Formal charge: A method for keeping track of charges, showing what charge would be on an atom in a particular Lewis structure is called a *formal charge*.

Bond length: *Bond length* is the internuclear distance between the two bonded atoms. It is expressed in angstrom units (Å). The bond length is obtained by electron diffraction and X-ray diffraction techniques. The magnitude of bond length depends on several factors such as hybridization and resonance effects.

Bond dissociation energy: It is the energy required to break a bond to produce two free radicals.

Molecular dipole moment: The vector sum of the individual bond dipole moments and any non bonding pairs of electrons in a molecule is called *molecular dipole moment*. It is a measure of the polarity of a molecule.

Atomic Orbital: It is a region in space where an electron is likely to be found.

Molecular orbital: An orbital formed by overlap of atomic orbitals on different atoms is called a *molecular orbital*.

Bonding orbital: A molecular orbital which has lower energy and greater stability than the atomic orbitals from which it is formed is known as bonding molecular orbital. A bonding orbital forms a σ-bond.

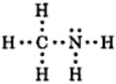
Anti-bonding orbital: A molecular orbital which has higher energy and lower stability than the atomic orbitals from which it is formed is known as anti-bonding orbital. Such an orbital forms a σ*-bond.

Problem 1.2:

Write a Lewis structure for each of the following:

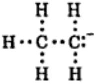
(*a*) Methylamine (*b*) Ethyl anion (*c*) Propanol (*d*) Acetylene (*e*) Acetic acid (*f*) Ethylmagnesium chloride.

Solution: (*a*)



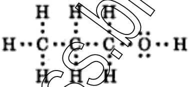
$H\cdot\cdot\overset{H}{\underset{H}{C}}\cdot\cdot\overset{\cdot\cdot}{\underset{H}{N}}\cdot\cdot H$

(*b*)



$H\cdot\cdot\overset{H}{\underset{H}{C}}\cdot\cdot\overset{H}{\underset{H}{C}}{:}^{-}$

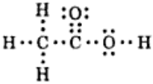
(*c*)



$H\cdot\cdot\overset{H}{\underset{H}{C}}\cdot\cdot\overset{H}{\underset{H}{C}}\cdot\cdot\overset{H}{\underset{H}{C}}\cdot\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\cdot\cdot H$

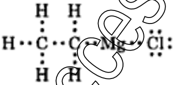
(*d*) $H\cdot\cdot C\vdots\vdots C\cdot\cdot H$

(*e*)



$H\cdot\cdot\overset{H}{\underset{H}{C}}\cdot\cdot\overset{:O:}{C}\cdot\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\cdot\cdot H$

(*f*)

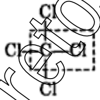


$H\cdot\cdot\overset{H}{\underset{H}{C}}\cdot\cdot\overset{H}{\underset{H}{C}}\cdot\cdot Mg\cdot\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}{:}$

Problem 1.3:

Indicate the polarity of the bonds between the atoms within the box of the following compounds:

(*a*) $CH_3-\boxed{C\equiv N}$ (*b*)



$Cl-\boxed{\overset{Cl}{\underset{Cl}{C}}-Cl}$

(*c*) $H_3-\boxed{C-C}-Cl_3$ (*d*) $\boxed{Cl-I}$

(*e*) $CH_3CH_2CH_2-\boxed{CH_2-I}$ (*f*) $H_3C-\boxed{C\equiv C}-CH_3$

Solution: In a polar bond, a pair of electrons is shared between two atoms with unequal attraction.

(*a*) Polar (*b*) Polar (*c*) Polar (*d*) Polar (*e*) Polar (*f*) Non-polar.

Problem 1.4:

Predict the hybridization and geometry of the following molecules:

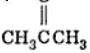
(*a*) NF_3 (*b*) $C_6H_5C\equiv CH$ (*c*) H_2O (*d*) CH_3CHO.

Solution: (*a*) sp^3, tetrahedral (*b*) *sp*, linear (*c*) sp^3, tetrahedral (*d*) sp^2, pyramidal.

Problem 1.5:

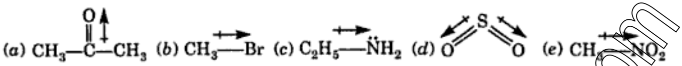
Show by a crossed arrow the direction of dipole moment of the following molecules:

(*a*)



$CH_3\overset{O}{\overset{\|}{C}}CH_3$ (*b*) CH_3Br (*c*) $C_2H_5NH_2$ (*d*) SO_2 (*e*) CH_3NO_2.

Solution:

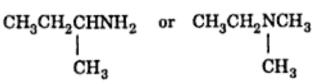


(a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (b) $CH_3\overset{\longleftrightarrow}{-}Br$ (c) $C_2H_5\overset{\longleftrightarrow}{-}\ddot{N}H_2$ (d) (e) $CH_3\overset{\longleftrightarrow}{-}NO_2$

Problem 1.6:

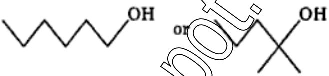
Indicate which of the following pairs of compounds is higher boiling:

(a)

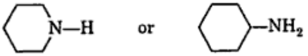


$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HNH_2$ or $CH_3CH_2\underset{CH_3}{\underset{|}{N}}CH_3$

(b)



(c)



Solution: (a) These are isomeric amines but $CH_3CH_2\underset{CH_3}{\underset{|}{C}}HNH_2$ being a primary amine can form H-bond. It is thus high boiling. The 3° amine lacks a H-atom on N.

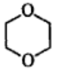
(b) These are isomers but the primary alcohol can form better H-bond and thus the former alcohol is high boiling.

(c) Cyclohexylamine (*i*) for the same reason as above can form better H-bond and is high boiling.

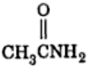
Problem 1.7:

Which of the following compounds can from hydrogen bonds with water?

(a)

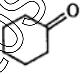


(b)



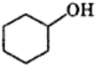
$CH_3\overset{O}{\overset{\|}{C}}NH_2$

(c)



(d) $(C_2H_5)_3\ddot{N}$ (e) $(CH_3)_2CHCH_3$

(f)



Solution: (a), (b), (c) and (f) can form H-bond with water, but (d) and (e) cannot.

In the latter two compounds one is 3° amine and the other is a hydrocarbon.

Problem 1.8:

Distinguish between *s*-orbital, *p*-orbital, *sp*, sp^2 and sp^3 hybridized orbitals. Give examples.

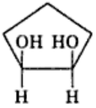
Solution: *s*-Orbital: An *s*-orbital is symmetrical about the nucleus and has a quantum number $l = 0$. The sign of 1*s* wave function is everywhere positive. For hydrogen the 1*s* atomic orbital is involved in bonding. For other elements such as sodium, lithium, carbon, oxygen, chlorine, *s* is always filled and is not involved in bonding.

***p*-Orbital:** A *p-orbital* is not symmetrical as the *s*-orbital. It rather consists of two lobes with a nodal plane at the center. For each *p*-orbital the quantum number *l* equals 1. These are three in number *i.e.*, p_x, p_y and p_z. Examples of hybridized orbitals are given in the table.

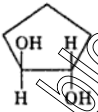
	Atomic orbitals	*Shape of molecule*	*Bond angle*	*Example*
sp	$s + p$	Linear	180°	$BeCl_2$, C_2H_2, $HgCl_2$
sp^2.	$s + 2p$	Trigonal planar	120°	BF_3, NO_3^-, C_2H_4
sp^3	$s + 3p$	Tetrahedral	109.5°	CH_4, NH_4^+, BH_4^-, $SnCl_4$

Problem 1.9:

Intramolecular hydrogen-bonding occurs in *cis*-1, 2-cyclopentanediol but not in the *trans*-isomer. Why?



cis



trans

Solution: In *cis*–diol, the hydroxy groups are close together while in the *trans*-isomer they are too far apart. The hydroxy groups in the former structure thus can form hydrogen-bond easily.

Problem 1.10:

o-Nitrophenol is steam volatile and less soluble than its other isomers. Why?

Solution: Due to intramolecular hydrogen-bond formation in *o*-nitrophenol, the intermolecular association is reduced, this makes it more volatile. Conversely because of intramolecular hydrogen-bond, *o*-nitrophenol is incapable of forming hydrogen-bond with water and is thus less soluble in water compared to the other isomers which can H-bond with water.

Problem 1.11:

(*a*) *p*-Nitroaniline has a dipole moment (6.10 D) greater than the sum of the dipole moments of nitrobenzene (3.95 D) and aniline (1.53 D). Explain.

(*b*) Explain the difference in the dipole moment of the following compounds:

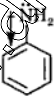
CH_3CHO and $CH_3CH{=}CH_2$

$\mu = 2.65$ D $\mu = 0.35$ D

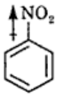
(*c*) Which of the following two compounds will have a larger dipole moment and why?

CH_3NO_2 or $C_6H_5NO_2$

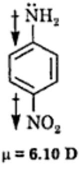
Solution: (*a*) The direction of dipole moments in these compounds is as follows:



$\mu = 1.53$ D



$\mu = 3.95$ D



$\mu = 6.10$ D

The dipole moment values for nitrobenzene and aniline show that NH_2 and NO_2 groups induce dipole moments in opposite directions with respect to the benzene ring. In *p*-nitroaniline the dipole moments of these groups reinforce each other to increase the net value.

(*b*) There is more charge separation in acetaldehyde $\left(CH_3-\overset{\overset{\textstyle H}{|}}{C^+}-O^-\right)$ than it is in propene $\left(CH_3-\overset{+}{C}H-CH_2^-\right)$. The larger *e* value thus increases dipole moment.

(*c*) Nitrobenzene would have a larger value of dipole moment than nitromethane because of a greater distance (*d*) of charge (*e*) separation, the dipole moment = $d \times e$.

Problem 1.12:

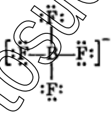
Describe formal charge and calculate the formal charges on the atoms indicated in parentheses.

H_2SO_4(S and O), CO_2(C and O), HCO_2^-(C and O), $CH_3^\bullet$(C and H),

CH_3O^-(C, H and O), CH_3OH(C, H and O), $:CF_2$(C and F),

HCO_2^-(C, H and O), CH_3NH_2(C and N), NH_4^+(N), H_3O^+(O), BF_4^-(B)

Solution: Formal charge: The Lewis structures described earlier are those of neutral molecules. But many ionic species such as BF_4^-, H_3O^+ also contain covalent bonds:



Tetrafluoroborate ion

Since the ion has a negative charge, one or more atoms within the ion must be charged-but which one? The charge is normally shared by all the atoms. A useful procedure has been adopted for electronic book-keeping that assigns a charge to specific atoms. The charge on each atom thus assigned is called its formal charge.

Note that the sum of the formal charges on the individual atoms must equal the total charge on the ion.

The formal charge on an atom can be calculated by the following equation:

$$\text{Formal charge} = \text{Valence electrons of the isolated atom} - \left[\text{unshared electrons} + \frac{1}{2}(\text{shared electrons})\right]$$

H_2SO_4 $\quad S=6-\left[0+\frac{1}{2}(12)\right]=0$ $\qquad CO_2$ $\quad C=4-\left[0+\frac{1}{2}(8)\right]=0$

$\quad O=6-\left[4+\frac{1}{2}(4)\right]=0$ $\qquad\quad O=6-\left[4+\frac{1}{2}(4)\right]=0$

$\dot{C}H_3$ $\quad C = 4 - \left[1 + \frac{1}{2}(6)\right] = 0$

$\quad H = 1 - \left[0 + \frac{1}{2}(2)\right] = 0$

CH_3O^- $\quad C = 4 - \left[0 + \frac{1}{2}(8)\right] = 0$

$\quad H = 1 - \left[0 + \frac{1}{2}(2)\right] = 0$

$\quad O = 6 - \left[6 + \frac{1}{2}(2)\right] = -1$

CH_3OH $\quad C = 4 - \left[0 + \frac{1}{2}(8)\right] = 0$

$\quad H = 1 - \left[0 + \frac{1}{2}(2)\right] = 0$

$\quad O = 6 - \left[4 + \frac{1}{2}(4)\right] = 0$

$:CF_2$ $\quad C = 4 - \left[2 + \frac{1}{2}(4)\right] = 0$

$\quad F = 7 - \left[6 + \frac{1}{2}(2)\right] = 0$

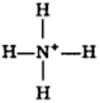
HCO_2^- $\quad C = 4 - \left[0 + \frac{1}{2}(8)\right] = 0$

$\quad H = 1 - \left[0 + \frac{1}{2}(2)\right] = 0$

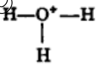
$\quad O = 6 - \left[6 + \frac{1}{2}(2)\right] = -1$

CH_3NH_2 $\quad C = 4 - \left[0 + \frac{1}{2}(8)\right] = 0$

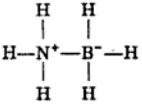
$\quad N = 5 - \left[2 + \frac{1}{2}(6)\right] = 0$



$H-N^+(H)_2-H$ $\quad N = 5 - \left[0 + \frac{1}{2}(8)\right] = +1$

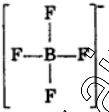


$H-O^+(H)-H$ $\quad O = 6 - \left[2 + \frac{1}{2}(6)\right] = +1$



$H_3N^+-B^-H_3$ $\quad N = 5 - \left[0 + \frac{1}{2}(8)\right] = +1, \quad B = 3 + \left[0 + \frac{1}{2}(8)\right] = -1$

(a neutral molecule)



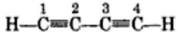
$[BF_4]^-$ $\quad B = 3 - \left[0 + \frac{1}{2}(8)\right] = -1$

Neutral molecules have zero formal charge.

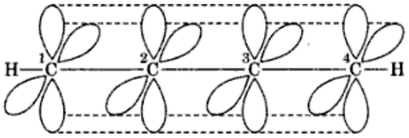
Problem 1.13:

The central bond of biacetylene is 1.37 Å, whereas a normal C—C bond distance is 1.54 Å. How do you account for this difference?

Solution: Because the following type of orbital overlap causes the central C—C bond to be shortened.

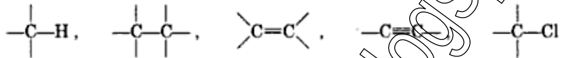


$$\mathrm{H{-}\overset{1}{C}{\equiv}\overset{2}{C}{-}\overset{3}{C}{\equiv}\overset{4}{C}{-}H}$$



Problem 1.14:

How do the bond lengths and bond angles vary in the following cases?



Solution: C—H, C—C and C—Cl bonds are sp^3 hybridized, therefore, they would be longer than C=C and C≡C bonds. The former set of compounds will have an angle of 109.5° whereas the last two an angle of 120°.

Problem 1.15:

Explain what is meant by dipole moment? Name two compounds which show dipole moment and two which do not.

Solution: Dipole Moment: Certain covalent bonds are polar. A bond which has any degree of polarity will have a corresponding dipole moment. The dipole moment abbreviated by the letter μ of a dipolar molecule (a molecule in which the centers of positive and negative charges are separated) is defined as the product of the charge (e) at one center and the distance (d) between the negative and the positive centers. Dipole moment is expressed in terms of e.s.u. or the Debye unit abbreviated D. Debye being equal to dipole moment of 1 × 10^{-18} e.s.u. cm/molecule. All dipole moments are of the order of 10^{-18} e.s.u.

$$\mu = e \times d$$

CH_3NH_2 and CH_3OH possess dipole moment while CCl_4 and *trans*-2-butene do not.

Problem 1.16:

Why is it necessary to invoke sp^2 hybridization to explain bonding in C_2H_4?

Solution: C_2H_4 contains a carbon-carbon double bond in which a carbon atom is bonded to only three other atoms and hence sp^2 hybridization takes place.

Problem 1.17:

Predict the direction of the dipole moment, if any, in the following molecules:

ICl, Br_2, HCl, H_2

Solution: Br_2 and H_2 have no dipole moment whereas ICl and HCl do. The dipole moment vector points towards Cl both in ICl and HCl.

$$\overset{+\!\!\longrightarrow}{\mathrm{I{-}Cl}} \qquad\qquad \overset{+\!\!\longrightarrow}{\mathrm{H{-}Cl}}$$

Problem 1.18:

Which C—C single bond is shortest in length among the following?

$CH_3{-}CH_2{-}CH_3$, $CH_3{-}CH{=}CH_2$, $CH_3C{\equiv}C{-}C{\equiv}CH$, $CH_3{-}C{\equiv}CH$

Solution: The C—C bond is shortest in $CH_3C{\equiv}C{-}C{\equiv}CCH_3$ because the C—C bond carbons are *sp* hybridized.

Problem 1.19:

Predict the shape of the following molecules:

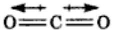
$$BeCl_2\,,\ NH_4^+\,,\ H_2O,\ BCl_3\,,\ SiF_4\,,\ PH_3$$

Solution: Linear, tetrahedral, tetrahedral, trigonal planar, tetrahedral, trigonal planar.

Problem 1.20:

Water has a dipole moment but carbon dioxide has not. Explain.

Solution:



In water there are two O—H bonds which are polar and inclined at an angle of 104.5°. The two bond dipoles do not cancel and the vector sum of bond dipoles give a resultant dipole moment.

The CO_2 molecule, on the other hand, is linear. The C—O bond dipoles are oriented in opposite directions. Since they also have equal magnitude, they cancel. Therefore CO_2 has no dipole moment and is also non-polar.

Problem 1.21:

Give an example of an element that undergoes sp hybridization in forming covalent bonds with other elements. What is the value of the angle between the bonds that result from *s* – *sp* overlap of atomic orbitals.

Solution: The element is carbon. The angle is 180°.

Problem 1.22:

Why does ice contract when it melts?

Solution: The hydrogen bonds formed between water molecules hold them in an "*open network*" structure in the ice crystal. As the ice melts, hydrogen bonds are broken and the resulting liquid occupies less space than the original solid ice, leading to its contraction.

Problem 1.23: What shape would you expect the following to have?

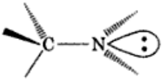
(*a*) CH_3^+ (*b*) CH_3NH_2 (*c*) CH_3^- (*d*) $(CH_3)_3\,B$ (*e*) BF_4^- (*f*) H_2S (*g*) CH_3OH (*h*) NH_2^-

Solution: To arrive at the shape of a molecule, we need to know how many orbitals the central atom can hold (not only the atoms alone attached to it but also unshared pair of electrons.) If it holds four orbitals then it is sp^3, if three than sp^2 and if two then *sp*. The shape given below in each case refers to if unshared pair of electrons are included and then if only atoms are included (this is given in parentheses).

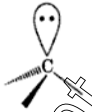
(*a*) Trigonal like BF_3

(trigonal because three are three hydrogens).

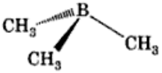
(*b*) Tetrahedral like NH_3
(pyramidal with tetrahedral angles)



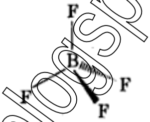
(*c*) Trigonal pyramidal like NH_3
(tetrahedral with tetrahedral angles)



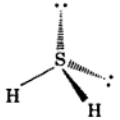
(*d*) Trigonal like BF_3 (trigonal)



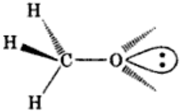
(*e*) Tetrahedral like CH_4 (tetrahedral)



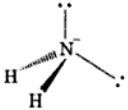
(*f*) Tetrahedral like H_2O
(flat with a tetrahedral angle)



(*g*) Tetrahedral like H_2O
(flat with a tetrahedral angle)



(*h*) Tetrahedral like H_2O
(flat with a tetrahedral angle).



Problem 1.24:

Explain why CH_3Cl ($\mu = 1.90$ D) and CH_3F ($\mu = 18.5$ D) have identical dipole moments although fluorine is more electronegative than chlorine.

Solution: The magnitude of dipole moment depends not only on the amount of charge (*e*) that is separated but also the distance between the charges. The C—Cl bond in CH_3Cl and the C—F bond in CH_3F have the same dipole moment because the large bond distance of C—Cl bond and the high electronegativity of F atom compensate each other. This results in both the molecules to possess the same dipole moment.

Problem 1.25:

Arrange the following in the order of decreasing bond energy:

H—F, H—Cl, H—Br, H—I

Solution: H—I < H—Cl < H—Br < H — F

Large size and lower electronegativity of halogen makes H—I bond longer and weaker.

Problem 1.26:

What are hybridized orbitals? Justify the introduction of the concept of hybridization in some cases and give an example of each type.

Solution: Hybrid orbitals are degenerate orbitals formed by mixing of orbitals differing in small amounts with each other, in energy. The concept of hybridization allows the "construction" of new orbitals on atoms, so that the bonding in a molecule is made consistent with its known geometry. For example, in BeH_2, the geometry is linear having bond angles of 180°. The two Be—H bonds also have same bond lengths. Now, the electron configuration of Be atom is $1s^2$ $2s^2$. If it is to form two bonds by sharing one electron with each of two other atoms then it must first be put into a state where each electron is in a different orbital, and each spin is uncoupled from the other and thus is ready to be paired with the spin of an electron on the atom to which bond is to be formed. Although the promotion of the Be atom to the valence state (unpaired spin state) prepares it to form two bonds to the H atoms it does not provide an explanation or a reason why molecule should be linear rather than bent. The 2*s* orbitals of Be have the same amplitude in all directions. Therefore, whichever of the 2*p* orbitals is used to form one Be—H bond, the other bond in which 2*s* orbitals is used could make any angle with it, in so far as overlap of H and Be 2*s* orbital is concerned. However, the preference for a linear structure can be attributed to the fact that if 2*s* and 2*p* orbitals are mixed so as to form two hybrid (*i.e.,* mixed) orbitals, better total overlap with H 1*s* orbitals can be obtained. Similarly planar character of $BeCl_3$ molecule with bond angle of 120° can be explained by introduction of sp^2 hybridization. The boron atom $(\text{electronic configuration } 1s^2\,2s^2\,2p_x^{\,1})$ in the ground state can be promoted to boron atom in excited state $(\text{electronic configuration } 1s^2\,2s^1\,2p_x^{\,1}\,2p_y^{\,1})$. Orbitals in the excited state are mixed to form $3sp^2$ orbitals of equal energy making an angle of 120° with each other. Hybridization also controls molecular shape. The tetrahedral nature of methane is explained by evolving sp^3 hybridization at carbon.

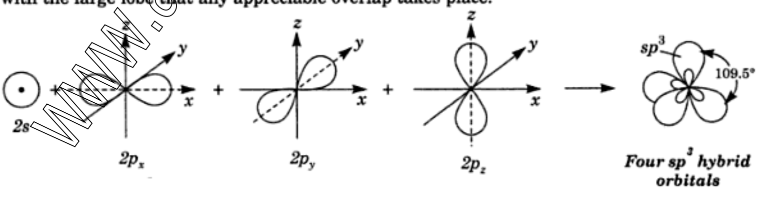
Problem 1.27:

Describe the formation and shape of an sp^3 hybridized orbital.

Solution: In carbon atom one electron from the 2*s* orbital is promoted in the excited state to the vacant p_z orbital as shown below.

	1*s*	2*s*	$2p_x$	$2p_y$	$2p_z$
C(excited state)	↑↓	↑	↑	↑	↑

Now, mixing of 2*s*, $2p_x$, $2p_y$, $2p_z$ orbitals occurs to form four new equivalent orbitals called the hybridized orbitals containing one electron each. These four hybridized orbitals point towards the four corners of a tetrahedron. The tetrahedral geometry is favorable for methane because the four hydrogen atoms and the four pairs of bonding electrons are as far apart as possible from one another but still close enough to form covalent bond. The shape of an sp^3 orbital is shown below and it consists of two lobes, one large and one small. It is only with the large lobe that any appreciable overlap takes place.



Problem 1.28:

Why do we not use the three *p*-orbitals $(2p_x, 2p_y, 2p_z)$ alone to form the three equivalent hybrid orbitals on carbon?

Solution: In general we should construct hybrid orbitals from the lowest energy atomic orbitals available. This involves the bonding electrons to have the lowest possible energies. The 2*s* orbitals are of lower energy than the 2*p* orbitals.

Problem 1.29:

Define a σ bond. How is a carbon-carbon σ bond formed? Why is a π bond weaker than a σ bond?

Solution: Sigma bonds are the most common bonds in organic compounds. The type of bond formed when the molecular orbital has its electron density centered along the line connecting the nuclei is called a σ *bond*. A σ bond is formed by the overlap of two hybrid orbitals along the internuclear axis. For instance, the sp^3 hybridized orbitals at two carbon atoms overlap to form a carbon-carbon σ bond.

Every double or triple bond contains one σ bond. A double bond results from the overlap between the *p*-orbitals oriented perpendicular to the nuclei connecting them. This lateral overlap is not as effective as the overlap along the internuclear axis. Therefore, a π bond is weaker than the σ bond.

Problem 1.30:

Which of the atoms in each of the following has a complete octet?

$$\ddot{N}H_3,\quad :CH_3^-,\quad CH_4,\quad BH_3$$

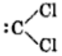
Solution: Only CH_4, because all the four valencies of C are satisfied.

Problem 1.31:

Predict the approximate bond angles in each of the following molecules.

$$CH_3^+,\quad :CCl_2,\quad BeH_2,\quad \underset{\cdot\cdot}{\ddot{O}}=\underset{\cdot\cdot}{\overset{+}{O}}-\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}:,\quad CH_2=C=CH_2$$

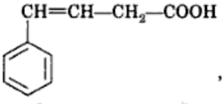
(ozone)

Solution: CH_3^+	sp^2 hybridized, 120°		sp^2 hybridized, 120°
BeH_2	sp hybridized, 180°	Ozone	Similar to H_2O, 104°
$CH_2=C=CH_2$	Linear, 180°		

Problem 1.32:

Select the correct answer.

(*a*) The type of hybridization exhibited by each carbon atom in



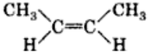
, is

A. *sp* and *sp* B. sp^2 only C. sp^2 and sp^3 D. *sp*, sp^2 and sp^3

(*b*) In the compound $CH_2{=}CH{-}CH_2{-}CH_2{-}C{\equiv}CH$, the $C_2{-}C_3$ bond is of the type:

A. $sp - sp^2$ B. $sp^3 - sp^3$ C. $sp - sp^3$ D. $sp^2 - sp^3$

(*c*) Which of the following hydrocarbons have the lowest dipole moment?

A. 
B. $CH_3{-}C{\equiv}C{-}CH_3$ C. $CH_3{-}CH_2{-}C{\equiv}CH$

D. $CH_2{=}CH{-}C{\equiv}CH$

(*d*) Which of the following represent the given mode of hybridization?

$$sp^2 - sp^2 - sp - sp$$

A. $CH_2{=}CH{-}C{\equiv}N$ B. $CH_2{=}CH{-}CH{=}CH_2$ C. $HC{\equiv}C{-}C{\equiv}CH$

D. $CH_2{=}C{=}C{=}CH$

(*e*) The Cl—C—Cl bond angle in 1, 1, 2, 2-tetrachloroethene and tetrachloromethane will be about:

A. 120° and 109.5° B. 90 and 109.5° C. 109.5° and 120° D. 109.5° and 90°

(*f*) Pick out the isoelectronic structures from the following:

$$CH_3^+,\ CH_3^-,\ NH_3,\ H_2O^+$$

A. CH_3^+ and H_3O^+ B. NH_3 and CH_3^- C. CH_3^+ and NH_3 D. H_3O^+, NH_3 and CH_3^-.

(*g*) Select the correct order of decreasing energy.

$$p,\ sp,\ sp^2,\ sp^3$$

A. $p > sp > sp^2 > sp^3$ B. $sp > sp^2 > sp^3 > p$ C. $p > sp^3 > sp^2 > sp$

D. $sp^3 > sp^2 > sp > p$

Solution: (*a*) C (*b*) D (*c*) B (*d*) A (*e*) A (*f*) D (*g*) C, the more the *s*-character in an orbital, the lower is its energy.

CHAPTER

2

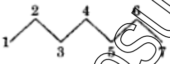
Nomenclature of Organic Compounds

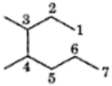
Problem 2.1:

Describe briefly the rules of IUPAC system of nomenclature for saturated hydrocarbons.

Solution: The following rules are followed to translate a structure into a name and *vice versa*.

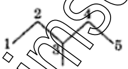
1. The generic name for paraffins or saturated hydrocarbons is *alkanes*.
2. In a compound to be named, first determine the longest straight chain of continuous carbon atoms. The name of the hydrocarbon is assigned by counting the number of carbon atoms in this chain. The selection of the carbon chain does not depend upon how it is written. Each of the following chains consist of seven carbon atoms and correspond to heptane.



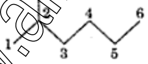


3. To specify the positions of the substituents, they are given names and numbers. The name of the alkyl substituent is derived by changing the paraffin hydrocarbon ending *-ane* to *-yl*.

   The carbon chain is numbered commencing at the end nearest the branching if any. This is done to assign the lowest number to the substituent or group attached to the chain.



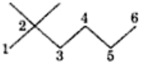
3-Methylpentane



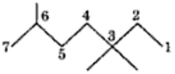
2-Methylhexane (written as one word)

2,2,4,4,6,8,8-Heptamethylnonane

4. When the carbon chain bears two similar substituents, their locations and numbers are represented by prefixing *di*-(2), *tri*-(3), *tetra*-(4), etc.

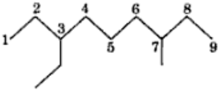


2,2-Dimethylhexane



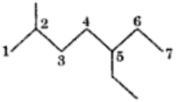
3,3,6-Trimethylheptane

5. When two or more substituents are present in equivalent positions in the carbon chain, the lower number is assigned to that group which is written first in the name of the compound in the alphabetical order.



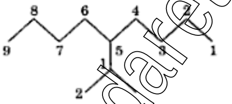
3-Ethyl-7-methylnonane

6. While writing the name of the compound, write the substituents in an alphabetical order, *i.e.* ethyl before methyl.

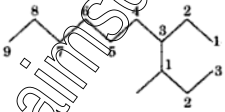


5-Ethyl-2-methylheptane

7. A complicated branched chain is named as a derivative of the longest chain (*i.e.* the base chain) in that compound. This chain is numbered starting from the carbon chain linked to the base chain. Its name is constructed on the basis of IUPAC rules and is enclosed within parenthesis to distinguish it from the base chain.



5-(1-Methylethyl) nonane

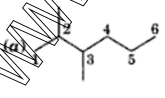


3-(1-Methylpropyl) nonane

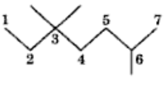
Problem 2.2:

Suggest IUPAC name for each of the following hydrocarbons :

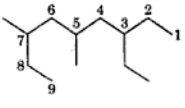
(*a*)



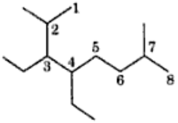
(*b*)



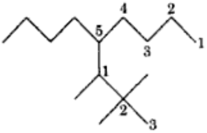
(*c*)



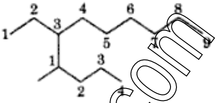
(*d*)



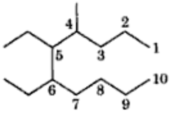
(*e*)



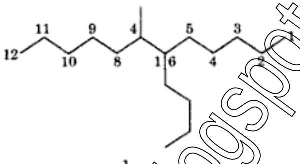
(*f*)



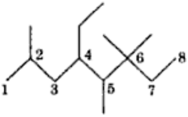
(*g*)



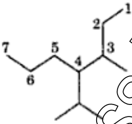
(*h*)



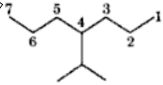
(*i*)



(*j*)



(*k*)



Solution: (*a*) 2,3-Dimethylhexane (*b*) 3,3,6-Trimethylheptane (*c*) 3-Ethyl-5,7-Dimethylnonane (*d*) 3,4-Diethyl-2,7-dimethylocatane (*e*) 5-(1,2,2-Trimethylpropyl) nonane (*f*) 3-(1-Methylbutyl) nonane (*g*) 5,6-Diethyl-4-methyldecane (*h*) 6-Butyl-7-methyldodecane (*i*) 4-Ethyl-2,5,6,6-tetramethyloctane (*j*) 4-Isopropyl-3-methylheptane (*k*) 4-Isopropylheptane.

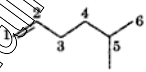
Problem 2.3:

Write briefly the IUPAC rules for naming compounds containing functional groups.

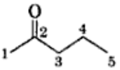
Solution: The following rules may be considered in naming compounds containing one functional group :

1. The name of a compound containing a single functional group is obtained by adding a *suffix* to the root derived from the name of the hydrocarbon of longest carbon chain. This suffix replaces the ending *-ane*. (For suffixes of functional groups, see A Textbook of Organic Chemistry by Dr. R.K. Bansal).
2. The chain is so numbered that the functional group always gets the lowest number.
3. A functional group containing a C-atom is always assigned position 1 and its location is not mentioned while writing the name of the compound.

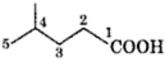
Examples:



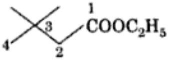
5-Methylhex-1-ene
(letter e is retained in terminal -ene
because of its terminal position)



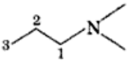
2-Pentanone (Pent-2-one)



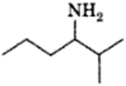
4-Methylpentanoic acid



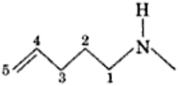
Ethyl 3,3-dimethylbutanoate



N,N-dimethylpropanamine
(N,N-dimethyl-1-aminopropane is wrong)



2-Methyl-3-hexanamine



N-methyl-4-pentenamine

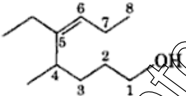
Similar rules as discussed above are also applicable for naming compounds containing two functional groups with some modifications.

1. Out of the two functional groups present in the carbon chain in a compound, one is chosen as the principal functional group and it is assigned the lowest number.

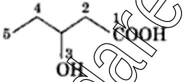
   (For priority of functional groups see, A Textbook of Organic Chemistry by Dr. R.K. Bansal).

2. The name of the compound ends with the suffix of the principal functional group. All other groups present are used as prefixes.

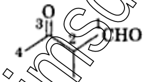
Examples:



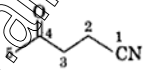
5-Ethyl-4-methyloct-5-en-1-ol
(-en in internal position)



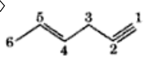
3-Hydroxypentanoic acid



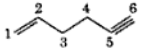
2-Methyl-3-oxobutanal



4-Ketopentanenitrile

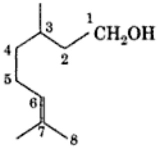


4-Hexen-1-yne



1-Hexene-5-yne
(5-Hexen-1-yne is wrong)

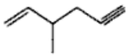
Note the difference in the above two structures. The carbon chain is numbered considering $C\equiv C$ as the principal group. In contrast, if there is a choice for numbering (as in the second structure) then $C=C$ gets the preference over $C\equiv C$ but the compound is still named as alkenyne.

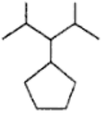


3,7-Dimethyl-6-octen-1-ol

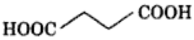
Problem 2.4:

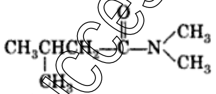
Write IUPAC names for the following structures:

(a)


(b)


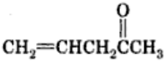
(c)


(d)


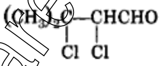
(e)

$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2-\overset{O}{\overset{\|}{C}}-N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$

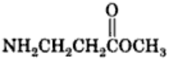
(f)

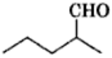

(g) $CH_3C\equiv CCH=CHCH=CH_2$ (h) $CH_2=CHCH_2OH$

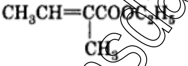
(i)

$CH_2=CHCH_2\overset{O}{\overset{\|}{C}}CH_3$

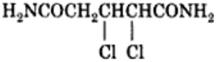
(j) $HOCH_2CH_2OH$

(k)

$(CH_3)_2\underset{Cl}{\underset{|}{C}}-\underset{Cl}{\underset{|}{C}}HCHO$

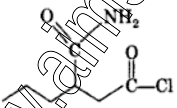
(l)

$NH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3$

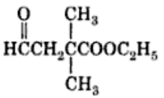
(m)


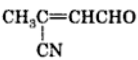
(n)

$CH_3CH=\underset{CH_3}{\underset{|}{C}}COOC_2H_5$

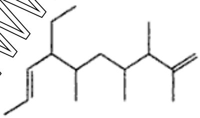
(o)

$H_2NCOCH_2\underset{Cl}{\underset{|}{C}}H\underset{Cl}{\underset{|}{C}}HCONH_2$

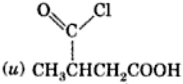
(p) $H_2C=CHCH_2Br$

(q)


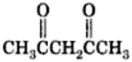
(r)

$H\overset{O}{\overset{\|}{C}}CH_2\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}COOC_2H_5$

(s)

$CH_3\underset{CN}{\underset{|}{C}}=CHCHO$

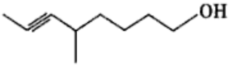
(t)


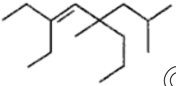
(u)

$CH_3\overset{O=C-Cl}{\overset{|}{C}}HCH_2COOH$

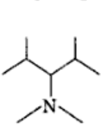
(v) $HOOCCH_2CH_2CN$

(*w*) 

$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$

(*x*) 

(*y*) 

(*z*) 

Solution: (*a*) 3-Methylhex-1-en-5-yne (*b*) 3-Cyclopentyl-2,4-dimethylpentane (*c*) 3-Methylpentanamide (*d*) 1,4-Butanedioic acid (*e*) N,N,3-trimethylbutanamide (*f*) 1,4-Pentadiyne (*g*) 2,6-Heptadien-2-yne (*h*) Propen-1-ol (*i*) 4-Penten-2-one (*j*) 1,2-Ethanedial (*k*) 2,3-Dichloro-3-methylbutanal (*l*) Methyl 3-aminopropanoate (*m*) 2-Methylpentanal (*n*) Ethyl 2-methylbutenoate (*o*) 2,3-Dichloro-1,5-dipentanamide (*p*) 3-Bromo-1-propene (*q*) 3-Carbamoylhexanoyl chloride (*r*) Ethyl 2,2-dimethyl-4-oxobutanoate (*s*) 2-Methyl-4-oxobutenonitrile (*t*) 7-Ethyl-2,3,4,6-tetramethyldeca-1,8-diene (*u*) 3-Chloroformylbutanoic acid (*v*) 3-Cyanopropanoic acid (*w*) 2,4-Pentanedione (*x*) 5-Methyl-6-octyn-1-al (*y*) 3-Ethyl-5,7-dimethyl-5-propyloct-3-ene (*z*) 2,4,N,N-tetramethyl-3-pentanamine.

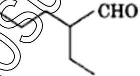
Problem 2.5:

Write the structures as well as the correct names for the following compounds:

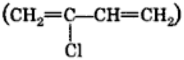
(*a*) 2-Pentyn-1-ene (*b*) 2-Allybutanal (*c*) 3-Chloro-1,3-butadiene (*d*) 5-Ethyl-3-methylheptane (*e*) 3-Butene (*f*) 3,3-Dimethyl-1-propyne (*g*) 1,3-Pentyne (*h*) Vinylacetic acid (*i*) 3-Oxo-7-octanol (*j*) Hex-2-en-6-ol (*k*) 3-Buten-1-yne (*l*) 2-Methyl propyl ethanoate.

Solution: (*a*) (2-Pentyn-4-ene)

(*b*) (2-Ethylpentanal)

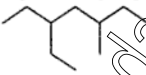


(*c*) 2-Chloro-1,3-butadiene



$(CH_2{=}\underset{\underset{Cl}{|}}{C}{-}CH{=}CH_2)$

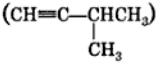
(*d*) 3-Ethyl-5-methylheptane



(*e*) 1-Butene

$(CH_2{=}CH{-}CH_2{-}CH_3)$

(*f*) 3-Methyl-1-butyne

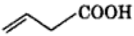


$(CH{\equiv}C{-}\underset{\underset{CH_3}{|}}{C}HCH_3)$

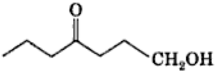
(*g*) 1,3-Pantadiyne

$(HC{\equiv}C{-}C{\equiv}C{-}CH_3)$

(*h*) 3-Butenoic acid



(*i*) 1-Hydroxy-5-heptanone



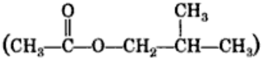
(*j*) Hex-4-en-1-ol

$(CH_3{-}CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2OH)$

(*k*) 1-Buten-3-yne

$(CH_2{=}CH{-}C{\equiv}CH)$

(*l*) 2-Methylpropyl ethanoate



$(CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}H{-}CH_3)$

Problem 2.6:

Define a functional group. Name some such groups containing an oxygen atom.

Solution: A *functional group* is defined as the chemically reactive part of a molecule. Examples of some functional groups containing oxygen atom are:

-COOH (Carboxyl) -OH (Hydroxy) -CHO (Aldehyde) -$CONH_2$ (Amide).

Problem 2.7:

Can homologues be isomers?

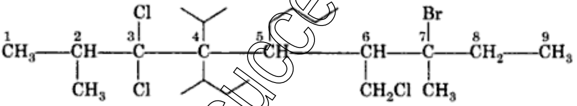
Solution: No, because homologues do not have the same molecular formula. They differ from one another by the possession of an additional CH_2 group. Homologues though have similar chemical properties.

Problem 2.8:

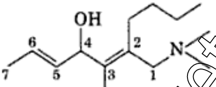
Write a structure corresponding to the following names:

(*a*) 2,7-Dimethyl-3,3-dichloro-4-sec-butyl-4-isopropyl-5-*n*-butyl-6-chloromethyl-7-bromononane. (*b*) 2-Butyl-4-hydroxy-3,N,N-trimethyl-2,5-heptadien-1-amine. (*c*) 2-Methyl-4-oxo-2-butenonitrile. (*d*) Methyl methyl propanedioate. (*e*) 2,N,N-trimethyl-3-ethoxy-propanamide.

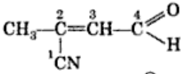
Solution: (*a*)



(*b*)

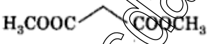


(*c*)

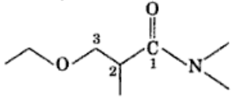


$\mathrm{CH_3{-}\underset{|\atop ^1CN}{\overset{2}{C}}{=}\overset{3}{C}H{-}\overset{4}{C}HO}$

(*d*)



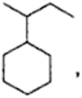
(*e*)



Problem 2.9:

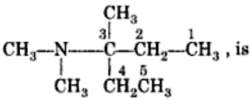
Select the correct answer from the following:

(*a*) The IUPAC name of



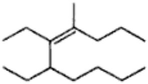
, is

A. 2-Phenylbutane B. 3-Phenylbutane C. 2-Cyclohexylbutane
D. 3-Cyclohexylbutane

(*b*) The IUPAC name of  $CH_3-N(CH_3)-\overset{3}{C}(CH_3)(\overset{4}{C}H_2\overset{5}{C}H_3)-\overset{2}{C}H_2-\overset{1}{C}H_3$, is

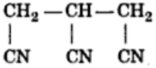
A. *3-Dimethylamine-3-methylpentane* B. 3,N,N-dimethylamino-3-ethylbutane

C. 3,N,N-trimethyl-3-pentanamine D. 3-Dimethylamino-3-ethylbutane

(*c*) The IUPAC name of  , is

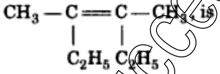
A. 5,6-Diethyl-8-methyl-7-decene B. 5,6-Diethyl-3-methyldec-4-ene

C. 3-Methyl-5,6-diethyl-6-decene D. 5,6-Diethyl-8-methyl-6-decene

(*d*) The IUPAC name of  $CH_2(CN)-CH(CN)-CH_2(CN)$, is

A. 1,2,3-Tricyanopropanedinitrile B. 3-Cyano-1,5-dinitrile

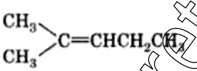
C. Propanetricarbylamine D. 3-Cyanopentan-1,5-dinitrile

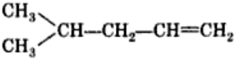
(*e*) The IUPAC name of  $CH_3-C(C_2H_5)=C(C_2H_5)-CH_3$, is

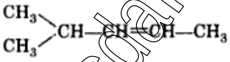
A. 3,4-Dimethylhex-3-ene B. 1,1-Diethylbutene

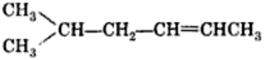
C. 2-Ethyl-3-methylpentene D. 2,4-Diethyl-2-butene

(*f*) The structure of 4-methylpent-2-ene, is

A.  $(CH_3)_2C=CHCH_2CH_3$

B.  $(CH_3)_2CH-CH_2-CH=CH_2$

C.  $(CH_3)_2CH-CH=CH-CH_3$

D.  $(CH_3)_2CH-CH_2-CH=CHCH_3$

(*g*) The IUPAC name of $CH_3-C\equiv N$, is

A. Acetonitrile B. Ethanenitrile C. Cyanoethane D. Methyl cyanide

Solution: (*a*) C (*b*) C (*c*) B (*d*) D (*e*) A (*f*) C (*g*) B.

CHAPTER

3

Factors Affecting Acid Base Strengths

Problem 3.1:

Write short notes on the following:

Solvation, resonance energy, electrophiles, nucleophiles, Lewis acids, tautomerism, resonance hybrid, inductive effect and steric effect.

Solution: Solvation: A solvent directly interacts with the dissolved ion. The ion is surrounded by the solvent molecules forming the solvation shell. This process is called *solvation*. The solvents affect the stabilities of ions in many cases. For example, polar protic solvents such as water and alcohols are capable of effectively solvating both cations and anions. Cations are solvated by dipolar interactions with lone pairs and the anions are solvated by hydrogen bonding. Polar aprotic solvents such as dimethylsulfoxide and dimethyl formamide solvate cations but do not effectively solvate anions. Thus anions tend to be more reactive in polar aprotic solvents.

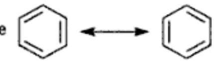
Resonance Energy: The extra stabilization provided by the delocalization of electrons compared to a non-delocalized structure is termed as *resonance energy*.

Electrophiles: *Electrophiles* are species capable of accepting electrons. Lewis acids are frequently called electrophiles. An electrophile tend to attack a site of high electron density.

Nucleophiles: *Nucleophiles* are species capable of donating electrons for bond formation. Lewis bases are called nucleophiles.

Lewis Acids: Species that are short of an electronic octet by one or more electron pairs are called *Lewis acids*.

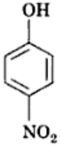
Tautomerism: The rapid equilibrium between two isomeric functional groups is called *tautomerism*.

Resonance Hybrid: The actual structure of a molecule is considered to be a *resonance hybrid* of all the possible Lewis structures which are referred to as contributing structures or canonical structures. For benzene the canonical forms are  and is a single compound that is the average of both these structures. Benzene is thus a hybrid of these structures and is represented by .

Inductive Effect: In the case of resonance effect the electrons are transmitted through an alternating system of single and double bonds. There is yet another way of electronic displacement and it takes place through a saturated carbon chain when an electron-donating or electron-withdrawing group is present on the chain. This is called the *inductive effect* and it is a polarization through a sigma bond. Most elements that are substituted for hydrogen in organic molecules are more electronegative than hydrogen. Therefore, most substituents such as $-NO_2$, $-NH_2$, $-OH$ and halogens exert electron-withdrawing inductive effects. For this reason chloroacetic acid is stronger than acetic acid. This effect falls off with distance from the substituent.

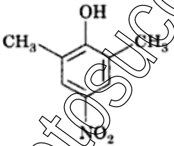
Steric Effect: An energetically unfavorable effect on any physical or chemical property that results from van der Waals repulsion is termed *a steric effect*. Thus when it is said that the energy barrier to rotation in butane is more than that of ethane, it is because there are two methyl groups in butane which interfere with the rotation. Steric effects are caused by interactions between atoms or groups that are non-bonded to each other. In other words it results from the presence of bulky groups.

From the K_a values of the following phenols, it is obvious that (C) has the lowest acidity. The reduced acidity is attributed to steric effects. In order for resonance interaction to operate between the substituent and the ring, the substituent must lie in the plane of the ring. Such a geometry is not available for phenol (C) because of the presence of two *ortho* methyl groups. As a result the nitro group is pushed out of the plane of the ring and effective delocalization of the resultant phenoxide ion does not take place. This effect is also termed as *steric inhibition to resonance*.



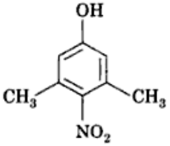
(*a*)

Ka 700×10^{-10}



(*b*)

700×10^{-10}



(*c*)

60×10^{-10}

Problem 3.2:

Predict the relative acidity of the following pairs:

(*a*) H_3O^+ and NH_4^+ (*b*) CH_3NH_2 and CH_3OH

Solution: We examine the conjugate base being formed when each acid loses a proton; the better the conjugate base accommodates the electron pair left behind, the weaker the base and hence stronger the acid.

(*a*) $H_3O^+ > NH_4^+$

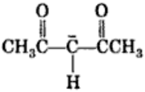
Oxygen is more electronegative than nitrogen and can hold on to electrons better. Therefore, H_3O^+ will tend to lose the proton more rapidly and more acidic.

(*b*) $CH_3\ddot{\underset{..}{O}}H > CH_2\ddot{N}H_2$

Again because oxygen is more electronegative than nitrogen, CH_3OH is more acidic.

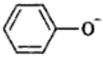
Problem 3.3:

Draw the resonance contributing structures of the following molecules:

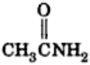
(*a*) 

$CH_3\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\bar{C}}}-\overset{O}{\overset{\|}{C}}CH_3$

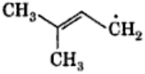
(*b*) CH_3NO_2

(*c*) 

(*d*) $CH_3CH_2CH{=}CHNO_2$

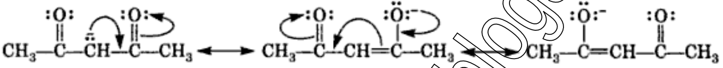
(*e*) 

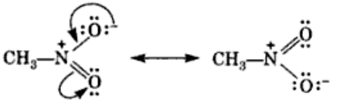
$CH_3\overset{O}{\overset{\|}{C}}NH_2$

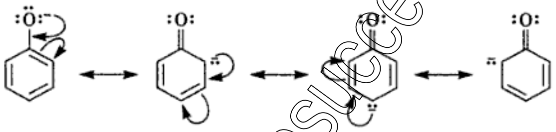
(*f*) 

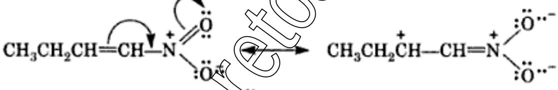
(a free radical).

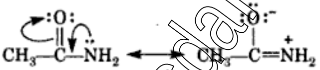
Solution:

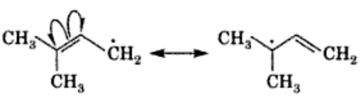
(*a*) 

(*b*) 

(*c*) 

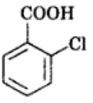
(*d*) 

(*e*) 

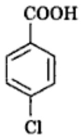
(*f*) 

Problem 3.4:

(*a*) Which is more acidic and why ?



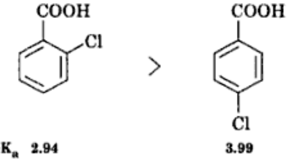
or



(*b*) Which is more basic and why ?

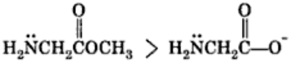
$H_2\ddot{N}CH_2COO^-$ or $H_2\ddot{N}CH_2COOH_3$

Solution: (*a*)



Because of the larger inductive electron-withdrawing effect of Cl in the *ortho* position, the negative charge on the carboxylate ion is stabilized, after the loss of a proton.

(*b*)



$$H_2\ddot{N}CH_2\overset{\overset{O}{\|}}{C}OCH_3 > H_2\ddot{N}CH_2\overset{\overset{O}{\|}}{C}—O^-$$

Because of the greater inductive electron-withdrawing effect of the carboxylate ion, the electron density on the nitrogen atom is decreased.

Problem 3.5:

(*a*) Would $Br\underset{\underset{Br}{|}}{C}HCH_2COOH$ be a stronger acid than $BrCH_2CH_2COOH$? Why ?

(*b*) Why is the compound $(CF_3)_3\ddot{N}$ virtually non-basic ?

Solution: (*a*) Yes, because the two β-Br groups are more effective in stabilizing the carboxylate ion inductively. (*b*) The trifluoromethyl groups withdraw electrons inductively making the electron pair on the N-atom virtually non-available for donation.

Problem 3.6:

(*a*) Write the following in the increasing order of acid strength:

$$CCl_3COOH,\ \ddot{N}H_3,\ HCOOH,\ CH_3COOH,\ CH_3\overset{\overset{O}{\|}}{C}NH_2,\ CF_3COOH$$

(*b*) Write the following in the decreasing order of base strength:

$$C_6H_5\ddot{N}H_2,\ :\ddot{O}H^-,\ \ddot{N}H_3,\ \ddot{N}H_2^-,\ (CH_3)_2\ddot{N}H,\ CH_3\ddot{O}H,\ CH_3\ddot{N}H_2$$

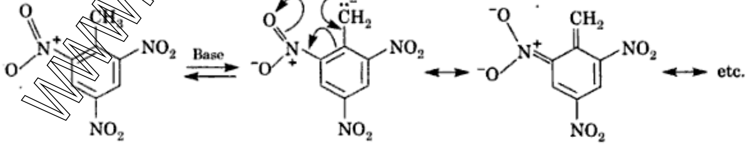
Solution: (*a*) $NH_3 < CH_3CONH_2 < CH_3COOH < HCOOH < CCl_3COOH < CF_3COOH$

(*b*) $NH_2^- > OH^- > (CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2 > CH_3OH$

Problem 3.7:

2,4,6-Trinitrotoluene is a relatively acidic compound. Explain why the proton is easily removed from the methyl group?

Solution:



The proton is removed easily because the anion formed after the removal of the proton is stabilized by resonance with the three $-NO_2$ groups as shown above.

Problem 3.8:

(*a*) State Lewis concept of acids and bases. (*b*) Can a proton (H^+) be regarded as an acid according to Brönsted and Lewis definitions ?

Solution: (*a*) Lewis acids are species that can accept a pair electrons, and those which donate are Lewis bases. (*b*) H^+ is not a Brönsted acid but is a Lewis acid because it can accept a pair of electrons.

Problem 3.9:

(*a*) The heat of hydrogenation of 1-butene is 30.3 Kcal/mole and that of 1,3-butadiene is 57.1 Kcal/mole. Calculate the resonance energy of 1,3-butadiene. (*b*) Can 2-butene be chosen as a model instead of 1-butene in the above case ?

Solution: (*a*) $\text{1-Butene} + H_2 \xrightarrow{\text{Catalyst}} \text{Butane} + 30.3\ \text{Kcal/mole}$

$\text{1,3-Butadiene} + 2H_2 \xrightarrow{\text{Catalyst}} \text{Butane} + 57.1\ \text{Kcal/mole}$

1,3-Butadiene might be expected to evolve twice the heat of 1-butene

($2 \times 30.3 = 60.6$ Kcal/mole). Therefore, the difference $60.6 - 57.1 = 3.5$ Kcal/mole is the resonance energy of 1,3-butadiene.

(*b*) No, because 2-butene has a lower heat of hydrogenation (28 Kcal/mole) due to its own stability.

Problem 3.10:

Classify the following into Lewis acids, bases or neither:

HF, BF_3, $HC{\equiv}CH$, NO_2^+, CH_3CN, H_2O, CH_3OH, C_2H_6, Ag^+, $SnCl_4$, I^-

Solution: Acids : BF_3, NO_2^+, Ag^+ Bases : CH_3CN, H_2O, CH_3OH

Neither : $HC{\equiv}CH$, C_2H_6, HF

Problem 3.11:

Arrange the following in decreasing order of acidity:

phenol, *p*-cresol and *p*-nitrophenol. Give reasons for your answer.

Solution: *p*-Nitrophenol > phenol > *p*-cresol

The nitro group is electron-withdrawing and stabilizes the phenoxide ion after the loss of a proton, while the $-CH_3$ group is electron-releasing and makes the phenoxide ion unstable.

Problem 3.12:

Trifluoroethanol is 1000 times more acidic than ethanol. Explain.

Solution: Because of the presence of three strong electronegative fluorine groups, the release of proton is facilitated or the trifluoroethoxide ion is inductively stabilized.

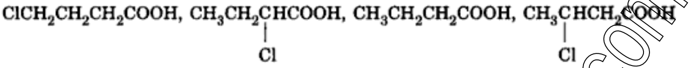
Problem 3.13:

Neither pure H_2SO_4 nor pure $HClO_4$ conduct an electric current. Explain.

Solution: None of the two acids is ionized in the pure form.

Problem 3.14:

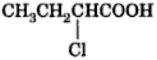
(*a*) Which is a strongest acid and why ?



$ClCH_2CH_2CH_2COOH$, $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH$, $CH_3CH_2CH_2COOH$, $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2COOH$

(*b*) Which is a strongest base and why ?

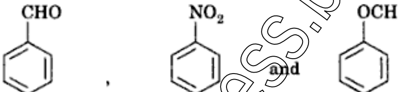
$$CH_3\ddot{N}H_2\ ,\ \ddot{N}H_3\ ,\ CH_3CH_2CH_2\ddot{N}H_2\ ,\ CH_3CH_2\ddot{N}H_2$$



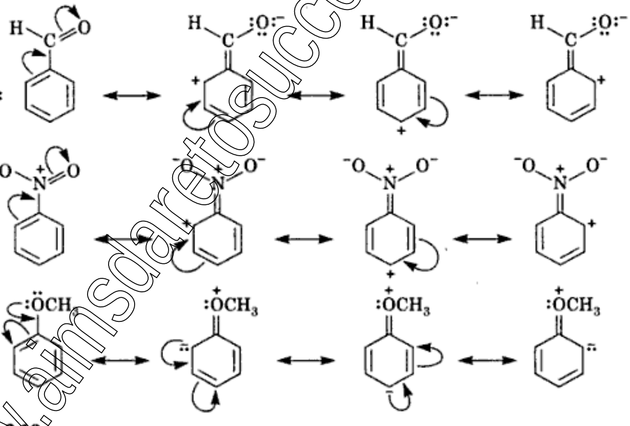
Solution: (*a*) $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH$ is the strongest acid because the electron-withdrawing Cl group is nearer to the carboxyl group. (*b*) Propylamine because the propyl group is a better electron donor than other alkyl groups.

Problem 3.15:

Write resonance contributing structures for the following molecules:



Solution:



Problem 3.16:

Write an expression for the acidity constant (K_a) of benzoic acid and show that pK_a is equal to the pH of a half-ionized aqueous solution.

Solution: $C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$

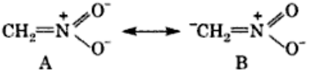
$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}$$

If the acid is half ionized, then $[C_6H_5COOH] = [C_6H_5COO^-]$. In this case

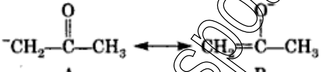
$$K_a = H_3O^+ \quad \text{or} \quad pH = pK_a$$

Problem 3.17:

Label the major and minor contributors in the following sets of resonance structures:

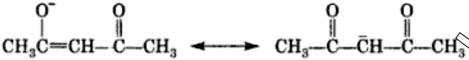
(a) 

A B

(b) 

$^{-}CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \longleftrightarrow CH_2=\overset{\overset{O^-}{|}}{C}-CH_3$

A B

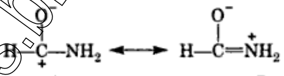
(c) 

$CH_3\overset{\overset{O^-}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-CH_3 \longleftrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\bar{C}H-\overset{\overset{O}{\|}}{C}-CH_3$

A B

(d) $CH_3-CH=C=N^- \longleftrightarrow CH_3-\bar{C}H-C\equiv N$

A B

(e) 

$H-\underset{+}{\overset{\overset{O^-}{|}}{C}}-NH_2 \longleftrightarrow H-\overset{\overset{O^-}{|}}{C}=\overset{+}{N}H_2$

A B

Solution: (a) A (b) B (c) A (d) A (e) B

Problem 3.18:

The K_a of acetic acid is 1.2×10^{-5} and the pK_a of phenylacetic acid is 4.31.

	CH_3COOH		$C_6H_5CH_2COOH$
K_a	1.2×10^{-5}	pK_a	4.31

Calculate the pK_a of acetic acid and K_a of phenylacetic acid. Which of the two acids is stronger ? Explain.

Solution:

	CH_3COOH		$C_6H_5CH_2COOH$
K_a	1.2×10^{-5}	pK_a	4.31

$$pK_a = -\log K_a$$

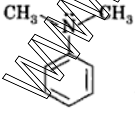
Substitute the values to obtain pK_a and K_a

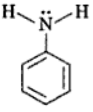
pK_a	4.76	K_a	5.1×10^{-5}

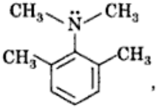
Phenylacetic acid is stronger because of the inductive electron-withdrawing effect of the phenyl group.

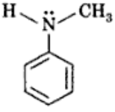
Problem 3.19:

Arrange the following amines in the order of their decreasing basicity. Justify your answer.

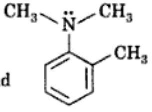

(1)


(2)


(3)


(4)

and


(5)

Solution: $3 > 5 > 1 > 4 > 2$

In (3) the resonance of the electron pair on the nitrogen atom is hindered by the two *ortho methyl* groups. In (1) and (4) there is more electron density on the nitrogen atom. In (2), which is least basic, there is extensive resonance of the electron pair with the ring.

Problem 3.20:

Arrange the following acids in the order of decreasing acidity. Give reasons for your answer.

H—F , H—I , H—Cl and H—Br

Solution:	HI	>	HBr	>	HCl	>	HF.
K_a	5.0×10^{10}		2.2×10^{10}		1.2×10^{8}		1.6×10^{-3}

As the size of the halo atom increases the bond length of hydron halide increases. The larger the bond, the weaker it is. Hence the hydrogen can be easily removed. HI having a larger bond length than others is the strongest acid. HF, on the other hand, has a high bond energy. Moreover, because of strong H-bond formation in HF, the H-atom is not easily ionized.

Problem 3.21:

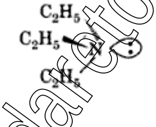
Name the tools for making qualitative estimates of structural features that might stabilize or destabilize the molecules with closely related structures.

Solution: At least the following four tools can be employed for this purpose:

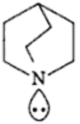
(*i*) The resonance effect
(*ii*) The Inductive effect
(*iii*) The steric effect
(*iv*) The hydrogen bonding effect.

Problem 3.22:

Triethylamine (*a*) gives no detectable adduct with trimethylborane whereas quinuclidine (*b*) forms a very stable adduct.



(*a*)



(*b*)

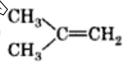
Solution: The ethyl groups shield the nitrogen atom of the amine to prevent any reaction of triethylamine with trimethylborane. In quinuclidine, in contrast, the carbon atoms are pinned at the back in the ring system. Therefore, the nitrogen atom is free to attack trimethylborane and hence form a stable adduct.

Problem 3.23:

Write the formula for the conjugate base of each of the following Brönsted acids.

(*a*) $(CH_3)_3C^+$ (*b*) H_2SO_4 (*c*) CH_4 (*d*) $C_2H_5OH_2^+$

Solution: (*a*)



$(CH_3)_2C{=}CH_2$ (*b*) HSO_4^- (*c*) CH_3^- (*d*) C_2H_5OH

Problem 3.24:

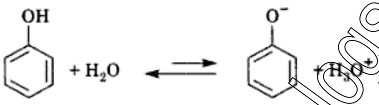
What are super acids ?

Solution: Super acids are mixture of fluorosulfonic acid and antimony pentafluoride (FSO_3H—SbF_5). Such mixtures are usually soluble in SO_2 and are among the strongest acid solution known. Alkyl cations can be kept indefinitely in stable form in super acids.

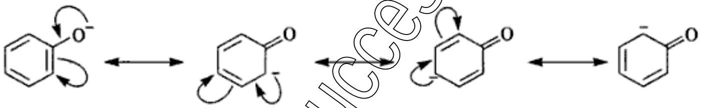
Problem 3.24:

Why is phenol acidic ?

Solution: Phenols, like alcohols can ionize.

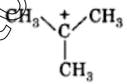


Phenols are considerably more acidic than alcohols of similar size and shape. Phenol, for instance, is 10^7 times more acidic than cyclohexanol. The enhanced acidity of phenol is due to the stabilization of its conjugate base anion. The anion is stabilized by resonance, and the negative charge is spread over ring C-atoms.



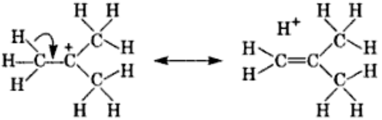
Problem 3.25:

What are the two ways by which the following cation can be stabilized.



Solution: The tertiary butyl carbocation may be stabilized by electron inductive effect. In this case the $-CH_3$ group being an electron donor, decreases the positive charge on the central carbon atom and thus increases its stability.

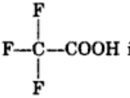
A second factor that accounts for its stabilization is hyperconjugation. This involves the overlap of bonding electrons from the adjacent σ bonds with the unoccupied 2*p* orbital of the carbocation. This is depicted as follows:



Similar structures are possible for a C—H bond in each methyl group. More the hyperconjugative structures, more stable is the cation.

Problem 3.26:

Is trifluoracetic acid the strongest aliphatic acid ? What is its pK_a ?

Solution:  $F-\underset{F}{\overset{F}{C}}-COOH$ is the strongest acid because of the powerful inductive electron-withdrawing effect of the three F groups. Its pK_a is zero.

Problem 3.27:

Why is the structure $R-C\equiv\overset{+}{O}:$, is more stable than $R-\overset{+}{C}=O$ for the acylium ion ?

Solution: In the structure $R-C\equiv\overset{+}{O}:$, each atom has complete octet and most of the positive charge resides on oxygen. While in $R-\overset{+}{C}=O$, the structure of the acylium ion usually written, the carbon atom has only six electrons, *i.e.* two short of octet.

Problem 3.28:

Would you expect the inductive effect to be dependent between two centres.

Solution: Yes. The effect decreases if the distance is increased.

Problem 3.29:

Describe the weighted average structure of a molecule.

Solution: If two resonance structures (unlike in benzene) are not identical then the molecule may represent a weighted average of the two. This implies that one of the structures is more important than the other in describing the molecule. For example, methoxymethyl cation can be written as:

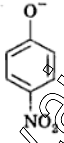
$$\overset{+}{C}H_2-\ddot{\underset{..}{O}}-CH_3 \longleftrightarrow CH_2=\underset{..}{\overset{+}{O}}-CH_3$$

The structure on the right is a better description of this cation because all atoms have complete octets. The C—O bond has significant double bond character and most of the positive charge resides on the oxygen.

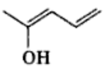
Problem 3.30:

Draw resonance contributing structures of:

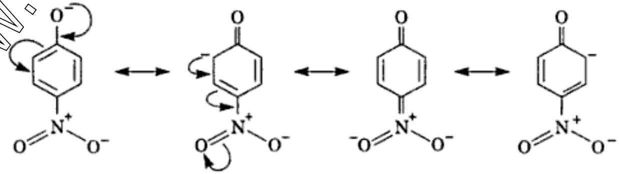
(*a*)



(*b*)



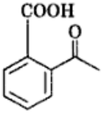
Solution: (*a*)



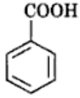
(*b*) 

Problem 3.31:

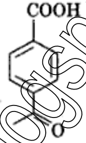
Arrange the following acids in increasing order of acid strength and explain your answer.



A



B



C

Solution: B < A < C

Occurrence of H-bond in (A) makes the loss of a proton difficult. Hence it is less acidic than (C).

Problem 3.32:

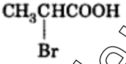
Which has a greater acidity,  or $CH_3—CH_2—CH_3$?

Solution: Cyclopropane, the C—H bonds in it have more *S* character. More the *s*-character, greater is the acidity and lower the basicity.

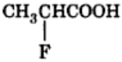
Problem 3.33:

Select the correct answer from the following:

(*a*) Which of the following acids has the lowest dissociation constant ?

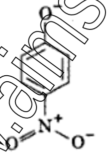
A. 
$CH_3\underset{\mathrm{Br}}{\underset{|}{C}}HCOOH$

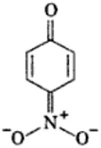
B. $BrCH_2CH_2COOH$

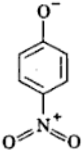
C. 
$CH_3\underset{\mathrm{F}}{\underset{|}{C}}HCOOH$

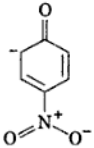
D. FCH_2CH_2COOH

(*b*) Which is the most unlikely resonance structure ?

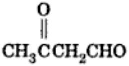
A. 

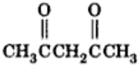
B. 

C. 

D. 

(*c*) Among the following which has the most acidic α-H ?

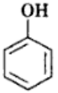
A. 
$CH_3\overset{\overset{O}{\|}}{C}CH_2CHO$

B. 
$CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}CH_3$

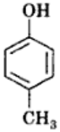
C. 
$CH_3\overset{\overset{O}{\|}}{C}CH_2COOCH_3$

D. CH_3CHO

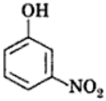
(*d*) The increasing order of acidity among phenol, *p*-methylphenol, *m*-nitrophenol and *p*-nitrophenol is:


I

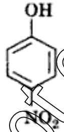
,


II

,

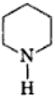

III

and

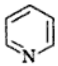

IV

A. III, IV, I, II B. IV, III, I, II C. II, I, III, IV D. I, II, IV, III.

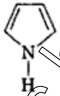
(*e*) In the following compounds the order of basicity is:


I

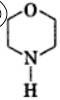
,


II

,


III

and


IV

A. I > IV > II > III B. II > I > IV > III C. III > I > IV > II

D. IV > I > III > II.

(*f*) Resonance structures of a molecule should have:

A. Identical arrangement of atoms B. Identical bonding

C. Nearly the same energy content D. Same number of paired electrons

Solution: (*a*) B, Br is less electronogative than F. Besides the distance between Br and COOH is large. (*b*) C, In this structure nitrogen is pentavalent. (*c*) B, the resultant anion has four resonance structures. (*d*) B, $-NO_2$ group is a powerful electron-withdrawing group. Moreover, the *p*-nitro phenoxide ion is also resonance stabilized. (*e*) A, I is a saturated compound, there is no delocalization of nitrogen electron pair in the ring. In II, the oxygen atom is electronegative. Compound III is virtually non-basic. (*f*) B, C, read the rules of resonance.

CHAPTER

4

Stereochemistry

Problem 4.1:

Describe the following terms:

Stereochemistry, mirror image, optical activity, *meso* compound, diastereoisomer, resolution, racemization, relative and absolute configurations, chiral center, conformation, *gauche* and *anti* conformation, stereospecific reaction, enantiomers, Fischer projection and stereoisomers.

Solution: Stereochemistry: Chemical studies that take into account the three-dimensional aspects of molecules is referred to as stereochemistry.

Mirror Image: The image that would be seen if an object or a molecule were viewed in a mirror.

Optical Activity: The rotation of polarized light by chiral molecules. One enantiomer must be present in excess of the other for optical activity to be observed.

Meso Compound: An optically inactive compound whose molecules are achiral even though they contain chiral centers.

Diastereoisomer: Stereoisomers that are not enantiomers are called *diastereoisomers.* The *meso* tartaric acid is diastereoisomer of the (d, l) enantiomers of the acid. Diastereoisomers contain two or more chiral carbon atoms.

Resolution: The process by which a mixture of two enantiomers is separated (resolved) into two individual optical enantiomeric forms is called *resolution*.

Racemization: The process when an optically active reagent gives a product that shows neither retention of the configuration nor inversion of configuration is called racemization.

Relative Configuration: Chemists have determined the absolute configuration of many chiral compounds by x-ray crystallography since 1951. Before that, however, it was possible to correlate the configuration of one compound with that of another and to show that the two compounds have the same or opposite configurations. For example, when we convert one compound into another using a reaction that does not affect the bonds to the chiral atom, we know that the product must have the same relative configuration as the reactant. The *relative configuration* is then the experimentally determined relationship between the configurations of two molecules.

Absolute Configuration: During our study of stereochemistry we have drawn three-dimensional representations and the Fischer projections, and also stated that the chiral carbons have the R and S configuration. All these methods of describing the configuration about a chiral atom are absolute, *i.e.* they give the actual orientations of atoms in space. Therefore these methods specify the *absolute configuration*.

Chiral Center: An atom in a molecule that is linked to four different groups.

Conformation: A spatial arrangement of the atoms of a molecule that can be converted into another arrangement by rotation around the single bonds.

Gauche Conformation: In butane, for instance at a dihedral angle of 60°, the molecule is staggered and the methyl groups are to the right and left of each other. Such a conformation with a dihedral angle of 60° between the largest groups is called the *gauche conformation*.

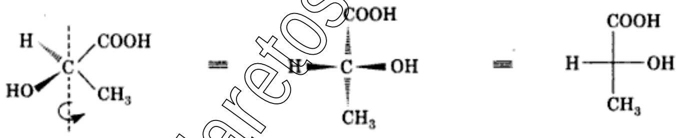
***Anti* Conformations:** For butane, there is another staggered conformation in which the two methyl groups are in opposite directions. Therefore, a conformation with a dihedral angle of 180° between the largest groups is in *anti conformation*. This is often the conformation with lowest energy.

Stereospecific Reaction: A reaction in which the stereochemistry of the reactants is retained in the products is called a *stereospecific reaction*.

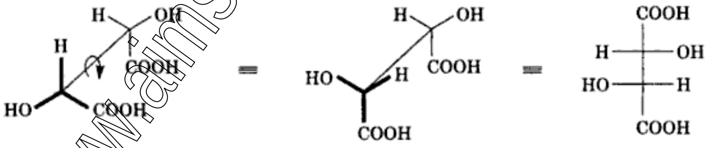
Enantiomers: Molecules that are non-superimposable mirror images are called *enantiomers*.

Fischer Projection: It is a method of writing two dimensional structure of molecules containing chiral atoms. In the *Fischer projection* we imagine that the longest chain containing the chiral atoms lies vertically in the plane of the paper in a conformation such that all groups and atoms are oriented horizontally in front of the paper. The vertical chain is then represented by a line and the groups are joined by crossbars.

The conversion of lactic and tartaric acids into Fischer projection is shown below:



(–) – Lactic acid **Fischer projection**

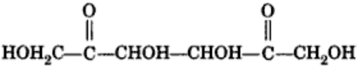


Tartaric acid **Fischer projection**

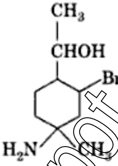
Stereoisomers: Isomers that have their atoms joined in the same order but differ in some respect of their three-dimensional structures are called *stereoisomers*. Stereoisomers are either enantiomers or diastereoisomers.

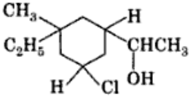
Problem 4.2:

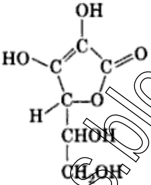
Circle all asymmetric carbon atoms in the following structures.

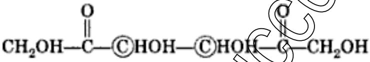
(a) 

$HOH_2C-\overset{\overset{O}{\|}}{C}-CHOH-CHOH-\overset{\overset{O}{\|}}{C}-CH_2OH$

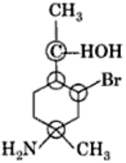
(b) 

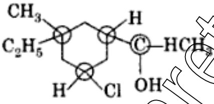
(c) 

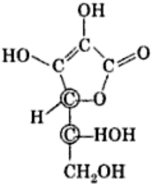
(d) 

Solution: (a) 

$CH_2OH-\overset{\overset{O}{\|}}{C}-\textcircled{C}HOH-\textcircled{C}HOH-\overset{\overset{O}{\|}}{C}-CH_2OH$

(b) 

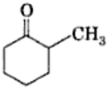
(c) 

(d) 

Problem 4.3:

Are the following molecules asymmetric ?

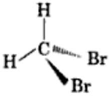
(a) 

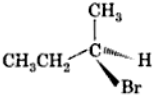
(b) 

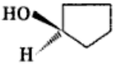
Solution: (a) No, because identical carbons are reached at each step in going around the ring and the Br atom is reached at the same time from both sides. (b) No, because no asymmetric carbon atom is present in this molecule.

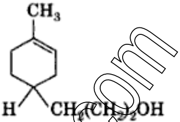
Problem 4.4:

State whether the following molecules are chiral or achiral.

(*a*) 

(*b*) 

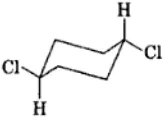
(*c*) 

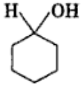
(*d*) 

Solution: (*a*) Achiral (*b*) Chiral (*c*) Chiral (*d*) Chiral.

Problem 4.5:

Which symmetry element is present in the following molecule.

(*a*) 

(*b*) 

Solution: (*a*) The molecule has a center of symmetry. (*b*) The molecule has a plane of symmetry.

Problem 4.6:

The observed rotation is found to be 4.05° counterclockwise when one of the enantiomers of 2-butanol is placed in a polarimeter. The sample was prepared by dissolving 6 g of (–)-2-butanol to a total of 40 ml and placed in a 200 mm polarimeter tube. Calculate the specific rotation of this 2-butanol enantiomer.

Solution: Since it is levorotatory, it must be (–)-2-butanol.

$$c = 69/40 \text{ ml} = 0.15 \text{ g/l}$$

$$l = 200 \text{ mm} = 2 \text{ dm}$$

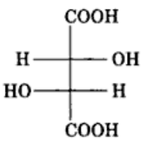
$$\text{The specific rotation } \left[\alpha\right]_D^{25} = \frac{4.05}{(0.15)(2)}$$

$$= -13.5^\circ$$

The specific rotation for the other enantiomer of 2-butanol obviously would be + 13.5°. Racemic (±)-2-butanol would be a mixture of equal amounts of (+)-2-butanol and (–)-2-butanol.

Problem 4.7:

Would you expect tartaric acid written below as D (+) or L (+) acid ?



Solution: L (+)-tartaric acid because –OH group is on the left hand side.

Problem 4.8:

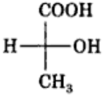
What would it imply if a mixture has an enantiomeric excess (ee) of 40% ?

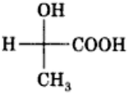
Solution: Enantiomeric excess (ee) of the mixture = 40%

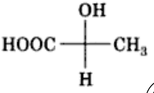
This means that (100-40)% is a racemic mixture. The enantiomer is thus [40 + 1/2 (60)] = 70% or the ratio of the isomers in the mixture is 70 : 30, *i.e.* 7 : 3.

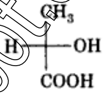
Problem 4.9:

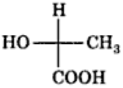
Mark identical structures (if any) in the following:

(*a*)


(*b*)


(*c*)


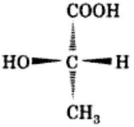
(*d*)


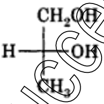
(*e*)


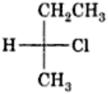
Solution: (*b*), (*d*) and (*e*) are identical structures. Work out according to Fischer projection.

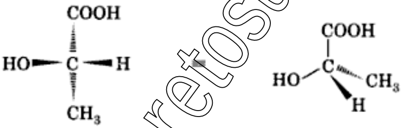
Problem 4.10:

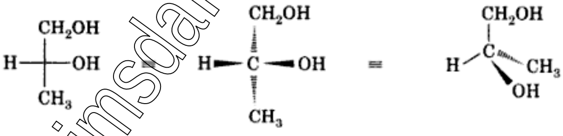
Draw three dimensional formula of the following structures:

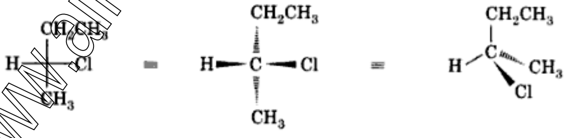
(*a*)


(*b*)


(*c*)


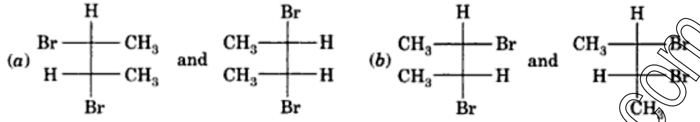
Solution: (*a*)


(*b*)


(*c*)


Problem 4.11:

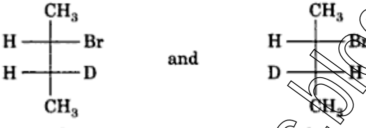
From each of the following pairs of structures, indicate whether they are identical or enantiomeric.



Solution: (*a*) same (*b*) enantiomeric

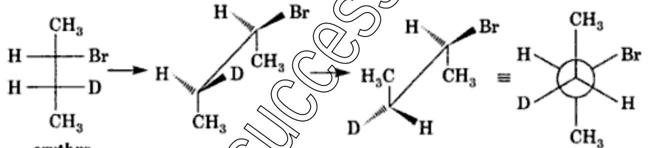
Problem 4.12:

Draw Newman projection formula for *erythro*- and *threo*-2-bromobutane-3-*d*, indicated below in Fischer projection.



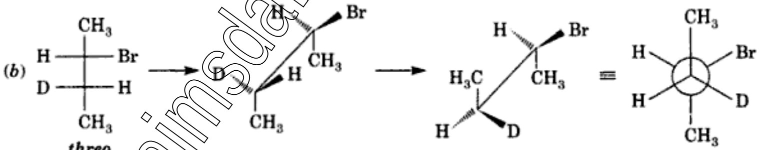
erythro *threo*

Solution: (*a*)



erythro

Fischer projection is first converted into the sawhorse representation. To do this the bottom chiral carbon is written at the front and the top at the rear as implied in Fischer formula. The resulting structure is a direct translation of Fischer representation. The front carbon in this structure is now rotated 180° clockwise to give another sawhorse formula. Now converseion of this form into Newman projection is easy.



threo

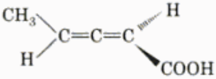
Proceed in the same manner as in (*a*).

Problem 4.13:

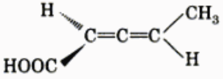
Indicate whether the following pairs of compounds are:

(*i*) Two different structures of the same molecule. (*ii*) Enantiomers (*iii*) Different compounds (*iv*) Diastereoisomers

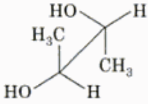
(*a*)



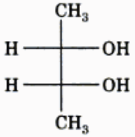
and



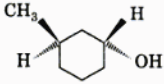
(*b*)



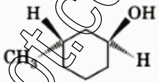
and



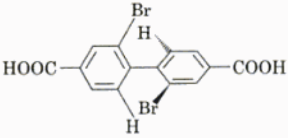
(*c*)



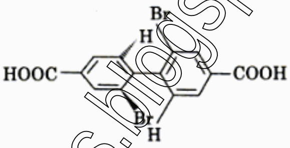
and



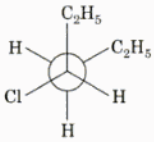
(*d*)



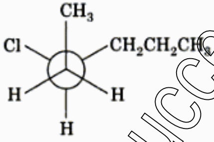
and



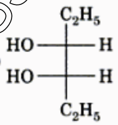
(*e*)



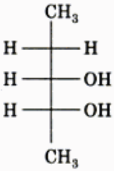
and



(*f*)

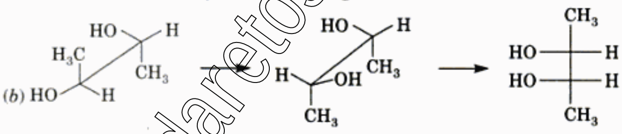


and



Solution: (*a*) Enantiomers, they are **mirror images.**

(*b*)



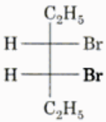
Diastereoisomers

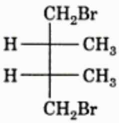
(*c*) Enantiomers (*d*) Can be **easily rotated, diastereoisomers** (*e*) **Drawings of the same molecule** (*f*) Different compounds, **not isomers.**

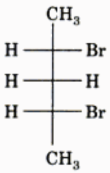
Problem 4.14:

Draw the structures of three *meso* diastereoisomers of $C_6H_{12}Br_2$.

Solution: *Meso* structures have a plane of symmetry

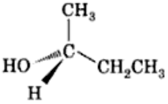


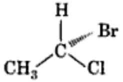


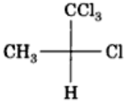


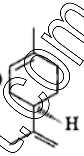
Problem 4.15:

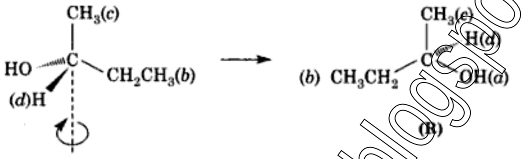
Determine the R/S configuration of each chiral carbon.

(a)


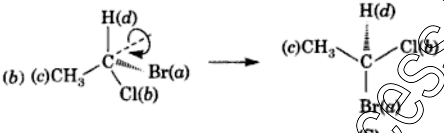
(b)


(c)


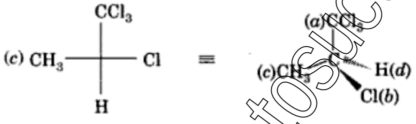
(d)


Solution: (a)


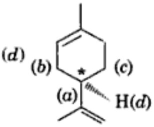
(R)



(S)

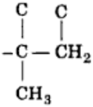


(S)

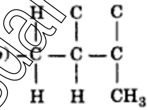


(R)

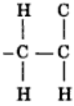
Priority of the groups is

(a)


$-\underset{\text{CH}_3}{\overset{\text{C}}{\text{C}}}-\overset{\text{C}}{\text{CH}_2}$

(b)


$-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{C}}{\text{C}}}-\underset{\text{CH}_3}{\overset{\text{C}}{\text{C}}}$

(c)


$-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{C}}{\text{C}}}$

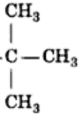
(d) –H

Problem 4.16:

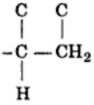
Arrange the following groups in order of increasing priority.

(a) $-\text{CH}=\text{CH}_2$, $-\text{C(CH}_3)_3$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{C(CH}_3)_3$ (b) $-\text{COOCH}_3$, $-\text{COOH}$, $-\text{CH(OCH}_3)$

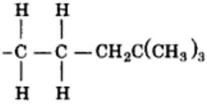
(c) $-\text{C(CH}_3)_2$, $-\text{CH(CH}_3)_2$, $-\text{CH}_2\text{Cl}$

Solution: (a) a.


$-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_3$

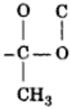
b.


$-\underset{\text{H}}{\overset{\text{C}}{\text{C}}}-\overset{\text{C}}{\text{CH}_2}$

c.


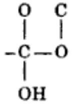
$-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\text{CH}_2\text{C(CH}_3)_3$

(*b*) *a.*



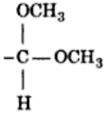
$$\begin{array}{ccc} & \mathrm{O} & \mathrm{C} \\ & | & | \\ - & \mathrm{C} - & \mathrm{O} \\ & | & \\ & \mathrm{CH_3} & \end{array}$$

b.



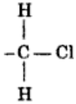
$$\begin{array}{ccc} & \mathrm{O} & \mathrm{C} \\ & | & | \\ - & \mathrm{C} - & \mathrm{O} \\ & | & \\ & \mathrm{OH} & \end{array}$$

c.



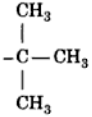
$$\begin{array}{ccc} & \mathrm{OCH_3} & \\ & | & \\ - & \mathrm{C} - & \mathrm{OCH_3} \\ & | & \\ & \mathrm{H} & \end{array}$$

(*c*) *a.*



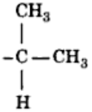
$$\begin{array}{ccc} & \mathrm{H} & \\ & | & \\ - & \mathrm{C} - & \mathrm{Cl} \\ & | & \\ & \mathrm{H} & \end{array}$$

b.



$$\begin{array}{ccc} & \mathrm{CH_3} & \\ & | & \\ - & \mathrm{C} - & \mathrm{CH_3} \\ & | & \\ & \mathrm{CH_3} & \end{array}$$

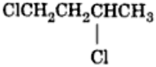
c.



$$\begin{array}{ccc} & \mathrm{CH_3} & \\ & | & \\ - & \mathrm{C} - & \mathrm{CH_3} \\ & | & \\ & \mathrm{H} & \end{array}$$

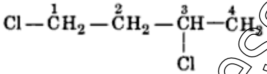
Problem 4.17:

Draw the enantiomers of 1,3-dichlorobutane and label them as (R) and (S).



$$\begin{array}{c} \mathrm{ClCH_2CH_2CHCH_3} \\ \quad\;\; | \\ \quad\;\; \mathrm{Cl} \end{array}$$

Solution:

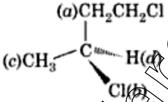


$$\mathrm{Cl}-\overset{1}{\mathrm{C}}\mathrm{H_2}-\overset{2}{\mathrm{C}}\mathrm{H_2}-\underset{\underset{\mathrm{Cl}}{|}}{\overset{3}{\mathrm{C}}\mathrm{H}}-\overset{4}{\mathrm{C}}\mathrm{H_3}$$

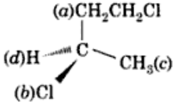
The third carbon of the compound is chiral. None is needed to determine the priority of the groups linked to the chiral carbon.

(*a*) $-CH_2CH_2Cl$ (*b*) $-Cl$ (*c*) $-CH_3$ and (*d*) $-H$

Based on the priority of the groups, the following mirror images are drawn with the hydrogen atom being directly behind the chiral carbon. Thus the two enantiomers are the following:



(R)

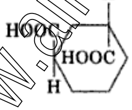


(S)

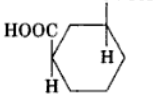
Problem 4.18:

Draw the optically active and *meso* form of 1,3-cyclohexandicarboxylic acid.

Solution:



optically active

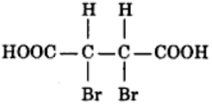


meso

Problem 4.19:

(*a*) Describe optical isomerism with suitable examples.

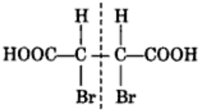
(*b*) Would you expect the following compounds to be optically active ? Explain.



$$HOOC-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-COOH$$

Solution: (*a*) Optical isomerism may be described as the existence of two or more non-superimposable mirror images of a compound leading to enantiomers, for instance, lactic acid, glyceraldehyde and alanine.

(*b*)



$$HOOC-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-COOH$$

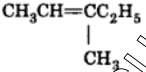
One half of the molecule is superimposable over the other. Therefore, the compound is not optically active but *meso*. *Meso* compounds always contain two or more chiral atoms but are symmetrical molecules which do not give any net rotation of polarized light.

Problem 4.20:

Indicate the possible types of isomerism exhibited by the following compounds.

(*a*) C_5H_{10} (*b*) $CH_3C{\equiv}CCH_3$ (*c*) $(CH_3)_2C{=}CHCH_3$ (*d*) C_4H_{10} (*e*) $ClCH{=}CHCl$

(*f*) C_3H_6O (*g*)



$$CH_3CH{=}\underset{CH_3}{C}C_2H_5$$

Solution: (*a*) Positional (Draw Structures) (*b*) None (*c*) None (*d*) Positional (*e*) Geometric (*f*) Functional (Draw Structures) (*g*) Geometric

Problem 4.21:

Which of the following structures exhibit *cis-trans*-isomerism ?

(*a*) 2-Methyl-2-pentene (*b*) 3-Methyl-3-pentene (*c*) 1,2-Dimethylcyclohexane

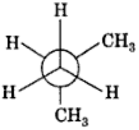
(*d*) Cyclohexene (*e*) 2-Hexene

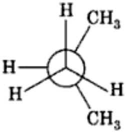
Solution: First draw the structures, then decide.

(*a*) No (*b*) Yes (*c*) Yes (*d*) No (*e*) Yes

Problem 4.22:

What type of isomers is the following pair ?



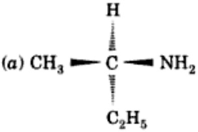


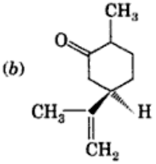
Solution: These are conformers.

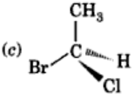
Conformers are molecules which differ from each other as a result of rotation about the C—C bond.

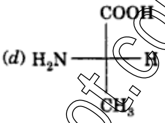
Problem 4.23:

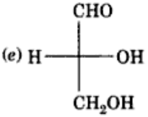
Write R/S configuration for the following compounds :



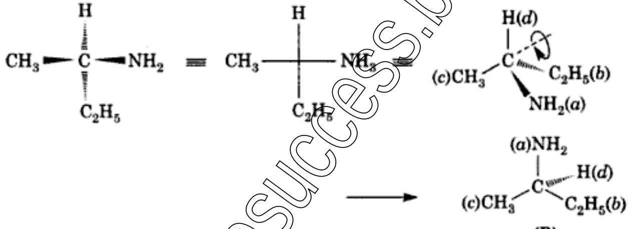




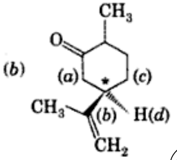




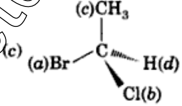
Solution: (a)



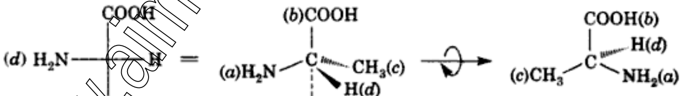
(R)



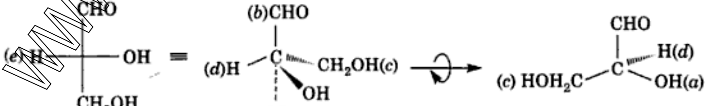
(S)



(S)



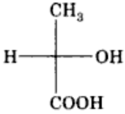
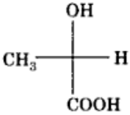
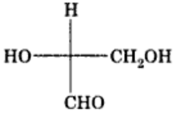
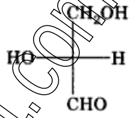
(S)



(S)

Problem 4.24:

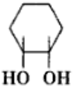
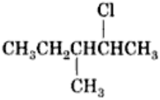
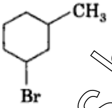
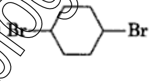
Show the relationship between the following pairs of compounds:

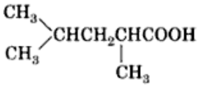
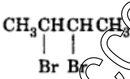
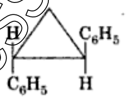
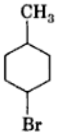
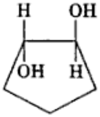
(*a*)

and

(*b*)

and


Solution: (*a*) Make two changes of groups, an identical structure is obtained. (*b*) Make one change of groups, enantiomeric structure is obtained.

Problem 4.25:

How many optically active isomers are possible for the following compounds ?

(*a*)

(*b*)

$CH_3CH_2\underset{CH_3}{CH}\overset{Cl}{CH}CH_3$
(*c*)

(*d*)


(*e*)

$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\!CHCH_2\underset{CH_3}{CH}COOH$
(*f*)

$CH_3\underset{Br}{CH}\underset{Br}{CH}CH_3$
(*g*)

(*h*)

(*i*)


Solution: The number of optically active isomers is given by 2^n, where n is the number of chiral centers.

(*a*) 2 (*b*) 4 (*c*) 4 (*d*) none (*e*) 2 (*f*) 2 (*g*) 2 (*h*) none (*i*) 2

Problem 4.26:

Indicate whether the following statements are true for false.

(*a*) R and S configurations correspond to the enantiomers of an optically active compound. (*b*) The process of converting an optically active compound into a racemate is called recemization. (*c*) Cyclic disubstituted compounds do not show geometric isomerism. (*d*) A molecule containing a plane of symmetry can be optically active. (*e*) Positional and chain isomerism are identical. (*f*) Optical isomers that are not enantiomers are called diastereoisomers. (*g*) All *ortho* substituted diphenyl compounds are optically active. (*h*) In the Fischer projection, any odd number of interchanges of substituents lead to an enantiomer. (*i*) All chiral objects are asymmetric.

Solution: (*a*) T (*b*) T (*c*) F (*d*) F (*e*) F (*f*) T (*g*) F (*h*) T (*i*) T

Problem 4.27:

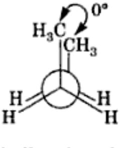
By drawing Newman projection formulas, show how do the potential energy changes occur in *n*-butane when the molecule is rotated around its C_2—C_3 bond axis through a complete cycle.

Solution: Conformation of *n*-Butane: Conformations are the result of free rotation about the carbon-carbon bond. In ethane the barrier to rotation is small and as a result the rotation about the carbon-carbon axis is free. If one of the hydrogens in ethane is replaced by a bulky group, the barrier to rotation increases. In monochloroethane, for instance, it amounts to 3.6 Kcal/mole while in butane it rises to 5.5 Kcal/mole.

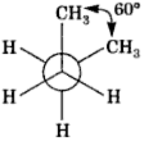
$$\overset{1}{C}H_3—\overset{2}{C}H_2—\overset{3}{C}H_2—\overset{4}{C}H_3$$

The conformation of butane can be evolved in a manner similar to those of ethane.

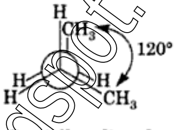
As in the case of ethane, the most unstable geometry of butane is the *fully eclipsed* conformation, a Newman projection (XI) looking along the $C_2—C_3$ bond is shown. In this case the two methyl groups are close to each other and $\theta = 0°$.



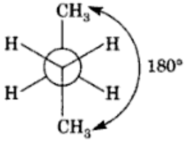
Fully eclisped
(XI)



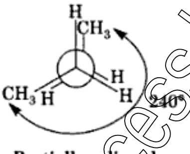
Gauche
(XII)



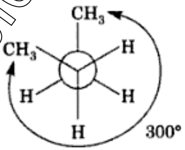
Partially eclipsed
(XIII)



Anti
(XIV)



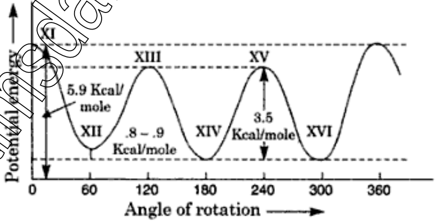
Partially eclipsed
(XV)



Gauche
(XVI)

Most stable conformation, however, is the staggered arrangement. But for butane there are two distinctive possibilities: the methyl group may be oriented in opposite direction or may be in much closer proximity. There are thus two minimum energy geometries which butane can adopt and they are known as the *anti* (XIII $\theta = 180°$) the two methyl groups are *trans*; and *gauche* (XII and XVI, $\theta = 60°$ and 300° respectively) conformations respectively. The remaining structures (XIII) and (XV) are partially eclipsed.

Figure below shows a graph of the torsional energy of butane as the molecule is rotated about the $C_2—C_3$ bond.



All the staggered conformations *anti* and *gauche* are lower in energy than any of the eclipsed conformations. The *anti* is more stable of the two *gauche* forms by about 0.9 Kcal/mole. The difference between the forms is that the methyl groups are closer together in the *gauche form*. The two kinds of eclipsed forms have also different energies. In the *fully eclipsed* form of higher energy, the methyl groups are very close together.

Problem 4.28:

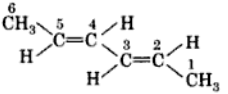
What do you understand by the terms R and S used for specifying the configuration of an optically active compound ? Do they throw any light on the direction of rotation of the compound ?

Solution: The only structural difference between enantiomers is the configuration at the chiral center (or centers). The R-S system of nomenclature includes a way of denoting the configuration at each chiral center. The configuration of any chiral center is named as *R* or *S*. The term *R* (*rectus* Latin for right) and *S* (*sinister*, Latin for left). The *R* and *S* specification has no connection with the direction of rotation of polarized light.

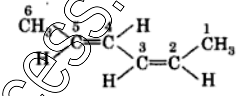
Problem 4.29:

(*a*) Is geometric isomerism possible in compounds which contain (*i*) Two double bonds (*ii*) No double bond ? (*b*) Solutions of optically active compounds showing positive rotation are called *dextro* and the ones showing negative rotation are called *levo*. Can these be denoted as D and L respectively ? Give reasons for your answer. (*c*) What is '*meso*' form ? How does it differ from racemic form ?

Solution: (*a*) (*i*) Yes, as in 1,3-butadiene derivatives

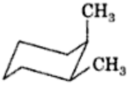


***trans, trans*-2, 4-Hexadiene**

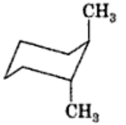


***cis, trans*-2, 4-Hexadiene**

(*ii*) Yes, as in cycloalkanes



***cis*-1, 2-Dimethylcyclohexane**



***trans*-1, 2-Dimethylcyclohexane**

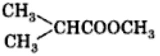
(*b*) The capital letters D and L refer to configuration and bear no relationship with the sign of rotation. (*c*) A *meso* form has a net rotation of zero, *i.e.*, optically inactive and is a diastereoisomer of each of enantiomeric form of the compound. It cannot be resolved into its optically active components. A *racemic* form also shows an overall rotation of zero but it can be separated into its optical isomers.

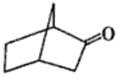
Problem 4.29:

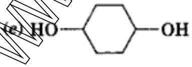
Which of the following compounds will exhibit optical isomerism ?

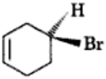
(*a*) 
$(CH_3)_2CHOH$

(*b*) $CH_3CHOHCOOH$

(*c*) 
$(CH_3)_2CHCOOCH_3$

(*d*) 

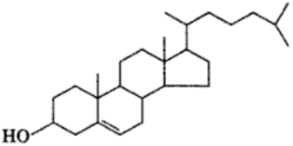
(*e*) 

(*f*) 

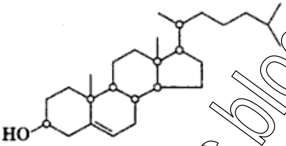
Solution: (*b*) and (*f*), these are the only compounds which are chiral.

Problem 4.31:

Circle all the chiral carbon atoms with a circle in cholesterol and state the number of optical isomers.



Solution:

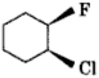


No. of isomers $2^8 = 256$

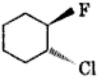
Problem 4.32:

What is the relationship between *cis*-1-chloro-2-fluorocyclohexane and *trans*-1-chloro-2-fluorocyclohexane ?

Solution:



***cis*-Isomer**



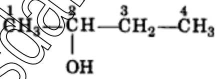
***trans*-Isomer**

The two isomers are diastereoisomers that are not enantiomeric. They differ in their three-dimensional structures but are not mirror images.

Problem 4.33:

Draw at least two Fischer projections of S-2-butanol.

Solution:



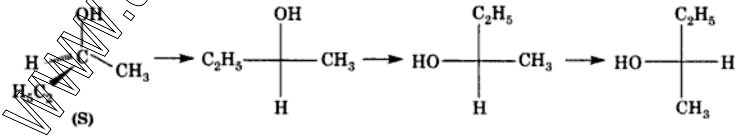
$$\overset{1}{C}H_3-\underset{\displaystyle OH}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_3$$

Carbon-2 is a chiral center.

The priority of groups is :

$$-OH \longrightarrow -CH_2CH_3 \longrightarrow -CH_3 \longrightarrow -H$$

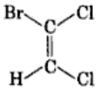
Therefore S-2-butanol is :

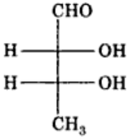


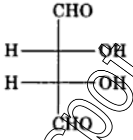
Problem 4.34:

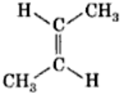
From the list of formulas below, select the one or two which best fit each description:

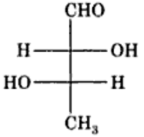
(*a*) A *cis* stereoisomer (*b*) A pair of enantiomers (*c*) A *meso* compound (*d*) A pair of diastereoisomer (*e*) A pair of compounds which might form a racemic mixture

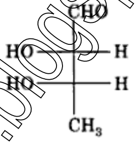




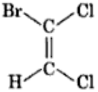




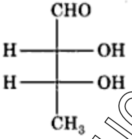




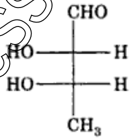
Solution: (*a*)



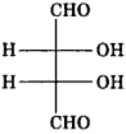
(*b*)



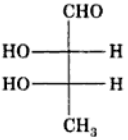
and



(*c*)



(*d*)



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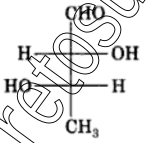


(*e*) Same as (*b*).

Problem 4.35:

List three types of asymmetry shown by organic compounds.

Solution: Organic molecules may show asymmetry:

(*i*) If they possess a chiral carbon atom (*ii*) Due to restricted rotation (*iii*) In allene derivatives.

Problem 4.36:

Distinguish D form *d* and L from *l*.

Solution: The symbols *d* and *l* pertain to the direction of rotation in the polarimeter. But the capital letters D and L refer to configuration. They have nothing to do with rotation.

Problem 4.37:

When 4.0 g of an optically active compound per 100 ml of solution was placed in a 20 cm tube, the plane of polarized light was rotated +5.8°. Calculate the specific rotation.

Solution: $\left[\alpha\right]_{\lambda}^{t} = \dfrac{\theta}{l \times c}$

$\theta = 5.8°$

$l = 20$ cm or 2 decimeter

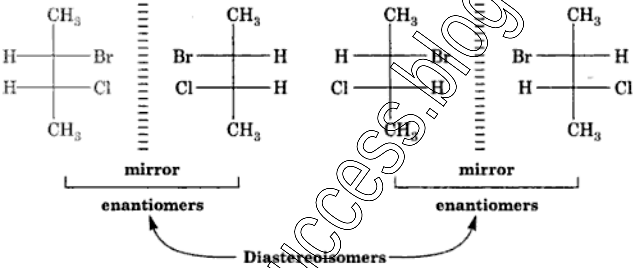
$c = 4/100$ g/ml

$$\therefore \text{ Specific rotation} = \frac{5.8}{2 \times 0.04} = 72.5°$$

Problem 4.38:

Write a formula for a **compound containing four carbon atoms which should be capable** of existence in 2^n optically active forms.

Solution: The compound is 2-bromo-3-chlorobutane and it has **the following four enantiomers.**



Compare the **molecule with tartaric acid.**

Problem 4.39:

A 0.1 M solution **of a compound (molecular weight 342) was placed in a one decimeter** tube and the plane of polarized **light was rotated to +2.2°. Calculate the specific rotation of the** compound.

Solution: $\left[\alpha\right]_{\lambda}^{t} = \dfrac{\theta}{l \times c}$

$\theta = +2.2°$

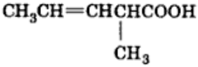
$l = 1$ decimeter

$c = 34.2$ g/1000 ml

$$\therefore \text{ Specific rotation} = \frac{2.2 \times 1000}{34.2} = +64.3$$

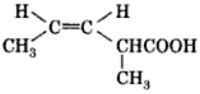
Problem 4.39:

Write all the **stereoisomers of the following acid :**

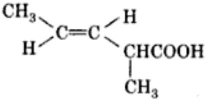


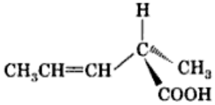
$$CH_3CH{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH$$

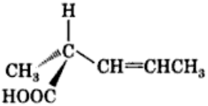
Solution: (*a*)



(*b*)



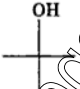
(*c*)


(*d*)


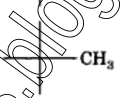
Problem 4.41:

Complete the following structures by placing the missing substituents in the correct positions.

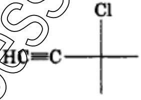
(*a*) S-Glyceric acid (HOCH$_2$CHOHCOOH)



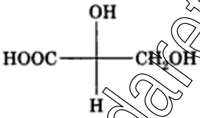
(*b*) S-Alanine (CH$_3$CHNH$_2$COOH)

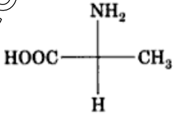


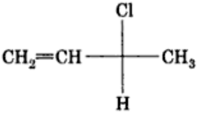
(*c*) S-3-chloro-1-butyne

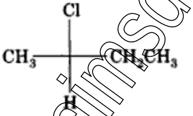


(*d*) R-2-chlorobutane

Solution: (*a*)


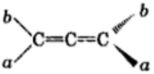
(*b*)


(*c*)


(*d*)


Problem 4.42:

(*a*) What is the hybridization state of an allene system ? (*b*) *H*ow many π-orbitals would be necessary in a $\sigma - \pi$ model of an allene ? What could be the relative orientation of π-oribitals ? (*c*) From your answer in (*b*) what orientation of the terminal substituents of the allene would you expect.

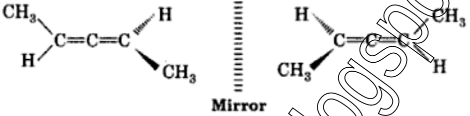


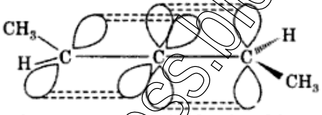
Solution: (*a*) sp^2, sp (*b*) Two oriented at right angle to each other. (*c*) The terminal substituents lie in a perpendicular plane.

Problem 4.43:

The allene 2,3-pentadiene does not have a chiral carbon but is resolvable into enantiomers. Draw an orbital picture that account for its chirality.

Solution: The allene has non planar character. The two double bond systems in 2,3-pentadiene are at right angle to each other. Due to this it has no plane of symmetry and its mirror images are not superimposable and this allene is capable of existence in (+) and (–) enantiomers.



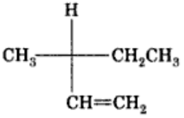


In allene, the central carbon atom is sp hybridized and linear while the two terminal carbon atoms are sp^2 hybridized and trigonal. The two unhybridized *p*-orbitals on a *sp* hybrid carbon atom are perpendicular. So the two π-bonds must also be perpendicular. Allene itself is achiral, however, if some substituents are added to allene, the situation is different and it becomes chiral as in the case of 2,3-pentadiene.

Problem 4.44:

Compound A (C_6H_{12}) is optically active. On catalytic hydrogenation it gives optically inactive compound C_6H_{14}. Identify the structure of A.

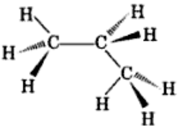
Solution: Since compound A gains two hydrogen atoms on hydrogenation, it must have a C=C bond. Therefore the structure of A is



Problem 4.45:

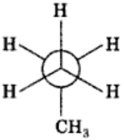
By drawing Newman projection, show how do potential energy changes occur in propane when the molecule is rotated around one of the C—C bond through a complete cycle.

Solution: The perspective and Newman projection of propane can be written as follows :



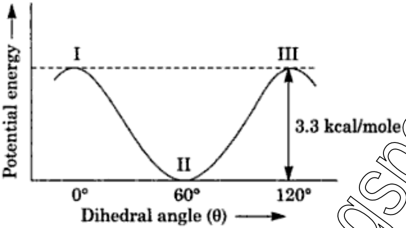
Perspective drawing

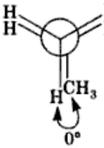
≡



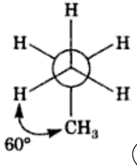
Newman projection

The following figures shows a graph of the torsional energy of propane as the molecule is rotated around the C—C bond.

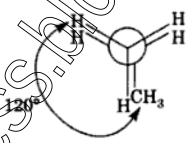




I



II



III

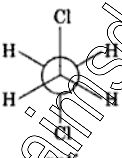
As in the case of ethane and *n*-butane, the unstable geometry of propane is also fully eclipsed. This is shown by structures I and III in the Newman projection drawn by looking along one of the C—C bonds. In these structures a hydrogen and the methyl group are close to each other if θ = 0 and 120°. The torsional energy of eclipsed conformation is 3.3. Kcal/mol more than that required for ethane. Structure II is the stable staggered conformation.

Problem 4.46:

Write the favored conformation (*gauche*, *anti* or eclipsed) for the following molecules.

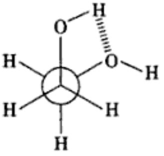
(*a*) 1,2-Dichloroethane (*b*) 1,2-Ethanediol (*c*) Propanaldehyde

Solution: (*a*)



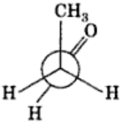
anti

(*b*)



Gauche
(due to H-bond formation)

(*c*)



Eclipsed

Problem 4.47:

Select the correct answer:

(*a*) An enantiomerically pure acid is treated with a racemic mixture of an alcohol having one chiral carbon. The ester formed will be

A. Optically active mixture B. Pure enantiomer C. *Meso* compound

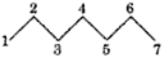
D. Racemic mixture

(*b*) Which of the following exhibit stereoisomerism ?

A. 2-Methylbuten-1 B. 3-Methylbutyn-1 C. 3-Methylbutanoic acid
D. 2-Methylbutanoic acid

(*c*) The most stable conformation of ethylene glycol is

A. *Anti* B. *Gauche* C. Partially eclipsed D. Fully eclipsed

(*d*) In this organic compound  methyl group be attached to which carbon to make it chiral.

A. 1 B. 4 C. 3 D. 7

(*e*) How many optical isomers are there for butan-2,3-diol ?

A. 1 B. 3 C. 2 D. 4

(*f*) An important chemical method to resolve a racemic mixture makes use of the formation of

A. Diastereoisomers B. Racemates C. A *meso* compound D. Enantiomers

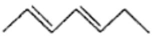
(*g*) How many structural isomers (including stereoisomers) would be obtained by replacing one H of propene by chlorine ?

A. 2 B. 4 C. 3 D. 5

(*h*) Meso tartaric acid is optically inactive due to

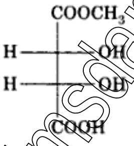
A. Two asymmetric carbon atoms B. Molecular symmetry
C. External combination D. Molecular asymmetry

(*i*) The number of geometric isomers in the case of the following compound

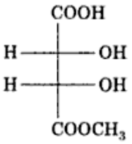
 , are

A. 3 B. 2 C. 5 D. 4

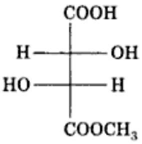
(*j*) The correct statement about *a*, *b*, *c* is



(*a*)



(*b*)



(*c*)

A. *a* and *b* are enantiomers B. *a* and *b* are identical
C. *a* and *b* are diastereoisomers D. *a* and *c* are enantiomers

(*k*) Which of the following pairs exhibit stereoisomerism ?

A. Geometric isomerism and tautomerism
B. Geometric isomerism and optical isomerism
C. Geometric isomerism and positional isomerism
D. Optical isomerism and metamerism

(*l*) Which of the following is not isomeric with diethyl ether ?

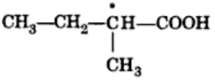
A. Butan-1-*ol* B. Butanone C. 2-Methylpropan-2-*ol*

D. *n*-Propylmethyl ether.

(*m*) The number of geometric isomers for the compound with molecular formula $C_2BrClFI$ is

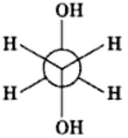
A. 3 B. 4 C. 5 D. 6

Solution: (*a*) A, this is the most general method for the resolution of a racemic mixture, using an acid as the resolving agent. In this case the racemic mixture is of an alcohol which is to be resolved.

(*b*) D, 

$CH_3—CH_2—\overset{\bullet}{C}H(\underset{CH_3}{|})—COOH$ contains a chiral carbon.

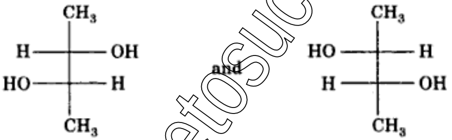
(*c*) A,



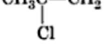
In the *anti* form the two – OH groups are situated opposite to each other.

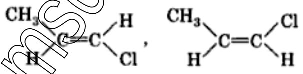
(*d*) C, the C–3 will become chiral.

(*e*) C,



This diol has similar symmetrical structure as tartaric acid.

(*f*) A (*g*) D, $CH_3CH{=}CHCl$,  $CH_3\underset{Cl}{\underset{|}{C}}{=}CH_2$, $ClCH_2CH{=}CH_2$,

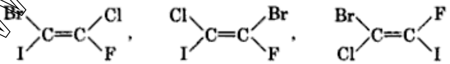


(*h*) B (*i*) D, two geometric isomers are obtained with each C=C bond.

(*j*) B, same structure one is written upside down. (*k*) B

(*l*) B, diethyl ether $(C_4H_{10}O)$, butanone (C_4H_8O).

(*m*) D,



cis and *trans* *cis* and *trans* *cis* and *trans*

CHAPTER

5

Reaction Intermediates and Mechanisms

Problem 5.1:

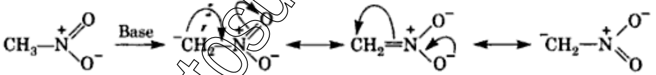
What do you understand when we say a carbocation is stable ?

Solution: It implies that there is a delocalization of the positive charge of the carbocation over other carbon atoms leading to its lower energy and hence its stability.

Problem 5.2:

Nitromethane is deprotonated in the presence of a strong base. Write the resonance structures of the resulting carbanion.

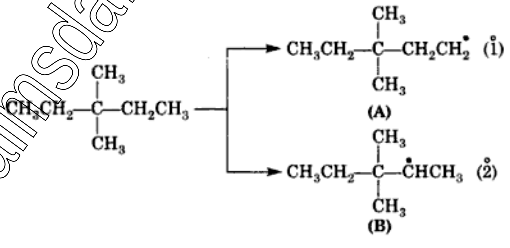
Solution:



Problem 5.3:

3,3-Dimethylpentane is likely to form two radicals on treatment with a suitable reagent. Indicate which radical would be more stable ?

Solution:



The two radicals (A) and (B) will be formed.

Out of these, (B) is a secondary (2°) radical and more stable.

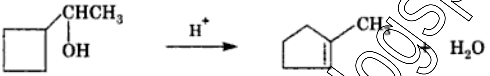
Problem 5.4:

What does a rate law tell us about the mechanism of a reaction ?

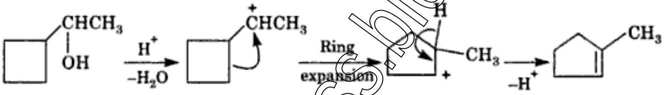
Solution: A rate law does not prove a proposed mechanism. But the rate law plays a role in ruling out some mechanisms while leaving others as possible alternatives.

Problem 5.5:

Suggest a mechanism for the following reaction.



Solution:



Problem 5.6:

Account for the following:

The species A, B and C are more stable than D, E and F respectively.

$CH_3CH{=}CHCH_2^+$ (A), $CH_3CH{=}CHCH_2^-$ (B), $CH_3CH{=}CHCH_2^{\bullet}$ (C)

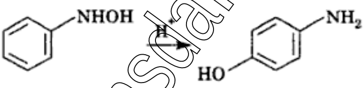
$CH_2{=}CHCH_2CH_2^+$ (D), $CH_2{=}CHCH_2CH_2^-$ (E), $CH_2{=}CHCH_2CH_2^{\bullet}$ (F)

Solution: Species A, B and C can be stabilized by resonance and hence more stable.

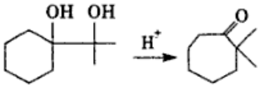
Problem 5.7:

Suggest a plausible mechanism for each of the following reactions :

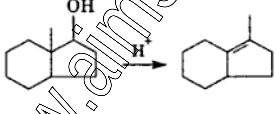
(*a*)



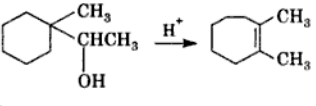
(*b*)



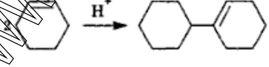
(*c*)



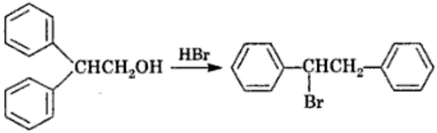
(*d*)



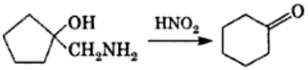
(*e*)



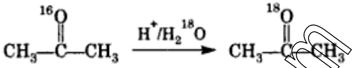
(*f*)



(*g*)

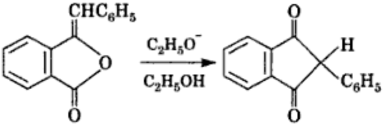


(*h*)

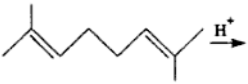


$$CH_3-\overset{\overset{^{16}O}{\|}}{C}-CH_3 \xrightarrow{H^+/H_2{}^{18}O} CH_3-\overset{\overset{^{18}O}{\|}}{C}-CH_3$$

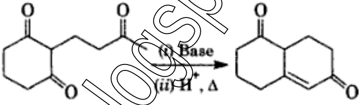
(*i*)



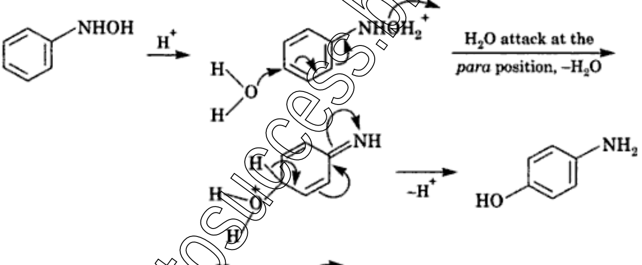
(*j*)



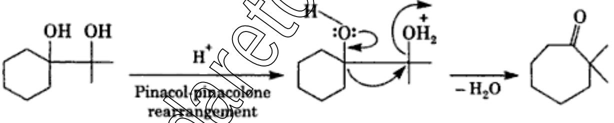
(*k*)



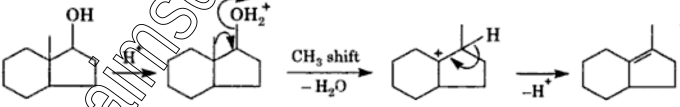
Solution: (*a*)



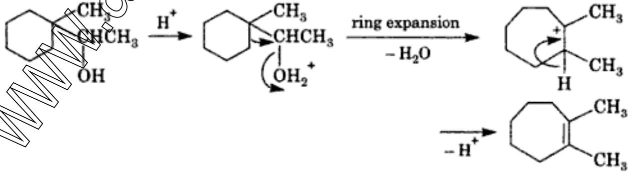
(*b*)



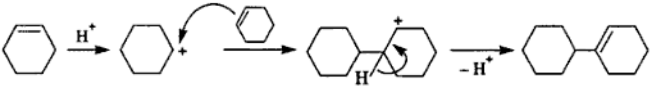
(*c*)



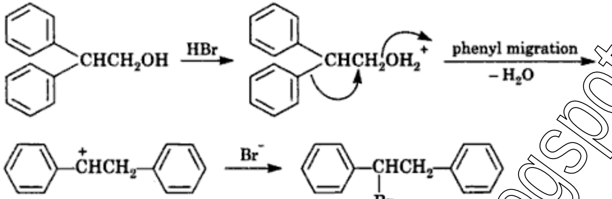
(*d*)



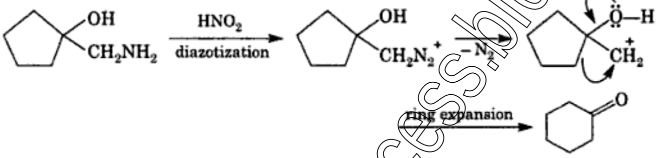
(e)


H⁺
H
– H⁺

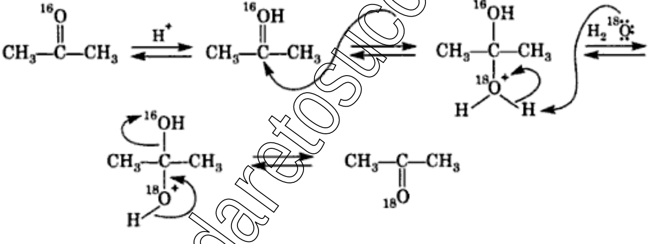
(f)


CHCH₂OH
HBr
CHCH₂OH₂⁺
phenyl migration
– H₂O
CHCH₂
Br⁻
CHCH₂
Br

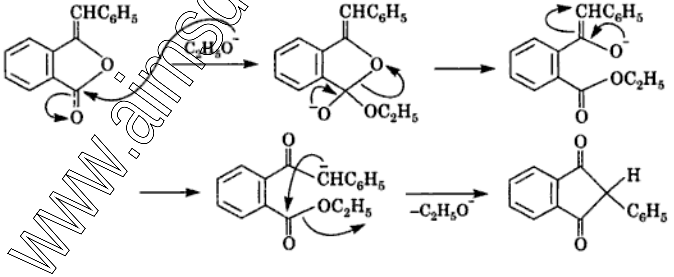
(g)


OH
CH₂NH₂
HNO₂
diazotization
OH
CH₂N₂⁺
– N₂
Ö—H
CH₂
ring expansion
O

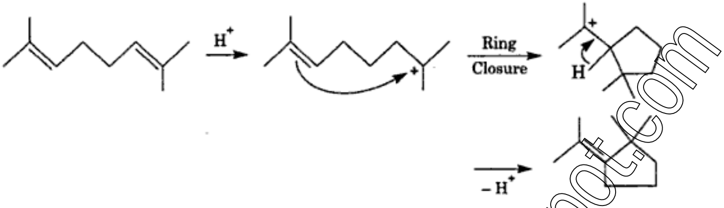
(h)


¹⁶O
CH₃—C—CH₃
H⁺
¹⁶OH
CH₃—C—CH₃
¹⁶OH
CH₃—C—CH₃
¹⁸O⁺
H
H
H₂¹⁸Ö
¹⁶OH
CH₃—C—CH₃
¹⁸O⁺
H
CH₃—C—CH₃
¹⁸O

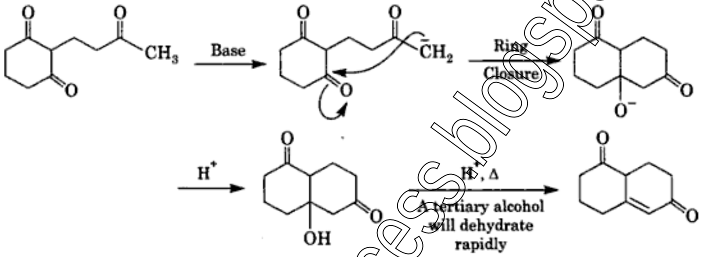
(i)


CHC₆H₅
O
O
C₂H₅O⁻
CHC₆H₅
O
⁻O
OC₂H₅
CHC₆H₅
O⁻
OC₂H₅
O
O
C̄HC₆H₅
OC₂H₅
O
–C₂H₅O⁻
O
H
C₆H₅
O

(j)

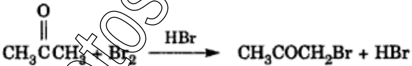


(k)



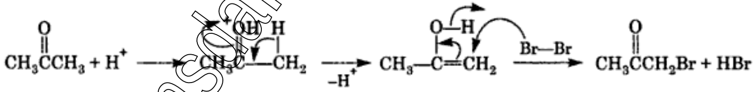
Problem 5.7:

The bromination of acetone in the presence of Br_2 and HBr has the rate law, rate = $k\,[CH_3COCH_3]\,[H^+]$. Suggest a mechanism for this reaction.



$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + Br_2 \xrightarrow{HBr} CH_3COCH_2Br + HBr$$

Solution: It is a second order reaction. Both acetone and bromine are involved in the slow step of the reaction.



Problem 5.8:

Arrange the following cations in the increasing order of stability:

$$(C_6H_5)_3C^+,\ (CF_3)_3^+,\ (CH_3)_3C^+,\ (CCl_3)_3C^+,\ (CH_3)_2C_6H_5C^+$$

Solution: $(CF_3)_3C^+ < (CCl_3)_3C^+ < (CH_3)_3C^+ < (CH_3)_2C_6H_5C^+ < (C_6H_5)_3C^+$

Problem 5.9:

Separate the following species into electrophiles and nucleophiles:

$$CH_3OH,\ SO_3,\ NO_2^+,\ RSH,\ H_2S,\ NH_3,\ OH^-,\ H_3O^+,\ Br^+$$

Solution: Electrophiles : SO_3, NO_2^+, H_3O^+, Br^+
Nucleophiles : CH_3OH, RSH, NH_3, OH^-, H_2S

Problem 5.10:

Sketch potential energy diagrams for the following reactions and label E_a and ΔH°:

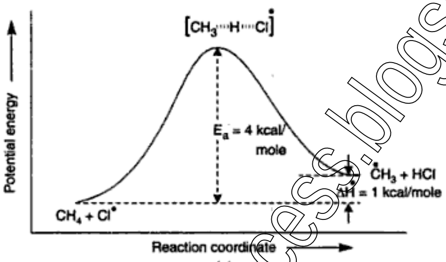
(*a*) $CH_4 + Cl^\bullet \longrightarrow CH_3^\bullet + HCl$

This reaction has an activation energy of + 4 Kcal/mole and ΔH° of + 1 Kcal/mole.

(*b*) $CH_3^\bullet + Cl_2 \longrightarrow CH_3Cl + Cl^\bullet$

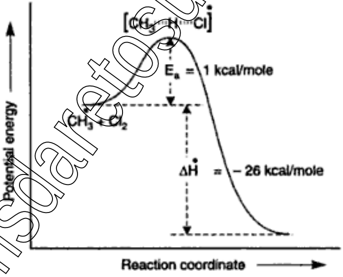
The activation energy is + 1 Kcal/mole and the ΔH° value of the reaction is – 26 Kcal/mole.

Solution: (*a*) Since ΔH° is positive, it is an endothermic reaction. The E_a is higher than ΔH° because the path from reactants to products is from lower to higher energy.



(a)

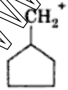
(*b*) It is an exothermic reaction.



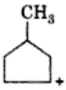
(b)

Problem 5.11:

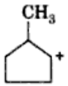
Arrange the following carbocations in order of increasing stability.



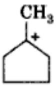
(*a*)



(*b*)



(*c*)



(*d*)

Solution: The order of increasing stability is the following:

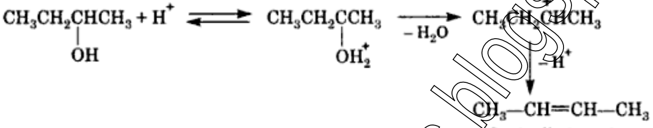
$$a < b < c < d$$

Carbocation (a) is least stable because it is primary.

Problem 5.12:

Optically active $CH_3CH_2CH(OH)CH_3$ was found to have lost its optical activity after standing in water containing a few drops of acid. Explain.

Solution: Addition of acid protonates the alcohol. Protonated alcohol subsequently eliminates water to form a carbocation. The resulting carbocation can either undergo rearrangement or elimination to yield an optically inactive product.

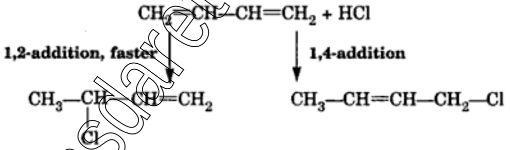


Optically inactive

Problem 5.13:

Define kinetic control and thermodynamic control of chemical reactions. Illustrate with a pertinent example.

Solution: In certain reactions the less stable product is formed faster than the one that is more stable. For instance, in the HBr addition to 1,3-butadiene, the less stable 1,2-addition product is formed in greater amount in hydrogen halide addition, provided the addition products are isolated before they can come to equilibrium. The formation of less stable product is governed by *kinetic control, i.e.,* the yields of the products are proportional to the rates at which they are formed. On the other hand, if the products of a reaction come to equilibrium under the reaction conditions the product distribution is said to be *thermodynamically controlled.*



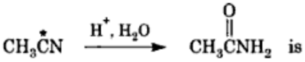
(less stable product) **(more stable product)**

Sulfonation of naphthalene is another familiar example.

Problem 5.14:

Select the correct answer.

(a) The change in hybridization state of the asterisked carbon in the following reaction :



$$CH_3\overset{*}{C}N \xrightarrow{H^+, H_2O} CH_3\overset{O}{\overset{\|}{C}}NH_2 \text{ is}$$

A. $sp^3 - sp^2$ B. $sp^3 - sp$ C. $sp - sp^2$ D. $sp^2 - sp^3$

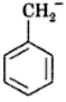
(*b*) The molecule which behaves both as electrophile and nucleophile is

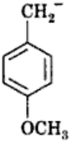
A. CH_3NH_2 B. CH_3Cl C. CH_3CN D. CH_3OH

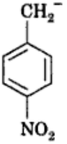
(*c*) Which type of reaction occurs when a reactant has a double bond ?

A. Addition B. Elimination C. Hydrolysis D. None

(*d*) The most stable carbanion among the following is :

A. 

B. 

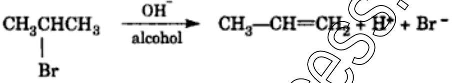
C. 

D. 

(*e*) Which of the following is most effective group in stabilizing inductively a free radical ?

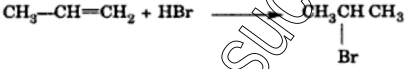
A. F B. I C. Br D. Cl

(*f*) Which of the following is an addition reaction ?

A. 

$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[\text{alcohol}]{OH^-} CH_3{-}CH{=}CH_2 + H^+ + Br^-$$

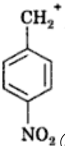
B. $CH_3CH_3 + Cl_2 \xrightarrow{h\nu} CH_3CH_2Cl + HCl$

C. 

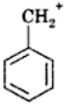
$$CH_3{-}CH{=}CH_2 + HBr \longrightarrow CH_3\underset{\displaystyle Br}{\underset{|}{C}}H\,CH_3$$

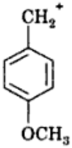
D. $CH_3CH_2Br + CN^- \longrightarrow CH_3CH_2CN + Br^-$

(*g*) Which of the following carbocation is most stable ?

A. 

B. 

C. 

D. 

(*h*) Write the true order of C—H bond weakness of the following alkanes :

R_3CH,	R_2CH_2 ,	RCH_3 ,	HCH_3
I	II	III	IV

A. I > II > III > IV B. II > III > IV > I

C. III > IV > I > III D. IV > III > II > I

Solution: (*a*) C (*b*) C (*c*) A (*d*) C, – NO_2 electron-withdrawing group (*e*) B, because I is the least electron–withdrawing inductively (*f*) C (*g*) D, -OCH_3 electron-donating group, stabilizes the cation. (*h*) A, The stability of the incipient alkyl radical is reflected in the C—H bond dissociation energies. The larger the alkyl groups attached, the greater is the stability of free radicals.

CHAPTER

6

Purification and Structure Determination of Organic Compounds

Problem 6.1:

Which diene would you expect to absorb at a higher wavelength ?

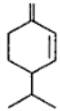
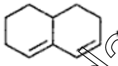
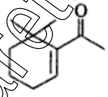
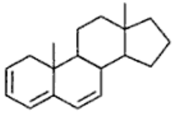
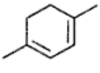
 or 

Solution: The diene  would absorb at a higher wavelength or lower energy because it is conjugated.

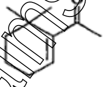
Problem 6.2:

Match the following *u.v.* absorption maxima (λ_{max}) with the corresponding compounds;

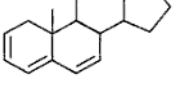
(*a*) 235 nm (*b*) 303 nm (*c*) 232 nm (*d*) 273 nm (*e*) 232 nm

,
,
,
,


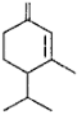
Solution:



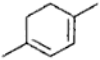
$215 + 2 \times 10 = 235$ nm



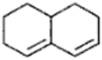
$253 + 30 + 3 \times 5 = 298$ nm



$217 + 3 \times 5 = 232$ nm



$253 + 4 \times 5 = 273$ nm

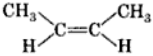


$217 + 3 \times 5 = 232$ nm

Problem 6.3:

Which of the following bonds would you expect to be *i.r.* active ?

(*a*) Cl—Cl (*b*) I—Cl (*c*) H—C≡C—H (C—C *triple bond*)

(*d*)  (C=C *bond*) (*e*) 

Solution:

Those bonds which have appreciable dipole moment will be *i.r.* active,

(*a*) Cl—Cl, No (*b*) I—Cl, Yes (*c*) —C≡C—, No (*d*) $-\underset{|}{C}=\underset{|}{C}-$, No

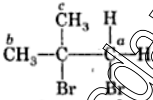
(*e*) C=O, Yes

Problem 6.4:

How many different types of protons are present in

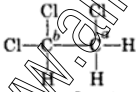
(*a*) 1,2-Dibromo-2-methylpropane (*b*) 1,1,2-Trichloroethane

Would you also observe splitting ?

Solution: (*a*) 

$\overset{b}{CH_3}-\underset{Br}{\overset{\overset{c}{CH_3}}{C}}-\underset{Br}{\overset{H}{\overset{a}{C}}}-H$

Two types of protons are present at C_a and C_b, and C_c. No splitting between -CH_3 and -CH_2 groups is observed as they are not on adjacent carbons. They would give rise to different *n.m.r.* signals.

(*b*) 

$Cl-\underset{H}{\overset{Cl}{\overset{b}{C}}}-\underset{H}{\overset{Cl}{\overset{a}{C}}}-H$

Two types of protons are present and there would be splitting.

Problem 6.5:

Describe the principle involved in the estimation of nitrogen by Kjeldahl's method.

Solution: The method is based on the principle that when an organic compound containing nitrogen is heated with conc. H_2SO_4, nitrogen evolved is converted to ammonium sulfate. The ammonium sulfate is treated with sodium hydroxide solution and the mixture is steam distilled. The liberated NH_3 gas is absorbed in excess standard H_2SO_4. The amount of NH_3 evolved and hence the nitrogen is determined by the amount of acid neutralized by back titration with standard NaOH solution.

Problem 6.6:

(*a*) Explain the various techniques used for the purification of a liquid. (*b*) If a liquid distils at a constant temperature, can an inference be drawn that it is pure?

Solution: (*a*) Distillation and chromatography. (*b*) No, it could be an azeotropic mixture.

Problem 6.7:

Chromatographic methods have been considered as the most viable techniques for the separation and purification of compounds. List the different chromatographic techniques.

Solution: Column chromatography, thin layer chromatography (TLC), paper chromatography, gas liquid chromatography (GLC), high performance liquid chromatography (HPLC) and exclusion chromatography.

Problem 6.8:

Predict the elution sequence of a mixture of compounds containing chlorobenzene, *p*-cresol and anthracene, developed on an alumina column using a solvent system of progressively increasing polarity.

Solution: Anthracene ⟶ chlorobenzene ⟶ *p*-cresol

Since the solvent system initially employed is non-polar and non-polar compounds are adsorbed usually on alumina, we expect the least polar compound to be eluted first, *i.e.*, anthracene. *p*-Cresol can form H-bond with the hydroxyl groups on alumina surface ($Al_2O_3.xH_2O$) so it is strongly adsorbed and will be eluted last.

Problem 6.9:

An organic compound on qualitative analysis was found to contain C, H and N. One gram of it on oxidation with CuO and oxygen gave 1.239 g of CO_2 and 0.1269 g of H_2O. A 2 g sample of the compound was digested with conc. H_2SO_4 and the residue was distilled after the addition of excess sodium hydroxide solution. The ammonia evolved was absorbed in 50 ml of 1 N sulfuric acid. The resulting solution was diluted to 500 ml in a measuring flask, 25 ml of this solution required 21.8 ml of 0.05 NaOH for complete neutralization. Calculate the empirical formula of the compound.

Solution:

$$\%C = \frac{1.239 \times 12 \times 100}{44 \times 1} = 33.79$$

$$\%H = \frac{0.1269 \times 2 \times 100}{18 \times 1} = 1.41$$

$$\%N = 25 \text{ ml of excess dil } H_2SO_4 = 21.8 \text{ ml of } 0.05 \text{ N NaOH}$$

$$500 \text{ ml of excess dil } H_2SO_4 = \frac{21.8 \times 500}{25}$$

$$= 436 \text{ ml of } 0.05 \text{ N NaOH}$$

$$\text{Volume of excess 1N } H_2SO_4 = 436 \text{ ml of } 0.05 \text{ N} - \text{NaOH}$$

$$= \frac{436 \times 0.05}{1} = 21.8 \text{ ml}$$

$$\text{Volume of 1N } H_2SO_4 \text{ consumed by } NH_3 = 50 - 21.8 = 28.2 \text{ ml}$$

Now, 28.2 ml of 1N H_2SO_4 = 28.2 ml of 1N NH_3

= 28.2 ml of 1N - combined nitrogen

$$= \frac{28.2 \times 1 \times 14}{1000} = 0.3948 \text{ g}$$

$$\% \text{ N} = \frac{0.3948}{2} \times 100 = 19.74$$

% O (By difference) = 45.06

Empirical formula :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	39.79	12	2.82	2
H	1.41	1	1.41	1
N	19.74	14	1.41	1
O	45.06	16	2.82	2

Empirical formula of the compound is C_2HNO_2

Problem 6.10:

A 0.2 g sample of an organic monobasic acid gave on combustion 0.505 g of CO_2 and 0.0892 g of H_2O; 0.183 g of the acid required 15 ml of 0.1 N NaOH for complete neutralization. Calculate the molecular weight and the molecular formula of the acid.

Solution:

$$\% \text{ C} = \frac{0.502}{44} \times \frac{12}{0.2} \times 100 = 68.45$$

$$\% \text{ H} = \frac{0.0892}{18} \times \frac{2 \times 1}{0.2} \times 100 = 4.9$$

% O (by difference) = 26.65

Empirical Formula :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	68.45	12	5.7	7
H	4.9	1	4.9	6
O	26.65	16	1.66	2

The empirical formula is $C_7H_6O_2$

Empirical formula weight is 122

$$\text{Molecular weight of the acid} = \frac{183}{15 \times 0.1} = 122$$

Since empirical formula weight and molecular formula weight are equal, the molecular formula of the acid is also $C_7H_6O_2$.

Problem 6.11:

A compound on analysis gave C = 54.55%; H = 9.09% and O = 36.26%. Its vapor density is 44. Find the molecular formula of the compound.

Solution: Empirical Formula :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	54.55	12	4.54	2
H	9.09	1	9.09	4
O	36.26	16	2.26	1

Empirical formula is C_2H_4O

$$\text{Molecular formula will be } (C_2H_4O)_n \text{ where } n = \frac{\text{Molecular formula weight}}{\text{Empirical formula weight}}$$

$$= \frac{2 \times \text{V.D.}}{44} = \frac{2 \times 44}{44} = 2$$

So molecular formula is $(C_2H_4O)_2$ or $C_4H_8O_2$.

Problem 6.12:

A monobasic acid gave the following data on combustion; 0.419 g of the acid gave 1.058 g of CO_2 and 0.185 g of H_2O, and 0.470 g of the silver salt of the acid produced on ignition 0.222 g of silver. Calculate the molecular formula of the acid.

Solution:

$$\% \text{ C} = \frac{1.058}{44} \times \frac{12}{0.419} \times 100 = 68.86$$

$$\% \text{ H} = \frac{0.185}{18} \times \frac{2 \times 1}{0.419} \times 100 = 4.9$$

% O (by difference) = 26.24

Empirical Formula :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	68.86	12	5.74	7
H	4.9	1	4.9	6
O	26.24	16	1.64	2

Empirical formula is $C_7H_6O_2$

Empirical formula weight = 122

$$\text{Molecular weight of the acid} = \left(\frac{0.470 \times 108}{0.22} - 107\right) \times 1$$

$$= 121.64$$

Since empirical and molecular formula weights are the same, so molecular formula of the acid is also $C_7H_6O_2$.

Problem 6.13:

Elemental analysis of an organic compound gave C = 39.98%, H = 6.72% and O = 53.3%; and 0.151 g of the compound on vaporization displaced 33.8 ml of air measured at 25° over water and at a pressure of 745 mm of Hg. Determine its empirical and molecular formula, given that the vapor pressure of water at 25° is 24 mm Hg.

Solution: Empirical Formula :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	39.98	12	3.33	1
H	6.72	1	6.72	2
O	53.3	16	3.33	1

Empirical formula is CH_2O

Empirical formula weight = 30

$$\text{Molecular weight} = \frac{\text{WRT}}{\text{PV}} = \frac{0.151 \times 0.082 \times 298 \times 1000}{\frac{1}{760}(745 - 24) \times 33.8}$$

$$= 116.6$$

$$\text{Molecular formula} = (CH_2O)_n \text{ where } n = \frac{116.6}{30} = 3.88 \approx 4$$

$$= (CH_2O)_4$$

$$= C_4H_8O_4$$

Problem 6.14:

A monoacid base contains C = 53.3%, H = 15.5% and N = 31.2%. One gram of the chloroplatinate salt of the base gave 0.32 g of platinum on ignition. Calculate its molecular formula.

Solution: Empirical Formula :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	53.3	12	4.44	2
H	15.5	1	15.5	6.95
N	31.2	14	2.23	1

Empirical formula is C_2H_7N

Empirical formula weight = 45

$$\text{Molecular weight of the mono acid base} = \frac{1}{2}\left(\frac{195 \times 1}{0.39} - 410\right)$$

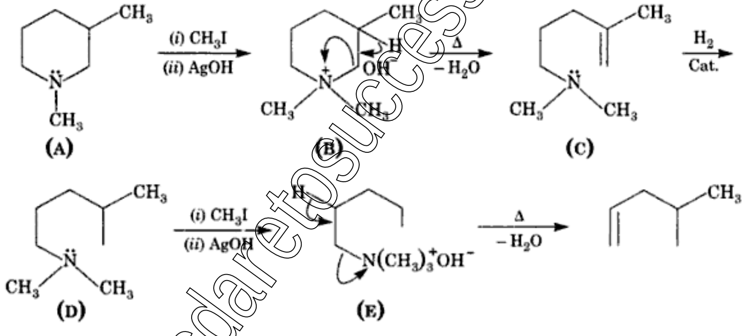
$$= 45$$

Since empirical and molecular weights are same it follows that molecular formula is also C_2H_7N.

Problem 6.15:

Compound A, $C_7H_{15}N$, is insoluble in water but dissolves in dil. hydrochloric acid. A, undergoes no reaction with nitrous acid. When A is treated with methyl iodide and then with silver oxide B, is formed. On heating, B forms C, $C_8H_{17}N$. C, adds hydrogen in the presence of a catalyst forming D, $C_8H_{19}N$. D, on treatment with methyl iodide and then with silver oxide yields $(CH_3)_3N$ and E. E can be hydrogenated to 2-methylpentane. Assign structures to compounds A to E.

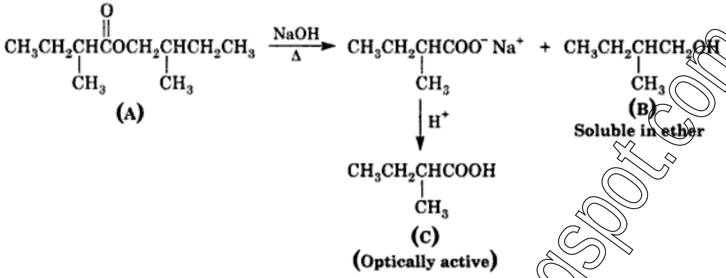
Solution: Since A dissolves in dil HCl, it must be an amine. A, does not undergo reaction with HNO_2, it is not primary or secondary amine. When A, is heated with CH_3I and Ag_2O, it forms quaternary ammonium hydroxide B. On heating B undergoes Hofmann degradation to form an alkene C. Since nitrogen appears in C, it follows that nitrogen atom is a part of the ring. C, on hydrogenation, becomes a saturated hydrocarbon. Further exhaustive degradation yields $(CH_3)_3N$ and E. E is hydrogenated to yield 4-methylpentane.



Problem 6.16:

Compound A, $C_{10}H_{20}O_2$, is not soluble in water or in sodium bicarbonate. It gives no reaction with $C_6H_5NHNH_2$. Refluxing A, with sod. hydroxide solution, extraction of the mixture with ether and evaporation of the solvent yields B, $C_5H_{12}O$. Acidification of the NaOH solution forms a new compound C, $C_5H_{10}O_2$ which is optically active. B gives a positive iodoform test. Suggest structures for A, B and C.

Solution: A is not an acid as it is insoluble in water and sodium bicarbonate. It is also not an aldehyde or ketone as it does not react with $C_6H_5NHNH_2$. A must be an ester as it is hydrolyzed by NaOH and the resulting alcohol (B) is soluble in ether and the acid (C) is soluble in NaOH.



$$\underset{\textbf{(A)}}{CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}\overset{\displaystyle O}{\overset{\|}{C}}OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2CH_3} \xrightarrow[\Delta]{NaOH} CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}COO^-\,Na^+ + \underset{\textbf{(B)}}{CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2OH}$$

Soluble in ether

$$\xrightarrow{H^+} \underset{\textbf{(C)}}{CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}COOH}$$

(Optically active)

Problem 6.17:

Two compounds A, and B, each containing C = 63.58%, H = 5.96% and N = 9.26% give benzoic acid on oxidation. Both dissolve in NaOH solution with a red coloration. On reduction A and B yield amines C and D respectively. C, but not D, can be resolved into optical isomers. What are A and B ?

Solution:

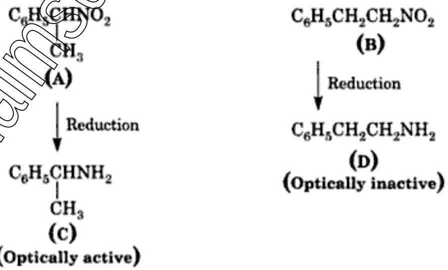
Empirical Formula of A and B

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	63.58	12	5.29	8
H	5.96	1	5.96	9
N	9.26	14	0.66	1
O	21.2	16	1.32	2

Empirical formula of A and B is $C_8H_9NO_2$

On reduction both A and B yield amines, therefore, they are isomeric nitroalkanes.

The sequence of reactions can be represented as follows :



$$\underset{\textbf{(A)}}{C_6H_5\underset{\displaystyle CH_3}{\underset{|}{CH}}NO_2} \xrightarrow{\text{Reduction}} \underset{\textbf{(C)}}{C_6H_5\underset{\displaystyle CH_3}{\underset{|}{CH}}NH_2}$$

(Optically active)

$$\underset{\textbf{(B)}}{C_6H_5CH_2CH_2NO_2} \xrightarrow{\text{Reduction}} \underset{\textbf{(D)}}{C_6H_5CH_2CH_2NH_2}$$

(Optically inactive)

Problem 6.18:

An organic compound A, contains C = 76.6%, H = 6.38% and gives a mixture of two isomers B and C when an alkaline solution of A was refluxed with chloroform at 60°. B, being steam volatile was separated by steam distillation which on oxidation gives an acid D, containing C = 60.67%, H = 4.34%. The acid D, was also obtained by heating sodium salt of A, at 125-140° under pressure. Assign structural formulae to the lettered compounds.

Solution: Empirical Formula of A :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	76.6	12	6.38	6
H	6.38	1	6.38	6
O	17.02	16	1.06	1

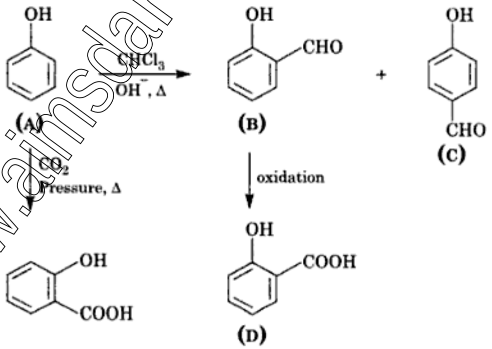
Empirical formula of A is C_6H_6O

Empirical formula of D :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	60.67	12	5.05	7
H	4.34	1	4.34	6
O	34.99	16	2.18	3

Empirical formula of D is $C_7H_6O_3$.

A is phenol which undergoes Reimer-Tiemann reaction when treated with chloroform and base. It forms *o*-hydroxy and *p*-hydroxybenzaldehydes. Since *ortho*-isomer can be steam distilled (due to intramolecular H-bonding), B is the *ortho* isomer and C the is *para*-isomer. B is oxidized to *ortho*-hydroxybenzoic acid (D) which is also obtained from A by Kolbe reaction. Reactions taking place can be represented as follows:

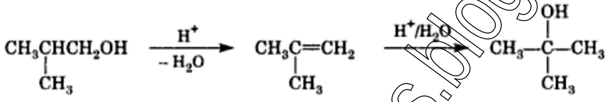


Problem 6.19:

A compound of formula, $C_4H_{10}O$, reacts rapidly with metallic sodium but not with Lucas reagent. Treatment of A, with hot conc. sulfuric acid yields a new compound B, C_4H_8. If B, is hydrated in aqueous sulfuric acid, a new compound C, $C_4H_{10}O$ is formed. Compound C, is almost inert to metallic sodium but reacts rapidly with Lucas reagent. Assign structures to A, B, and C.

Solution: As A reacts with metallic sodium it is an alcohol. Since it does not react with Lucas reagent it is 1° alcohol. With conc. H_2SO_4 dehydration of A takes place and an alkene B is formed. Hydration of B again leads to an alcohol C. Since C reacts rapidly with Lucas reagent, it is a tertiary alcohol.

Sequence of reactions is depicted below :



$$\underset{\underset{CH_3}{|}}{CH_3CHCH_2OH} \xrightarrow[-H_2O]{H^+} \underset{\underset{CH_3}{|}}{CH_3C{=}CH_2} \xrightarrow{H^+/H_2O} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

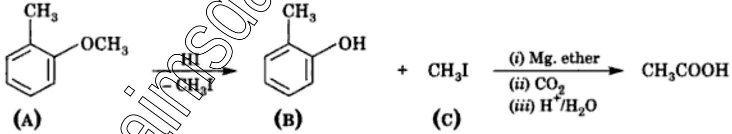
(A) (B) (C)

Problem 6.20:

An organic compound A, $C_8H_{10}O$, does not react with sodium. On treatment with HI, it yields two compounds B and C. B reacts with sodium to liberate hydrogen and also forms a salt with sodium hydroxide. B can also be brominated and the major product contains two bromine atoms. The compound C, contains iodine. On treatment with magnesium in ether, followed by CO_2, it forms acetic acid. What are A, B and C ?

Solution: A is not alcohol as it does not react with Na. A may be an ether. On treatment with HI, A forms alcohol and a halide. As B reacts with Na to liberate hydrogen, B is alcohol (phenol) and thus C is halide. C reacts with Mg to form Grignard reagent which reacts with CO_2 to form acetic acid.

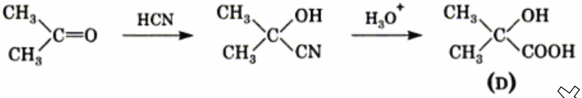
Sequence of reactions can be represented as follows:



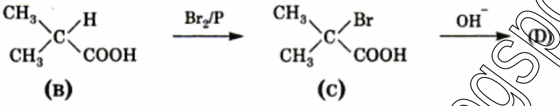
Problem 6.21:

An alkene A, on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid B. When B is treated with bromine in the presence of phosphorus, it yeilds a compound C which on hydrolysis gives a hydroxy acid D. This acid can also be obtained from acetone by reacting it with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D.

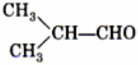
Solution: When acetone is treated with HCN followed by hydrolysis, D is formed by the following reactions :



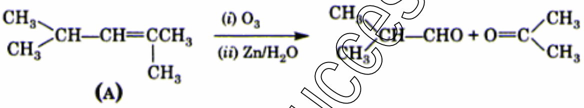
D can also be formed from B by the following sequence of reactions :



B is the oxidation product of the following aldehyde



Since the alkene on ozonolysis gives this aldehyde and an acetone, the alkene is



Problem 6.22:

An organic compound contains C = 81.55%, H = 4.88% and N = 13.6% and has a vapor density of 51.5. It evolves ammonia when heated with KOH and reduction with sodium and alcohol forms a base which reacts with nitrous acid giving off nitrogen gas yielding an alcohol. This alcohol can be oxidized to benzoic acid. What is the original substance ? Explain the above changes.

Solution: Empirical Formula :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	81.55	12	6.79	7
H	4.85	1	4.85	5
N	13.6	14	0.97	1

Empirical formula is C_7H_5N

$$\text{Molecular formula} = (C_7H_5N)_n \text{ where } n = \frac{\text{Molecular formula weight}}{\text{Empirical formula weight}}$$

$$= \frac{2 \times 51.5}{103} = 1$$

So, molecular formula is $(C_7H_5N)_1$ or C_7H_5N

A 1° amine reacts with HNO_2 to give N_2 and alcohol. 1° amine is formed by reduction of a nitriles by sodium and alcohol. Nitriles also evolve NH_3 when heated with KOH.

$$\begin{tikzcd}
C_6H_5CN \arrow[r, "Na,\ C_2H_5OH"] \arrow[d, "KOH"] & C_6H_5CH_2NH_2 \arrow[r, "HNO_2"] & C_6H_5CH_2OH \arrow[d, "oxi"] \\
C_6H_5COO^- K^+ + NH_3 & & C_6H_5COOH
\end{tikzcd}$$

The evidence suggests that the original substance is benzonitrile.

Problem 6.23:

An aromatic monobasic acid A, contain C = 70.6% and H = 5.71%. Its methyl ester has a V.D. of 75. When A is distilled with soda lime it gives a hydrocarbon. On oxidation with $KMnO_4$ it gives a diabasic acid B. Name the compound and three of its isomers. How will you distinguish between these isomers ?

Solution: Empirical Formula :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	70.6	12	5.88	4.0
H	5.71	1	5.71	3.86
O	23.7	16	1.48	1

The Empirical formula of the monoacid is C_4H_4N

Molecular weight of the methyl ester = 2 × V.D. = 2 × 75 = 150

Molecular weight of acid = 150 – (12 + 2) = 136 (-CH_3 of the methyl ester is replaced by H)

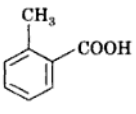
Empirical formula weight of the acid = 68

Molecular formula of the acid = $(C_4H_4O)_n$ where $n = \frac{136}{68} = 2$

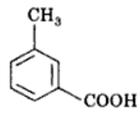
$$= (C_4H_4O)_2 = C_8H_8O_2$$

The acid on distillation with soda lime gives toluene.

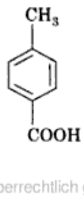
Since A on oxidation with $KMnO_4$ gives a dibasic acid, A could be any one of following isomers.



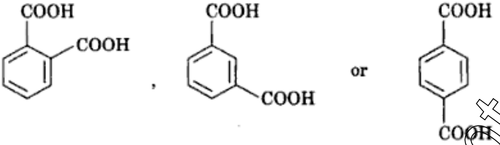
,



or



B could be any of the following isomers :

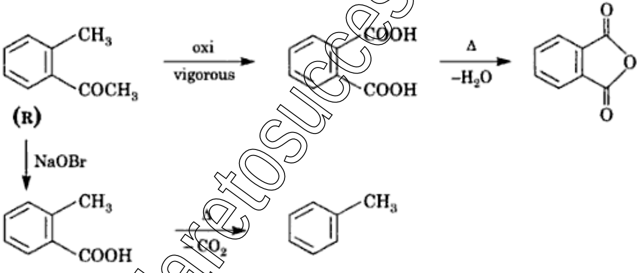


Problem 6.24:

A compound R, with molecular formula, $C_9H_{10}O$ is insoluble in dil. acid and base. It does not reduce Tollens' reagent but forms a 2,4-dinitrophenylhydrazone. On vigorous oxidation an acidic product $C_8H_6O_4$ is formed which forms an acid anhydride on heating. Treatment of R, with sodium hypobromite gives a different acid which, when heated with soda-lime, yields toluene. Propose a structural formula for R.

Solution: R is not an aldehyde as it does not reduce Tollens' reagent. It must be a ketone as it forms 2,4-dinitrophenylhydrazone. Since the acid anhydride is formed so the two carboxyl groups on benzene ring are in the *ortho* positions.

The sequence of reactions is as follows :



Problem 6.25:

An organic compound A, contains C = 90.56% and H = 9.43%. Its vapor density is 53. On oxidation A, yeilds a dibasic acid B, containing 57.8% C and 3.6% H. The silver salt of the acid contains 56.8% of silver. The acid on heating forms a compound C, of molecular formula $C_8H_4O_3$. On distillation with soda-lime, the acid B, forms benzene. Explain the above reactions and assign structural formulae to A, B and C.

Solution: Empirical Formula :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	90.56	12	1	4
H	9.43	1	1.25	5

Empirical formula of A is C_4H_5

Molecular formula of A = $(C_4H_5)_n$ where $n = \frac{53 \times 2}{53} = 2$

$= (C_4H_5)_2 = C_8H_{10}$

Empirical Formula of the dibasic acid (B) :

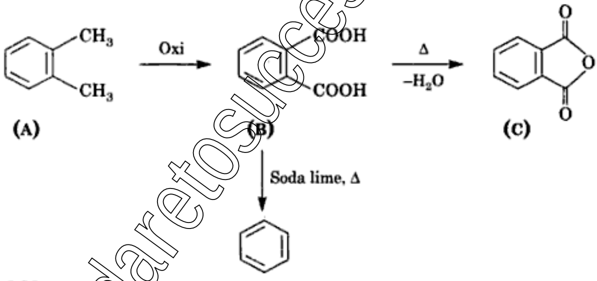
Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	57.8	12	4.82	4
H	3.6	1	3.6	3
O	38.6	16	2.41	2

Empirical formula of B is $C_4H_3O_2$

Molecular weight of B = $\left(\frac{100 \times 108}{56.8} - 107\right) \times 2 = 166.3$

Molecular formula of B = $(C_4H_3O_2)_2 = C_8H_6O_4$

The sequence of reactions is as follows :



Problem 6.26:

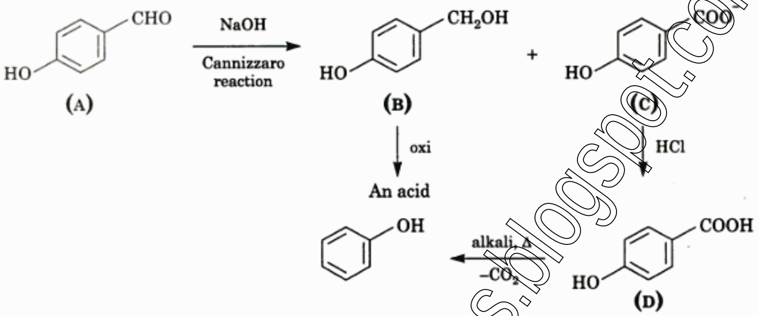
An organic compound A, contains C = 68.85%, H = 4.9% and reacts with NH_2OH; on treatment with NaOH, it forms two compounds B and C. Compound B, is soluble in HCl and can be oxidized to compound C, with alkaline $KMnO_4$. The compound C, on treatment with conc. HCl forms an acid D, which on heating with an alkali gives phenol. Identify the compounds A, B, C and D. Explain the reactions.

Solution: Empirical Formula of A :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	68.85	12	5.74	7
H	4.9	1	4.9	6
O	26.25	16	1.64	2

Empirical formula of **A is $C_7H_6O_2$**

Since A reacts with NH_2OH hence it contains **an aldehyde group. The sequence of reactions** can be represented as follows :



Problem 6.27:

An organic halogen **compound A, contains C = 66.41%, H = 5.53% and Cl = 28.04%. On** treatment with potassium **hydroxide solution gave a hydroxy compound B, containing** C = 77.77%, H = 7.40% but **no halogen. B, on oxidation yields a monobasic acid C, which on** distillation with soda lime gave **benzene. Assign structures to A, B and C and describe a method** for the preparation of **compound A.**

Solution: Empirical Formula **of A :**

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	66.41	12	5.53	7
H	5.53	1	5.53	7
Cl	28.04	35.5	0.789	1

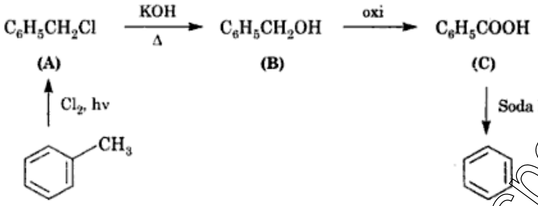
Empirical formula **of A is C_7H_7Cl**

Empirical Formula of **B :**

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	77.77	12	6.48	6.9
H	7.40	1	7.40	7.9
O	14.83	16	0.93	1

Empirical formula **of B is C_7H_8Cl**

Reactions involved are represented below :



Compound A can be prepared by photo chlorination of toluene.

Problem 6.28:

A 1.06 g sample of an organic compound gave on combustion 3.08 g of CO_2 and 0.54 g of H_2O. This compound on heating with caustic soda yields an alcohol and the sodium salt of an acid. Distillation of the sodium salt of the acid with soda lime gives benzene. Determine the formula for the compound, the alcohol and the acid.

Solution:

$$\% \text{ C} = \frac{3.08}{44} \times \frac{12}{1.06} \times 100 = 79.2$$

$$\% \text{ H} = \frac{0.54}{18} \times \frac{2}{1.06} \times 100 = 5.66$$

% O (by difference) = 15.14

Empirical Formula of the organic compound :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*
C	79.2	12	6.6	6.95
H	5.66	1	5.66	5.96
O	15.14	16	0.95	1

Empirical formula is C_7H_6O

Molecular formula $(C_7H_8O)_n$ where $n = \frac{2 \times 53}{106} = 1$

Molecular formula is C_7H_6O

The formula of the compound is C_6H_5CHO

The formula of alcohol is $C_6H_5CH_2OH$

The formula of acid is C_6H_5COOH.

Problem 6.29:

An organic compound A, molecular formula $C_3H_6O_2$ when treated with excess ammonia and then heated formed B, molecular formula C_3H_7ON. B, when heated with P_2O_5 formed C molecular formula C_3H_5N. C, on complete hydrolysis formed A. C, on reduction with a complex metal hydride formed a basic nitrogenous compound, D, molecular formula C_3H_9N. D, on treatment with nitrous acid formed an alcohol E, molecular formula C_3H_8O. E, on oxidation formed compound A. Give the structures of compounds A, B, C, D and E and explain the reactions.

Solution: With ammonia A forms amide B. Hence A may be an acid. P_2O_5 is a dehydrating agent, removes H_2O from amide B and forms nitrile. A nitrile on hydrolysis yields a carboxylic acid.

$$\underset{\substack{\textbf{(acid)}\\ \textbf{(A)}}}{C_3H_6O_2} \xrightarrow[-H_2O]{NH_3} \underset{\substack{\textbf{(amide)}\\ \textbf{(B)}}}{C_3H_7ON} \xrightarrow{P_2O_5} \underset{\substack{\textbf{(nitrile)}\\ \textbf{(C)}}}{C_3H_5N}$$

$$H_3O^+$$

Nitrile on reduction yields 1° amine (D). 1° amine can be converted to alcohol (E) by HNO_2 and the alcohol on oxidation yields an acid.

$$\underset{\substack{\textbf{Nitrile}\\ \textbf{(C)}}}{C_3H_5N} \xrightarrow{\text{Reduction}} \underset{\substack{\textbf{1° amine}\\ \textbf{(D)}}}{C_3H_9N} \xrightarrow[-N_2]{HNO_2} \underset{\substack{\textbf{alcohol}\\ \textbf{(E)}}}{C_3H_8O} \xrightarrow{\text{Oxidation}} \underset{\substack{\textbf{acid}\\ \textbf{(A)}}}{C_3H_6O_2}$$

From above reactions, it follows that

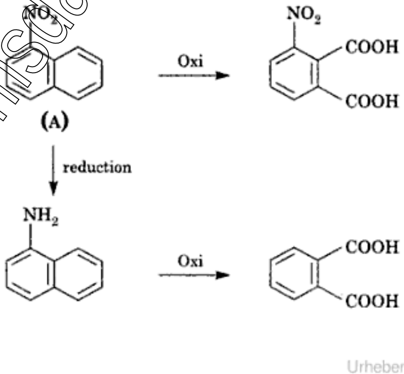
$A = CH_3CH_2COOH$ $B = CH_3CH_2CONH_2$ $C = CH_3CH_2CN$

$D = CH_3CH_2CH_2NH_2$ $E = CH_3CH_2CH_2ON$

Problem 6.30:

A neutral solid A, has the formula $C_{10}H_7O_2N$. Vigorous oxidation of A, gives a dibasic acid B, $C_8H_5O_6N$. A, can be reduced to a compound C, $C_{10}H_9N$ which on oxidation gives a dibasic acid D, $C_8H_6O_4$. Compound A, can be obtained by direct nitration of a particular aromatic hydrocarbon. Identify compounds A to D.

Solution: A, is a nitro compound having two benzene ring fused together. On oxidation the NO_2 group remains in one benzene ring while the other ring is oxidized. Since dibasic acid is formed, A must be nitronaphthalene



Problem 6.31:

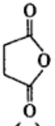
A compound A, contains C = 48%, H = 4%. Sodium fusion of A reveals the absence of halogen, sulfur and nitrogen. What is the empirical formula of A ? Draw structure of A.

Solution: Empirical Formula of A :

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*
C	48	12	4
H	4	1	4
O	48	16	3

The empirical formula is $C_4H_4O_3$

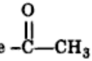
The compound is succinic anhydride.

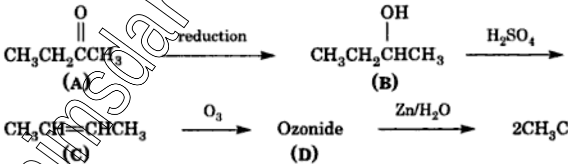


(A)

Problem 6.32:

A ketone A, undergoes the haloform reaction and on reduction gives a compound B. On heating with sulfuric acid B, yields C which forms a mono ozonide D, with ozone. D on hydrolysis in the presence of zinc dust gives only acetaldehyde. Identify compounds A, B, C and write the chemical reactions involved.

Solution: Since the ketone undergoes the haloform reaction, it should contain the  $-\overset{\overset{O}{\|}}{C}-CH_3$ grouping. The formation of only acetaldehyde on ozonolysis suggests that the alkene is symmetrical. The sequence of reactions is the following :



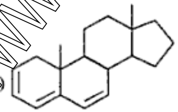
$$\underset{(A)}{CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3} \xrightarrow{\text{reduction}} \underset{(B)}{CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_3} \xrightarrow{H_2SO_4}$$

$$\underset{(C)}{CH_3CH{=}CHCH_3} \xrightarrow{O_3} \underset{(D)}{\text{Ozonide}} \xrightarrow{Zn/H_2O} 2CH_3CHO$$

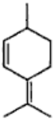
Problem 6.33:

Estimate the λ_{max} of the following compounds :

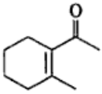
(*a*)



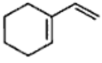
(*b*)



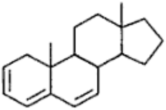
(*c*)



(*d*)

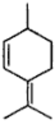


Solution: (*a*)



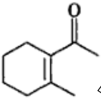
$253 + 30 + 3 \times 5 + 5 = 303$ nm

(*b*)



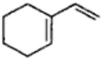
$217 + 4 \times 5 + 5 = 242$ nm

(*c*)



$215 + 3 \times 10 = 245$ nm

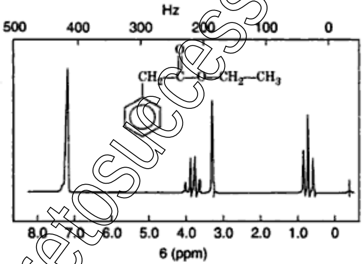
(*d*)



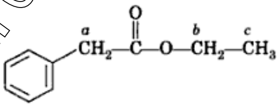
$217 + 2 \times 5 = 227$ nm

Problem 6.34:

Interpret the following *n.m.r.* spectra of ethyl phenylacetate.



Solution:



(*a*) singlet (*b*) triplet (*c*) quartet

Problem 6.35:

Identify the two geometric isomers of stilbene, $C_6H_5CH{=}CHC_6H_5$, from their λ_{max} values of 294 nm and 278 nm.

Solution: Coplanarity is needed for most effective overlap of the π-orbitals and increased ease of the $\pi \rightarrow \pi^*$ transition. *Cis - isomer* is forced into a nonplanar conformation due to steric effects and hence it absorbs at higher energy than the *trans*-isomer. Considering these aspects, the two isomers of stilbene and their λ_{max} values are.

Isomer - stilbene	Absorption
Cis - stilbene	278 nm
Trans - stilbene	294 nm

Problem 6.36:

What do you understand by chemical shift ?

Solution: It is the difference (in ppm) between resonance frequency of proton being observed and that of tetramethylsilane (TMS).

$$\text{Chemical shift (ppm)} = \frac{\text{Shift downfield from TMS (Hz)}}{\text{Total spectrometer frequency (MHz)}}$$

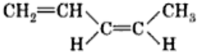
For example, if 60 MHz spectrometer records a proton that absorbs at a frequency 426 Hz downfield from tMS then the chemical shift is :

$$426\ \frac{\text{Hz}}{60\ \text{MHz}} = 7.10\ \text{ppm.}$$

Problem 6.37:

The following dienes have λ_{max} at 176 mm, 211 mm and 215 mm respectively. Find out which is which and why ?

(*i*)



(*ii*)

(*iii*) $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

Solution:

Isomer	Absorption
(*i*)	211 nm
(*ii*)	215 nm
(*iii*)	176 nm

Coplanarity is needed for the most effective overlap of the π-orbitals and increased ease of the π → π* transition. *Cis*-isomer (*i*) is forced into a non planar conformation due to steric effects and hence it absorbs at higher energy than the trans-isomer (*ii*).

Isomer (*iii*) doesn't have conjugated double bonds so energy difference between HOMO and LUMO is considerable increased compared to other two conjugated isomer. Therefore, it absorbs at the highest energy (lowest wavelength).

Problem 6.38:

How can you differentiate between CH_3COOH and CH_3COCH_3 by *i.r.* spectroscopy ?

Solution: We will look for the absorption at about 3200-3600 cm^{-1} wavenumber region in the spectra of both acetic acid and acetone. A broad O—H stretching band is observed in case of acetic acid due to intermolecular hydrogen bonding. The broad band is absent in case of acetone.

Problem 6.39:

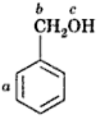
What compound (C_7H_8O) has *n.m.r.* signals at δ 7.3, 4.4. and 3.7 ppm with relative intensities of 7 : 2.9 : 1.4 ?

Solution: Molecular formula suggests the compound contains a benzene ring. Three signals signify that there are three types of protons.

The ratio of intensities is :

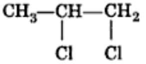
a	:	*b*	:	*c*
7	:	2.9	:	1.4
5	:	2	:	1

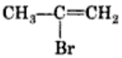
The 5H of a (δ 7.3) are in the aromatic range, suggesting a monosubstituted benzene. The 1H of *c* has a shift expected of alcoholic protons. The 2H of *b* (δ 4.4.) corresponds to $-CH_2-$ unit. So the compound is benzyl alcohol :



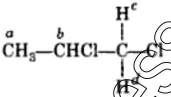
Problem 6.40:

How many *n.m.r.* signals would you expect in each of the following :

(*i*) 
$CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2}$

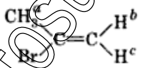
(*ii*) 
$CH_3-\underset{Br}{C}=CH_2$

Solution: (*i*) 1,2-Dichloropropane (optically active or inactive) gives four *n.m.r.* signals.



The environments of the two protons on C–1 are not the same (and no amount of rotation about single bonds will make them so); the protons are not equivalent and will absorb at different field strengths.

(*ii*) 2-Bromopropene gives three signals in *n.m.r.* spectrum.



The environments of the two protons on C–1 are not same; these protons are non equivalent and we expect a *n.m.r.* signal from each proton.

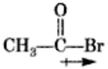
Problem 6.41:

Explain the importance of finger print region in *i.r.* spectroscopy. How is the carbonyl frequency in acetone affected when one of the methyl groups in acetone is replaced by (*i*) -Br and (*ii*) $-NH_2$ group.

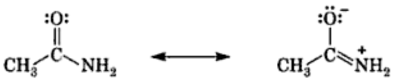
Solution: Importance of finger print region (900 – 1400 cm^{-1}) : or (7μ to 11μ)

Each organic compound has its own unique absorption pattern in this region. So by comparing the *i.r.* spectra of an unknown compound with a standard spectra recorded under identical conditions, the identity of the unknown compound can be guessed. The pattern of *i.r.* spectrum in the finger print region is very sensitive and differs with minor chemical or stereochemical alterations in a molecule.

(*i*) When one of the methyl groups in acetone is replaced by –Br the absorption frequency of the C=O bond is increased due to electronic withdrawing effect of Br.



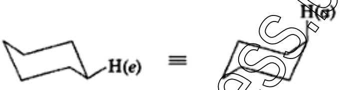
(*ii*) When one of the methyl groups in acetone is replaced by NH_2 the absorption frequency of the C—O bond is decreased due to resonance of the following type as a result of which C-O bond becomes less than a full double bond.



Problem 6.42:

The sharp peak in the *n.m.r.* spectrum of cyclohexane broadens on cooling and separates into two peaks when the *n.m.r.* is taken at – 100°C. Explain.

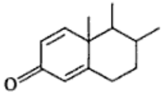
Solution: Cyclohexane displays itself in its spectrum as a singlet at room temperature because of rapid inversion (10^6 times per second). At – 100°C the molecule is frozen and the energy available for interconversion is reduced, which occurs for each conformer to exist long enough to be detected by *n.m.r.* The axial protons have different chemical shifts compared to the equatorial protons. As a result of this two signals are displayed each corresponding to the axial and equatorial hydrogens of the two chair conformations.



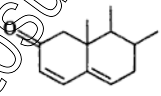
Problem 6.43:

Calculate λ_{max} for the following compounds. The base value given for enones is 215 nm, increments for extended conjugation 30, α 10; β 12; γ, δ 18 nm and homoannular diene component 30.

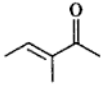
(*a*)



(*b*)



(*c*)



Solution: (*a*) Base value = 215 nm

Exocylic double bond = 5

2 × β substituents = 24

λ_{max} = 244 nm

(*b*) Base value = 215

Homoannular diene component = 30

Exocylic double bond = 5

γ substituent = 18

δ substituent = 18

λ_{max} = 286 nm

(*c*) Base value = 215

α substituent = 10

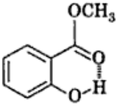
β substituent = 12

λ_{max} = 237 nm

Problem 6.44:

Discuss briefly how the O—H and C—O stretching frequencies in the *i.r.* will be shifted from their routine values in case of methyl salicylate.

Solution: O—H stretching and C—O stretching frequencies will be lowered in methyl salicylate when compared to their routine values. This is due to intramolecular hydrogen bond present in methyl salicylate.



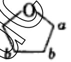
The O—H stretching frequencies may be as low as 2800 cm^{-1} compared to around 3600 cm^{-1} in ordinary hydroxy compounds.

Problem 6.45:

An organic compound A, C_4H_8O shows strong absorption at 1070 cm^{-1} but no absorption in the region 1600-1800 cm^{-1} in its *i.r.* spectrum. Its *n.m.r.* consists of two multiplets of ratio 1 : 1, centered at δ 1.8 and δ 3.7 respectively. What is the structure of A ?

Solution:

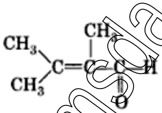
No absorption in 1600-1800 cm^{-1} range in *i.r.* spectrum indicates the absence of a carbonyl group. Two multiplets in the ratio of 1 : 1 in *n.m.r.* indicate symmetrical nature of the compound. The proposed structure is THF.



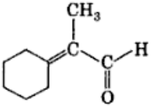
1070 cm^{-1} in *i.r.* corresponds to C—O stretching. Signal at δ 1.8 and δ 3.7 in *n.m.r.* corresponds to absorption by H^a and H^b respectively.

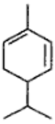
Problem 6.47:

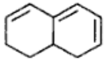
Using Woodward-Fieser rules, calculate λ_{max} values for π-π* transitions for the following :

(*i*)


$$(CH_3)_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}H$$

(*ii*)


(*iii*)


(*iv*)


Solution: (*i*) Base value = 210
a substituent = 10
2 × β substituent = 24
λ_{max} = 244 nm

(*ii*) Base value = 210
a substituent = 10
2 × b substituent = 24

Exocyclic double bond = 5

λ_{max} = 249 nm

(*iii*) Base value = 253 (*cissoid* cyclic diene)

Three alkyl groups = 15

λ_{max} = 268 nm

(*iv*) Base value = 253

Conjugated C═C = 30

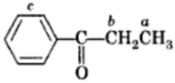
Three alkyl groups = 15

Exocyclic C═C = 5

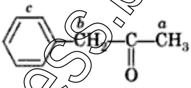
λ_{max} = 303 nm

Problem 6.47:

How would you distinguish between the following ketones on the basis of their *n.m.r.* spectra ?



(A)



(B)

Solution: Although both compounds show the same number of signals (three), they differ in the multiplicity of peaks.

Signal due to proton	Multiplicity A	Multiplicity B
a	Triplet	Singlet
b	Quartet	Singlet
c	Singlet	Singlet

In (B) all the signals appear as singlet unlike in (A) where signals of different multiplicities are observed.

Problem 6.48:

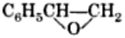
How will you differentiate between salicylic acid and *m*-hydroxybenzoic acid by *i.r.* spectroscopy ?

Solution: Absorption band of >C═O group in salicylic acid appears at a lower frequency than in *m*-hydroxybenzoic acid due to greater predominance of intramolecular hydrogen bond formation in salicylic acid.

Problem 6.49:

An organic compound X (mol. formula C_8H_8O) shows a strong *i.r.* peak at 1690 cm^{-1}. Which of the following structure would you assign to X ?

(*i*) $C_6H_5CH_2CHO$ (*ii*) $C_6H_5—O—CH═CH_2$ (*iii*)



$C_6H_5CH{-}CH_2$ (with O bridging, epoxide) (*iv*) $C_6H_5COCH_3$

Justify your answer.

Solution: X is the ketone (*iv*). Ethers show absorption band between 1080 – 1300 cm^{-1} and an aldehyde shows around 1725 cm^{-1}. Only ketones show strong *i.r.* peak at 1690 cm^{-1}.

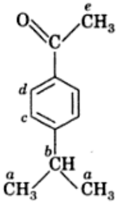
Problem 6.50:

(*a*) Indicate the splitting pattern in the *n.m.r.* spectrum of *p*-isopropylacetophenone.

(*b*) Between acetophenone and cyclohexyl methyl ketone which will absorb at a lower wave number ?

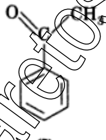
Solution:

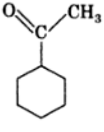
(*a*) There are five signals in *n.m.r.* spectrum. Spin-spin splitting is observed only between non-equivalent neighbouring protons *i.e.*, with different chemical shifts.



Signal	Multiplicity
a	Doublet
b	Heptet
c	Doublet
d	Doublet
e	Singlet

(*b*)


(I)


(II)

(I) absorbs at lower wave number (lower energy as $E = hc\nu$). $>C{=}O$ group conjugates with phenyl ring. This effect increases the bond distance of C—O bond and hence lowers the energy of absorption. The carbonyl group in acetyl cyclohexane cannot conjugate with cyclohexyl group and hence absorbs at higher wave number (higher energy).

CHAPTER

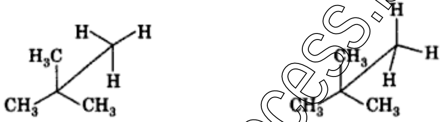
7

Alkanes

Problem 7.1:

Draw the staggered and eclipsed sawhorse drawings and Newman projections of 1,1,1-trimethylethane.

Solution:



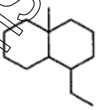
Staggered **Eclipsed**

Sawhorse drawings

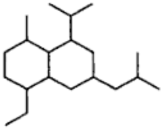
Newman projections

Problem 7.2:

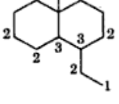
Label each carbon atom in the following molecules as primary, secondary and tertiary.



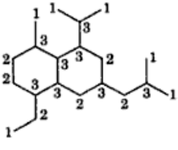
and



Solution:



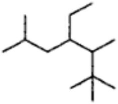
,



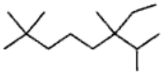
Problem 7.3:

Suggest IUPAC name for each of the following alkanes.

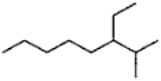
(a)



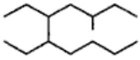
(b)



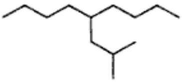
(c)



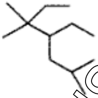
(d)



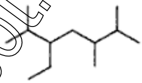
(e)



(f)



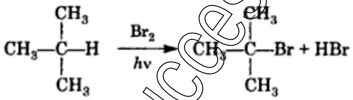
(g)



Solution: (a) 4-Ethyl-2,2,3.6-tetramethylheptane (b) 2,2,6,6,7-Pentamethyloctane (c) 3-Ethyl-2-methyloctane (d) 5,6-Diethyl-3-methyldecane (e) 5-(2-Methylpropyl) nonane (f) 4-Ethyl-3,3,6-trimethylheptane (g) 3-Ethyl-2,5,6-trimethylheptane

Problem 7.4:

Write a complete reaction mechanism for the formation of 2-bromo-2-methylpropane by the free radical bromination of 2-methylpropane.

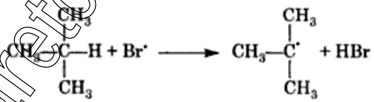


$$CH_3C(CH_3)_2H \xrightarrow[h\nu]{Br_2} CH_3C(CH_3)_2Br + HBr$$

Solution: A free radical mechanism takes place in three steps.

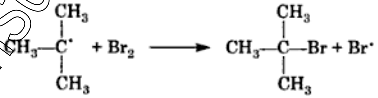
Initiation step : $Br_2 \xrightarrow{h\nu} 2\ Br^{\cdot}$

Propagation step :



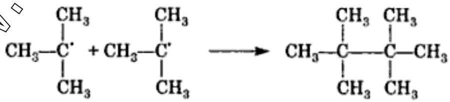
$$CH_3C(CH_3)_2H + Br^{\cdot} \longrightarrow CH_3\dot{C}(CH_3)_2 + HBr$$

The $Br^{\cdot}$ pulls a $H^{\cdot}$ to generate the most stable radical.



$$CH_3\dot{C}(CH_3)_2 + Br_2 \longrightarrow CH_3C(CH_3)_2Br + Br^{\cdot}$$

Termination ste[: $Br^{\cdot} + Br^{\cdot} \longrightarrow Br_2$



$$CH_3\dot{C}(CH_3)_2 + CH_3\dot{C}(CH_3)_2 \longrightarrow CH_3C(CH_3)_2\text{—}C(CH_3)_2CH_3$$

Problem 7.5:

What is cracking ? How is it useful in the petroleum industry ?

Solution: Crude oil on fractional distillation yields 20-25% gasoline that can be used as motor fuel. The yield of heavier petroleum fractions is very high. Because of the increasing demand of high quality petrol, cracking of heavier fuel oils is undertaken to obtain petrol. Cracking is the process of heating of high boiling fractions of petroleum at a high temperature to produce lighter fractions. Cracking involves the cleavage of C—C and C—H bonds. Cracking can be achieved either thermally or using catalysts. The resulting low molecular weight hydrocarbons can be used as raw materials for other industrial processes. Ethylene is a petroleum product. It is not obtained from oil wells directly. Ethylene, a raw material of commercial importance is produced by thermal cracking.

Problem 7.6:

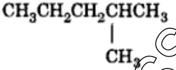
Write structures and names for all the isomers of the alkane of formula C_6H_{14}.

Solution: Isomers of formula C_6H_{14}

(1) $CH_3CH_2CH_2CH_2CH_2CH_3$

(*n*-Hexane)

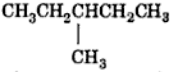
(2)



$$\begin{array}{l} CH_3CH_2CH_2CHCH_3 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\; CH_3 \end{array}$$

(2-Methylpentane)

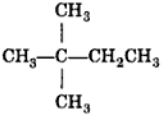
(3)



$$\begin{array}{l} CH_3CH_2CHCH_2CH_3 \\ \qquad\qquad\; | \\ \qquad\quad\; CH_3 \end{array}$$

(3-Methylpentane)

(4)



$$\begin{array}{c} \qquad CH_3 \\ \qquad | \\ CH_3—C—CH_2CH_3 \\ \qquad | \\ \qquad CH_3 \end{array}$$

(2,2-Dimethylbutane)

(5)

$$\begin{array}{l} CH_3CH—CHCH_3 \\ \qquad\; | \qquad | \\ \qquad CH_3 \; CH_3 \end{array}$$

(2,3-Dimethylbutane)

Problem 7.7:

Write structural formulas for the following compounds :

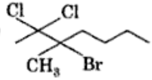
(*a*) 3,3-Dimethyl-4-ethylhexane (*b*) 2,2-Dichloro-3-bromo-3-methylheptane

(*c*) *neo-Pentane* (*d*) isobutane (*e*) 2-Cyclobutyl-3,3-dimethylheptane (*f*) iso-Octane

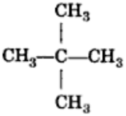
(*g*) 5-(2-Methylpropyl)-3-methyldecane (*h*) 4-Isopropyl-3-methylheptane

Solution: (*a*)

(*b*)

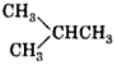


(*c*)



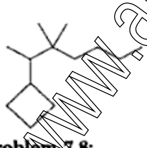
$$\begin{array}{c} \qquad CH_3 \\ \qquad | \\ CH_3—C—CH_3 \\ \qquad | \\ \qquad CH_3 \end{array}$$

(*d*)

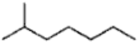


$$\begin{array}{l} CH_3\diagdown \\ \qquad\quad CHCH_3 \\ CH_3\diagup \end{array}$$

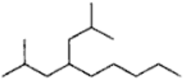
(*e*)



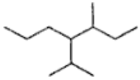
(*f*)



(*g*)



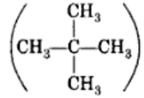
(*h*)



Problem 7.8:

Which of the isomeric pentanes can form only one monochloro substitution product ?

Solution: Only neopentane :



$\left(CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3\right)$. This compound is symmetrical.

Problem 7.9:

What is meant by the term octane number ? Also what does it mean by a certain gasoline having an octane rating of 85.

Solution: Octane number is defined as the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane which has the same knocking tendency as the fuel under examination.

The octane number is a measure of the quality of a motor fuel, the higher the octane number the better the fuel. Octane numbers of 0 and 100 are assigned to heptane and 2,2,4-trimethylpentane respectively. Mixture of these two compounds are used to define octane number. An octane number of 85 means that the iso-octane and octane mixture contains 85% and 15% n-heptane.

Problem 7.10:

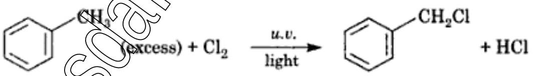
Give reasons for the following :

(*a*) Octane has a m.p. – 57°C while 2,2,3,3-tetramethylbutane 101°C. (*b*) A tertiary free radical is more easily formed than a primary free radical. (*c*) Ethanol is soluble in water but ethane is not. (*d*) Methane is more stable than other higher alkanes. (*e*) The quality of a fuel is improved by the addition of tetraethyllead.

Solution: (*a*) The latter hydrocarbon has a larger surface area. (*b*) Because a tertiary free radical is more stable. (*c*) Ethanol forms H-bond with water. (*d*) Methane is incapable of being fragmented into smaller fragments. (*e*) It functions as an anti-knock agent and it boosts the octane rating of gasoline.

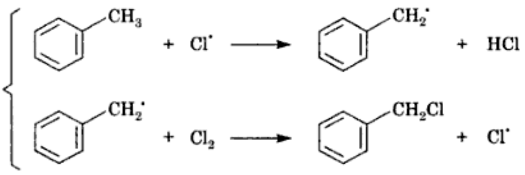
Problem 7.11:

Describe a mechanism for the formation of benzyl chloride from toluene by photochlorination.

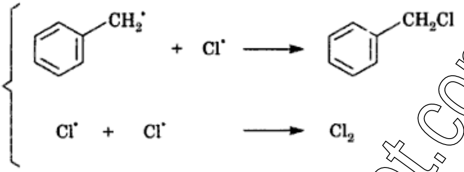


Solution: **Initiation step :** $Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$

Propagation step :

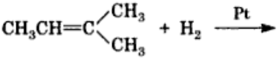


Termination step :



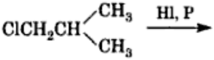
Problem 7.12:

Write the major product of each of the following reactions :

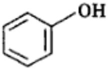
(*a*) 
$CH_3CH{=}C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} + H_2 \xrightarrow{Pt}$

(*b*) $CH_3CH_2CH_2MgBr \xrightarrow{RNH_2}$

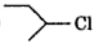
(*c*) $(CH_3)_4C + Cl_2 \xrightarrow{h\nu}$

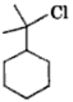
(*d*) 
$ClCH_2CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} \xrightarrow{HI,\ P}$

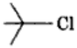
(*e*)  $+ CH_3CH_2I \xrightarrow{Na}$

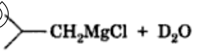
(*f*)  $+ CH_3CH_2MgBr \longrightarrow$

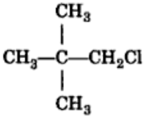
(*g*) $CH_3CH_2CH_3 \xrightarrow{500°}$

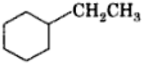
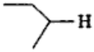
(*h*)  $\xrightarrow{NaBH_4}$

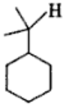
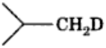
(*i*)  $\xrightarrow{NaBH_4}$

(*j*)  $\xrightarrow{LiAlH_4}$

(*k*)  $+ D_2O \longrightarrow$

Solution: (*a*) $CH_3CH_2CH(CH_3)_2$ (*b*) $CH_3CH_2CH_3$ (*c*) 
$CH_3{-}\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}{-}CH_2Cl$
(*d*) $CH_3CH(CH_3)_2$

(*e*)  (*f*) CH_3CH_3 (*g*) $CH_4 + CH_3CH_3 + CH_3CH{=}CH_2 + H_2$ (*h*) 

(*i*)  (*j*) No reaction (*k*) 

Problem 7.13:

A sample of gaseous hydrocarbon occupying 1.12 litres at N.T.P. when completely burnt in air produced 2.2 of CO_2 and 1.8 g of H_2O. Calculate the weight of the compound taken and the volume of oxygen at N.T.P., required for its burning. Find the molecular formula of the hydrocarbon.

Solution: Weight of CO_2 = 2.2 g

$$\text{weight of carbon} = \frac{2.2}{44} \times 12 = 0.8 \text{ g}$$

$$\text{weight of water} = 1.8 \text{ g}$$

$$\text{weight of H} = \frac{1.0}{18} \times 1 = 0.2 \text{ g}$$

$$\text{Atomic ratio : C : H} = \frac{0.6}{12} : \frac{0.2}{1} = 1 : 4$$

Therefore, empirical formula is CH_4

Weight of the hydrocarbon : 0.6 + 0.2 = 0.8 g

In 22.4*l* (1 molar volume) the hydrocarbon is $\frac{0.8}{0.12} \times 22.4$ or 16 g

Weight of 1 mole of the hydrocarbon = 16 g

Molecular formula is CH_4

Moles of oxygen required for C = $\frac{0.6}{12}$ and for H = $\frac{0.2}{2}$

Total oxygen required = 0.05 + 0.05 = 0.1 mole.

Problem 7.14:

A mixture of ethyl- and isopropyl-iodides is heated with metallic sodium in dry ether. Predict the products.

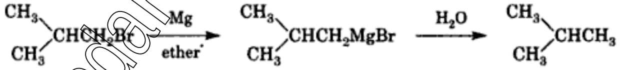
Solution: Three products are formed according to the Wurtz reaction :

$$CH_3CH_2CH_2CH_3\,,\quad (CH_3)_2CHCH(CH_3)_2 \quad \text{and} \quad CH_3CH_2CH(CH_3)_2$$

Problem 7.15:

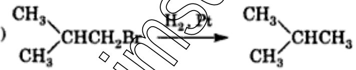
Indicate with relevant equations three different methods for the conversion of isobutyl bromide to isobutane.

Solution: (1)



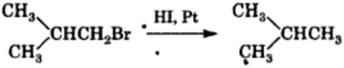
$$(CH_3)_2CHCH_2Br \xrightarrow[\text{ether}]{Mg} (CH_3)_2CHCH_2MgBr \xrightarrow{H_2O} (CH_3)_2CHCH_3$$

(2)



$$(CH_3)_2CHCH_2Br \xrightarrow{H_2,\ Pt} (CH_3)_2CHCH_3$$

(3)

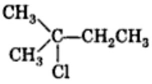


$$(CH_3)_2CHCH_2Br \xrightarrow{HI,\ Pt} (CH_3)_2CHCH_3$$

Problem 7.16:

Write the possible mono-substitution products that would be obtained by the chlorination of isopentane at 300°C. Which isomer would you expect to predominate ?

Solution: Total number of mono-substituted products will be five. The folowing isomer will predominate being a tertiary alkyl chloride :



$$(CH_3)_2C(Cl)CH_2CH_3$$

Problem 7.17:

Write a balanced equation for the combustion of *n*-butane and show that it is consistent with the general equation (7.1) [See A Textbook of Organic Chemistry by R.K. Bansal].

Solution:

$$C_4H_{10} + 6\frac{1}{2}O_2 \longrightarrow 5H_2O + 4CO_2$$

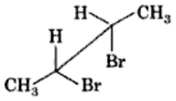
$$n = 4$$

$$C_nH_{2n+2} + \frac{(3n+1)}{2}\,O_2 \longrightarrow (n+1)H_2O + nCO_2$$

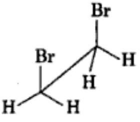
Problem 7.18:

State the dihedral angle between the bromine atoms in each of the following compounds.

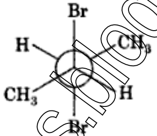
(*a*)



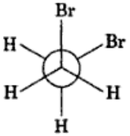
(*b*)



(*c*)



(*d*)



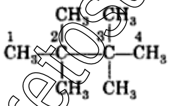
Solution: Any conformation of a compound can be specified by a dihedral angle—the angle between the C—H bonds on the front carbon and C—H bonds on the back carbon atom in the Newman projection.

(*a*) 60° (*b*) 0° (*c*) 180° (*d*) 60°

Problem 7.19:

Name one isomer of octane which on chlorination will give only one octyl chloride.

Solution:



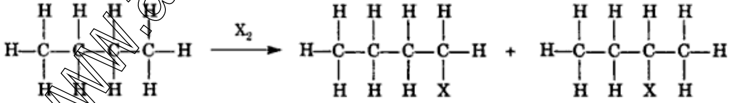
$$\overset{1}{C}H_3-\overset{2}{C}(CH_3)_2-\overset{3}{C}(CH_3)_2-\overset{4}{C}H_3$$

2, 2, 3, 3-Tetramethylbutane

Problem 7.20:

Discuss the Hammond postulate.

Solution: The Hammond postulate provides a convenient and straight forward method for correlation of reactivity and selectivity. Reactivity implies the tendency of the reagent to react with a substrate while selectivity means preference for one out of several reaction pathways. The selectivity of free radical halogenation of alkanes differs considerably toward various halogens. This is demonstrated for the halogenation of *n*-butane.

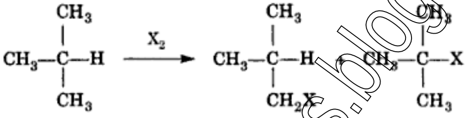


F_2	56 ± 2%	44 ± 2%
Cl_2	31 ± 1%	69 ± 1%
Br_2	2 ± 0.5%	98 ± 1%

The relative rates of formation of the isomeric products is primarily controlled by the probability factor and the energy factors. Butane has six primary hydrogen and four secondary hydrogen atoms. Thus the probability factor results in the formation of primary halide in fluorination in the ratio of 3 : 2. In other words, no selectivity for fluorination is obtained.

In chlorination of *n*-butane, the secondary halide is obtained in a yield twice that of the primary product. Chlorination is still non-selective. Bromination of *n*-butane, however, produces the primary to secondary product in the ratio of 2 : 98. This shows the energy factor must enhance the rate of formation of secondary product. In short, bromination is more selective but less reactive. In other words, bromine shows much greater ability to discriminate among the different types of hydrogens.

The selectivity of halogenation is even greater for abstraction for the tertiary hydrogen atoms as shown for 2-methylpropane.



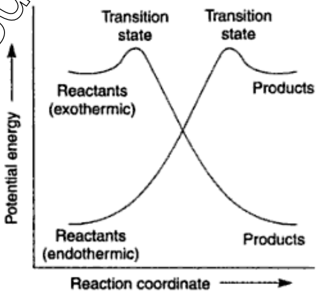
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H \xrightarrow{X_2} CH_3-\overset{CH_3}{\underset{CH_2X}{C}}-H + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-X$$

F_2	90%	10%
Cl_2	70%	30%
Br_2	1%	99%

In this case there is no selectivity for fluorination. But a substantial fraction of chlorination is tertiary. In contrast, bromination yeidls the tertiary product almost exclusively.

The greater selectivity of bromine can be explained in terms of the structure of the transition state, which is a point of highest energy on the energy on the energy profile diagram.

A useful quantitative guide in this regard is the Hammond postulate. It states that in a highly exothermic reaction the reactants are higher in energy and transition state will be reached early and resembles the reactants (reactant like). In a highly endothermic reaction, the products are high in energy and the transition state will be late and resembles the products (product like). In short the location of the transition state of the reactant coordinate will vary with the relative energies of the reagent, transition state and the product. This is depicted in the following diagram.



In the highly exothermic reaction, the energy level of the reactants and the transition states are close together. The transition state is also close to the reactants or it is reached earlier. In the highly endothermic reaction, the transition state is close to the product or it is reached late (a high value cf energy of activation).

Problem 7.21:

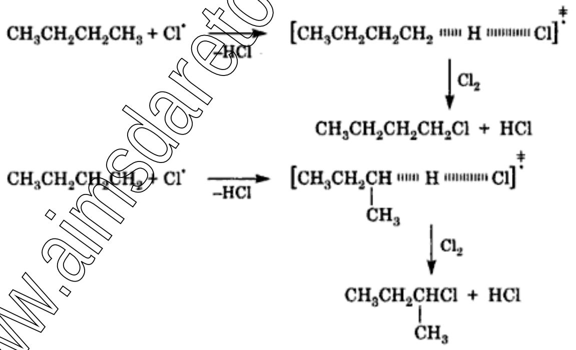
Explain the structures of the transition states for the chlorination and bromination of the *n*-butane on the basis of the Hammond postulate.

Solution: The following reactions take place for the chlorination and bromination of *n*-butane :

$$CH_3CH_2CH_2CH_3 + Cl^{\bullet} \xrightarrow[-HCl]{} \underset{\Delta H\ -\ 5\ \text{Kcal/mole}}{CH_3CH_2CH_2\dot{C}H_2} + \underset{-\ 8\ \text{Kcal/mole}}{CH_3CH_2\dot{C}HCH_3}$$

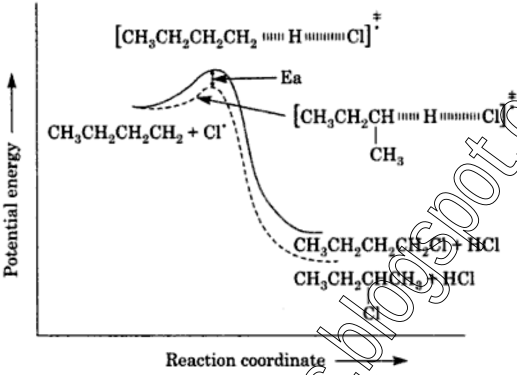
$$CH_3CH_2CH_2CH_3 + Br^{\bullet} \xrightarrow[-HBr]{} \underset{\Delta H\ +\ 10\ \text{Kcal/mole}}{CH_3CH_2CH_2\dot{C}H_2} + \underset{+\ 7\ \text{Kcal/mole}}{CH_3CH_2\dot{C}HCH_3}$$

According to ΔH data the first propagation step (abstraction of a hydrogen by a halogen atom) for chlorination is exothermic while for bromination it is endothermic. Therefore, we expect that the transition state for chlorination will resemble the chlorine radical. This is the same species in both reactions (primary as well as secondary hydrogen abstractions so we would expect the energies of the transition states to be very similar. The energy levels of the reactants and the transition state are close to each other. The transition state lies closer to the reactants along the reaction coordinate. This means that in the exothermic step, bond-breaking has not proceeded very far when the transition state is reached (or the transition state has achieved very little alkyl radical character).



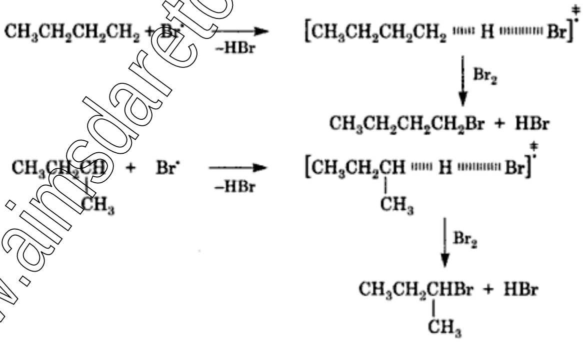
$$CH_3CH_2CH_2CH_3 + Cl^{\bullet} \xrightarrow[-HCl]{} [CH_3CH_2CH_2CH_2 \cdots H \cdots Cl]^{\ddagger\bullet} \xrightarrow{Cl_2} CH_3CH_2CH_2CH_2Cl + HCl$$

$$CH_3CH_2CH_2CH_2 + Cl^{\bullet} \xrightarrow[-HCl]{} [CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}} \cdots H \cdots Cl]^{\ddagger\bullet} \xrightarrow{Cl_2} CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCl + HCl$$



Since the transition states in both cases are reactantlike in structure and energy, they show little resemblance to products of the hydrogen abstraction step a 1° or a 2° radical. Since the reactants in both cases are the same the exact type of C—H bond being broken (primary or secondary) has a relatively small influence on the relative rates of reaction. The two reactions thus proceed with small (though not identical secondary : primary = 3 : 1) rates because their respective energies of activation are quite similar. Chlorination is thus non-selective.

The case for bromination of *n*-butane can be argued in the same manner. The hydrogen abstraction step (both primary and secondary) is endothermic and the bond has broken to a considerable extent by the time the transition state is reached. The transition state resembles an alkyl radical or the transition state lies closer to the products.



$$CH_3CH_2CH_2CH_2 + Br^{\bullet} \xrightarrow[-HBr]{} [CH_3CH_2CH_2CH_2 \cdots H \cdots Br]^{\ddagger\bullet} \xrightarrow{Br_2} CH_3CH_2CH_2CH_2Br + HBr$$

$$CH_3CH_2\underset{\overset{|}{CH_3}}{CH} + Br^{\bullet} \xrightarrow[-HBr]{} [CH_3CH_2\underset{\overset{|}{CH_3}}{CH} \cdots H \cdots Br]^{\ddagger\bullet} \xrightarrow{Br_2} CH_3CH_2\underset{\overset{|}{CH_3}}{CH}Br + HBr$$

The transition state stability will be a direct reflection of the alkyl radical stability. There is a marked influence on the relative rates of these reactions. In fact they proceed with very different rates. Abstraction of a secondary hydrogen takes place much faster than that of primary (80 : 1). Thus bromine is selective in its reaction.

Problem 7.22:

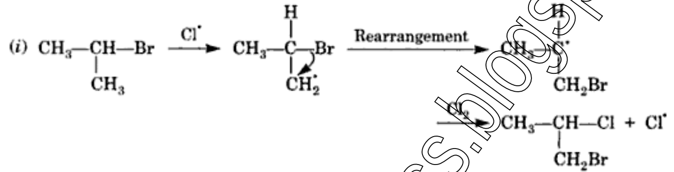
It is believed that the side-chain carbon of benzyl radical lies in the same plane as the ring. Why ?

Solution: In order to permit the overlap of π electron cloud and the *p*-orbital.

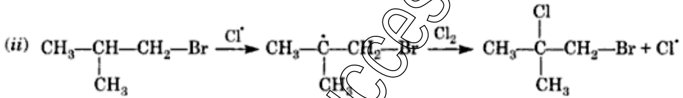
Problem 7.23:

Isopropyl bromide on photochlorination gives 1-bromo-2-chloropropane but isobutyl bromide gives 1-bromo-2-chloro-2-methyl-propane. Account for this observation.

Solution: $Cl_2 \xrightarrow{h\nu} 2Cl^{\cdot}$



$$(i)\ CH_3—\underset{\underset{CH_3}{|}}{C}H—Br \xrightarrow{Cl^{\cdot}} CH_3—\overset{\overset{H}{|}}{\underset{\underset{\dot{C}H_2}{|}}{C}}—Br \xrightarrow{\text{Rearrangement}} CH_3—\overset{\overset{H}{|}}{\underset{\underset{CH_2Br}{|}}{\dot{C}}} \xrightarrow{Cl_2} CH_3—\underset{\underset{CH_2Br}{|}}{C}H—Cl + Cl^{\cdot}$$



$$(ii)\ CH_3—\underset{\underset{CH_3}{|}}{C}H—CH_2—Br \xrightarrow{Cl^{\cdot}} CH_3—\underset{\underset{CH_3}{|}}{\dot{C}}—CH_2—Br \xrightarrow{Cl_2} CH_3—\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2—Br + Cl^{\cdot}$$

It is known that alkyl free radicals do not rearrange by migration of an alkyl group. However in case (*i*), it seems that radicals can rearrange by migration of the halogen atom resulting in a 2° free radical. In case (*ii*) even such a rearrangement is not possible because the intermediate radical is already 3°. This explains the difference in product formation.

Problem 7.24:

Describe briefly what is meant by the following terms : Reforming, scrubbing, petrochemicals, unleaded petrol, sour petrol, CNG and power alcohol.

Solution: Reforming : To improve the quality of gasoline it s subjected to reforming. It is the process of bringing about changes in the molecular structure of fuel thermally or catalytically. The major reactions in reforming operation are : formation of aromatic hydrocarbons by dehydrogenation, isomerization and cracking into higher hydrocarbons.

Scrubbing : Removal of low boiling constituents, propane, butane, etc. from crude oil is known as *scrubbing*. This involves the dissolution of these substances into a high boiling liquid and subsequent separation by distillation.

Petrochemicals : The name *petrochemicals* is assigned to those compounds which are obtained either directly or indirectly from petroleum and natural gas and are used in the manufacture of commodities other than fuels. These compounds have a common origin and are isolated from petroleum in a high state of purity. Such compounds serve as industrial raw materials in the plastic, rubber and synthetic fibre industries. New developments in the manufacture of paints, pesticides, plasticizers and detergents are made possible in a large manner by the ready availability of the chemicals from the petroleum industry. Important petrochemicals obtained from petroleum are benzene, toluene and their derived products.

Unleaded Petrol : Lead compound, tetraethyl lead $(C_2H_5)_4Pb$ is added to petrol as an antiknocking agent, but this compound is also a source of pollution. Petrol whose octane number is increased without the addition of lead compounds is referred to as *unleaded petrol*.

Sour Petrol : Sulfur compounds containing gasoline is termed as *sour petrol*. Thiols are one of such compounds.

CNG : Compressed natural gas (CNG) contains 95% methane. It is considered less polluting than petrol or diesel. Methane contains only one C-atom and it gets completely oxidized under ordinary conditions. On the other hand, petrol contains 6-12 carbon atoms while diesel contains 15-18 carbon atoms. Due to their high carbon content, they do not get oxidized completely and thus cause extensive pollution.

Power Alcohol : Power alcohol is an alternative source of energy. Absolute alcohol (100% ethanol) and rectified spirit (95% ethanol) are not used as prime fuels but they are only mixed with petrol. Power alcohol has petrol and alcohol in the ratio of 4 : 1. By the way alcohol mixes well with petrol in the presence of benzene. Therefore, benzene as a solvent is also used. Power alcohol has good antiknocking properties. Its octane number is 90. Alcohol thus increases the octane number of alcohol.

Problem 7.25:

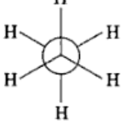
Write a short note on photochemical reaction.

Solution: A photochemical reaction is any reaction initiated by ultraviolet or visible light. These reactions differ from thermal reactions where the reaction is promoted by heat alone. Photosynthesis is a familiar photochemical reaction in nature. For a photochemical reaction to take place, a molecule must absorb energy in the wavelength region in which it is irradiated. This can be determined by the absorption spectrum of the molecule. Photochemical reactions are largely those of π-electron systems in which case the molecule absorbs a photon and one bonding π-electron is excited to an antibonding orbital, *i.e.* π^*. This is also known as π–π^* *transition*. The reaction which are examined by photochemical means are the Diels-Alder reaction, the Fries rearrangement, nucleophilic displacements and Grignard reagents. In photochemical reactions, it is feasible to cleave a specific bond in contrast to thermal reactions which involves a complex formation of free radicals. Both photochemical and thermal reactions have one feature in common—they involve homolytic cleavage into fragments which subsequently recombine to yield stable products. Photochemical reactions are insensitive to the influence of catalyst, solvents and electronic nature of the substituents.

Problem 7.26:

Define conformational isomerism.

Solution: The conversion of one spatial arrangement of atoms into another through rotation about a C—C bond is called conformational isomerism and the two isomers are called conformational isomers. Ethane has two such conformations.



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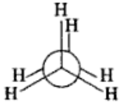

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Problem 7.27:

Select the correct answer.

(*a*) Methane is produced by the hydrolysis of :

A. CaC_2 B. Al_4C_3 C. Dry ice D. *n*-C_2H_5MgBr

(*b*) A mixture of ethyl iodide and *n*-propyl iodide is subjected to Wurtz reaction. The hydrocarbon which will not be formed is

A. Butane B. Propane C. Pentane D. Hexane

(*c*) Pure methane can be produced by

A. Wurtz reaction B. Kolbe electrolysis C. Soda lime decarboxylation

D. Reduction with H_2

(*d*) Fomation of alkanes by action of Zn on alkyl halides is called

A. Frankland reaction B. Cannizzaro reaction C. Wurtz reaction

D. Kolbe reaction

(*e*) A hydrocarbon with molecular formula C_8H_{18} gives only one monochloro derivative. The hydrocarbon is :

A. *n*-Octane B. 2,2,4-Trimethylpentane C. 2-Methylpentane

D. 2,2,3,3-Tetramethylbutane

(*f*) The reaction conditions leading to the best yield of C_2H_5Cl are

A. $C_2H_6 + Cl_2 \xrightarrow{\text{dark}}$ B. $C_2H_6 + Cl_2 \xrightarrow[\text{light}]{uv}$

C. $C_2H_6 + Cl_2\,(\text{excess}) \xrightarrow[\text{light}]{uv}$ D. $C_2H_6\,(\text{excess}) + Cl_2 \xrightarrow[\text{light}]{uv}$

(*g*) Which of the following in considered less polluting ?

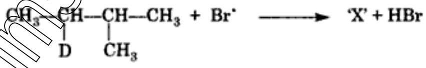
A. Petrol B. Diesel C. CNG D. Mixture of CO_2 and hydrocarbons

(*h*) Which gives a racemic mixture on monochlorination ?

A. Neopentane B. 2-Methylbutane C. 2,3-Dimethylbutane

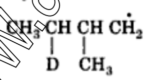
D. 2,2,3,3-Tetramethylbutane

(*i*) Consider the following reaction

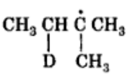


$$CH_3-\underset{D}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3 + Br^{\bullet} \longrightarrow \text{'X'} + HBr$$

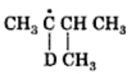
Identify the structure of the major product 'X'.

A. 

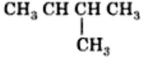
$CH_3\,\underset{D}{\underset{|}{CH}}\,\underset{CH_3}{\underset{|}{CH}}\,\dot{C}H_2$

B. 

$CH_3\,\underset{D}{\underset{|}{CH}}\,\underset{CH_3}{\underset{|}{\dot{C}}}\,CH_3$

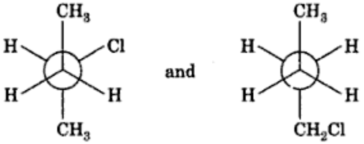
C. 

$CH_3\,\underset{D}{\underset{|}{\dot{C}}}\,\underset{CH_3}{\underset{|}{CH}}\,CH_3$

D. 

$CH_3\,\dot{C}H\,\underset{CH_3}{\underset{|}{CH}}\,CH_3$

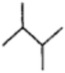
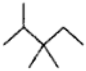
(*j*) The pair of structurs given below represents



A. Constitutional isomers B. Enantiomers C. Diastereoisomers

D. Same compound

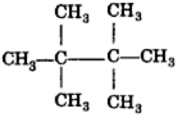
(*k*) Which of the following compound is assigned octane number 100 ?

A. 
B. 
C. 
D. 

(*l*) Sodium formate on Kolbe electrolysis gives :

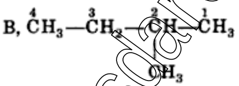
A. CH_4 B. CH_3CH_3 C. H_2 D. None of those

Solution: (*a*) B, $Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$ (*b*) B, because no such coupling combination is possible. (*c*) C, other methods do not produce CH_4 (*d*) A (*e*) D,



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

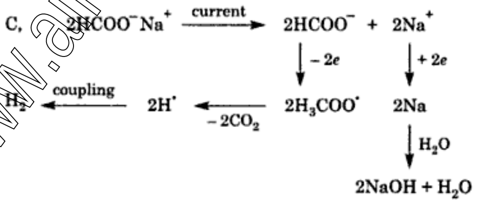
(*f*) D (*g*) C, CNG contains upto 95% methane, and it gets completely oxidized under ordinary conditions, petrol, on the other hand, contains 6–12 carbon atoms while deisel contains 15–18 carbon atoms. Due to the high carbon content they do not get completely oxidized.

(*h*) B, 

$$\overset{4}{C}H_3-\overset{3}{C}H_2-\underset{CH_3}{\overset{2}{C}H}-\overset{1}{C}H_3$$

Chlorination at position-2 will give an enantiomeric mixture.

(*i*) B, a tertiary free rdical formed is more stable. (*j*) A (*k*) C, It is called iso-octane

(*l*) C, 

CHAPTER

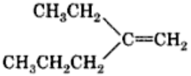
8

Alkenes

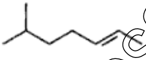
Problem 8.1:

Suggest an IUPAC name for each of the following structures :

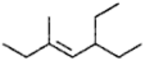
(*a*)



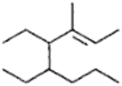
(*b*)



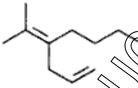
(*c*)



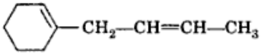
(*d*)



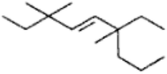
(*e*)



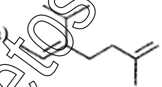
(*f*)



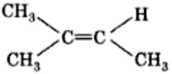
(*h*)



(*h*)



(*i*)



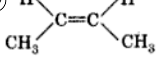
Solution: (*a*) 2-Ethyl-1-pentene (*b*) 6-Methyl-2-heptene (*c*) 5-Ethyl-3-metylhept-3-en (*d*) 4, 5-Diethyl-3-methyloct-2-en (*e*) 4-Butyl-5-methyl-1, 4-hexadiene (*f*) 1-(2-Butenyl) cyclohexene (*g*) 6-Ethyl-3, 3, 6-trimethyl-4-nonene (*h*) 2-Methyl-5-(1-methylethyl)-1, 5-heptadiene (*i*) 2-Methyl-2-butene.

Problem 8.2:

For each pair of compounds, predict the one with a higher boiling point.

(*a*) *cis*- and *trans*-2-Butene (*b*) *cis*- and *trans*-1, 2-Dichloroethene

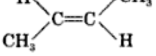
Solution: (*a*)



cis

μ = 0.33 D

bp. 4°C



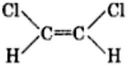
trans

μ = 0 D

bp. 1°C

***cis*-Isomer is high boiling**

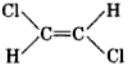
(*b*)



cis

μ = 2.95 D

bp. 60°C



trans

μ = 0 D

bp. 48°C

***cis*-isomer is high boiling**

The boiling points of *cis*- and *trans*-isomers reflect the difference in their dipole moments. Compounds with permanent dipole moments engage in dipole-dipole attractions while those without permanent dipole moments only in van der Waals attractions. The *cis*- and *trans*-2-butenes have similar van der Waals attractions but in addition the *cis*-isomer has dipole-dipole attractions. The *cis*-2-butenes thus have higher boiling points because of this intermolecular attractions.

Problem 8.3:

Why are all *trans*-alkenes more stable than the *cis*- isomers ?

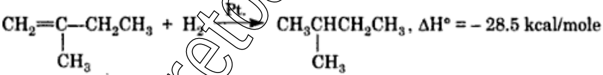
Solution: In the *cis*- isomer the two alkyl groups are forced to occupy the same plane on the same side of the C—C double bond. One hydrogen in each of the *cis* methyl groups is within a van der Waals radius of the other. Therefore, van der Waals repulsions occur between the methyl groups. No such repulsions occur in the *trans*- isomer. Such a van der Waals repulsion is also given the name of steric effect.

Problem 8.4:

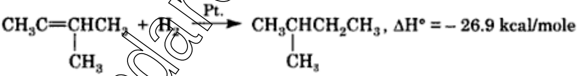
Which of the following alkenes is more stable ?

2-Methyl-1-butene	ΔH° = – 28.5 kcal/mole
2-Methyl-2-butene	ΔH° = – 26.9 kcal/mole

Solution:



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2CH_3 + H_2 \xrightarrow{Pt.} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3,\ \Delta H^\circ = -28.5\ \text{kcal/mole}$$

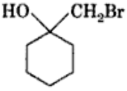


$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_3 + H_2 \xrightarrow{Pt.} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3,\ \Delta H^\circ = -26.9\ \text{kcal/mole}$$

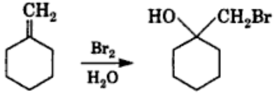
2-Methyl-1-butene evolves more energy than 2-methyl-2-butene, the latter thus has less potential energy and more stable. The alkene with the greatest number of alkyl groups on the double bond is usually the most stable.

Problem 8.5:

Give the structure of the alkene that would yield the following product (a bromohydrin) when allowed to react with bromine water.

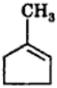
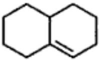
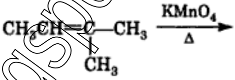


Solution: The alkene is methylenecyclohexane. The addition of $Br_2 + H_2O$ takes place according to Markownikoff's rule to give the product.

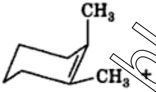


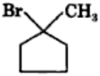
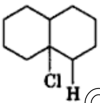
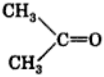
Problem 8.6 :

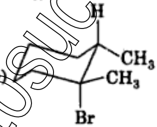
Write the product of the following reactions :

(a)  + HBr ⟶ (b)  + HCl ⟶ (c) 

$CH_3CH{=}C(CH_3){-}CH_3 \xrightarrow[\Delta]{KMnO_4}$

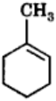
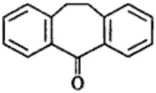
(d) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[\Delta]{KMnO_4}$ (e)  + HBr ⟶

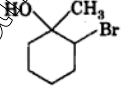
Solution: (a)  (b)  (c) CH_3COOH + 

(d) $CH_3CH_2CH_2COOH + CO_2$ (e) 

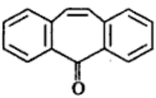
Problem 8.7:

Write the product of the following reactions :

(a)  + HOBr ⟶ (b)  $\xrightarrow[(ii)\ (CH_2H_5)_3N]{(i)\ NBS,\ CHCl_3,\ \Delta}$

Solution: (a) 

(Addition takes place according to Markownikoff rule)

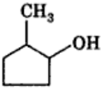
(b) 

(Allylic bromination followed by HBr elimination)

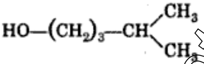
Problem 8.8:

From which alkenes could one synthesize the following alcohols by hydroboration-oxidation ?

(*a*)

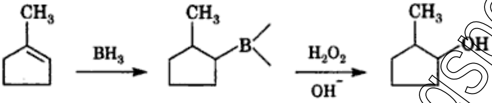


(*b*)

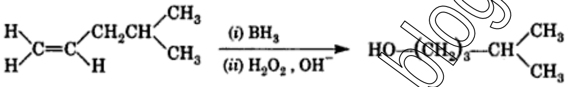


$HO-(CH_2)_3-CH(CH_3)_2$

Solution: (*a*)



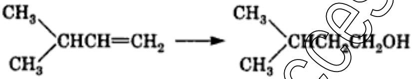
(*b*)



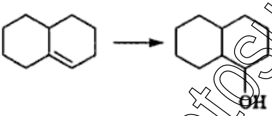
Problem 8.9:

How will you synthesize the following ?

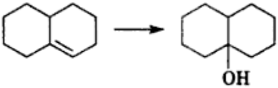
(*a*)



(*b*)



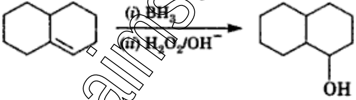
(*c*)



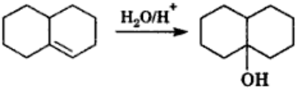
Solution: Note the attachment of the -OH group.

(*a*)

(*b*)



(*c*)



Problem 8.10:

Write the structures of all the lettered compounds.

$$\underset{C_6H_{12}}{[A]} \xrightarrow{HCl} \underset{C_6H_{13}Cl}{[B]} + \underset{C_8H_{13}Cl}{[C]}$$

$$[B] \xrightarrow{\text{alc. KOH}} [D] \text{ (an isomer of A)}$$

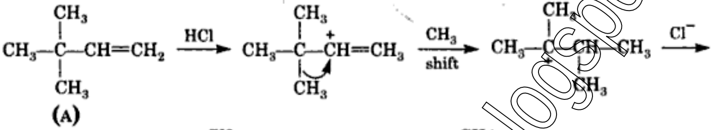
$$[D] \xrightarrow{\text{ozonolysis}} [E] \text{ (gives positive iodoform test but not Tollens' test)}$$

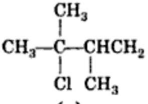
$$[A] \xrightarrow{\text{ozonolysis}} [F] + [G]$$

(Both give positive Tollens' test)

$$[F] + [G] \xrightarrow{\text{conc. NaOH}} HCOONa + \text{Primary alcohol}$$

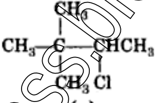
Solution: A is an alkene which on addition of HCl gives two products





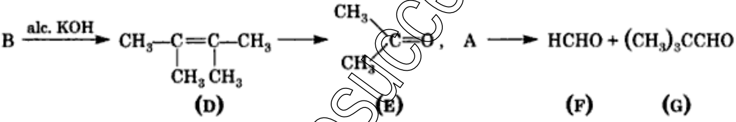
$CH_3-\underset{Cl}{\overset{CH_3}{\overset{|}{C}}}-\underset{CH_3}{CH}CH_2$

(B)



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Cl}{CH}CH_3$

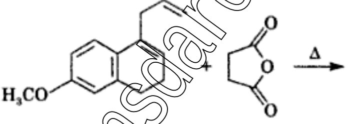
(C)



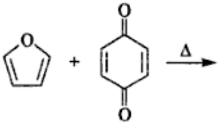
Problem 8.11:

What products are formed in the Diels-Alder reaction from the following dienes and dienophiles.

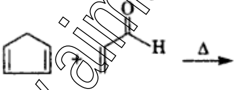
(*a*)



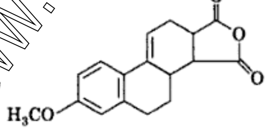
(*b*)



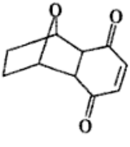
(*c*)



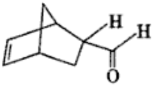
Solution: (*a*)



(*b*)



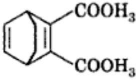
(*c*)



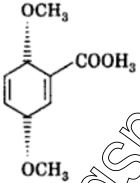
Problem 8.12:

Write the structure of the diene and the dienophilic that would react in the Diels-Alder reaction to yield each of the following Diels-Alder adducts :

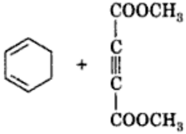
(*a*)



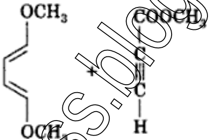
(*b*)



Solution: (*a*)



(*b*)

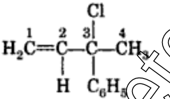


Problem 8.13:

Write a structure corresponding to the following names :

(*a*) 3-Chloro-3-phenyl-1-butene (*b*) 4-Nonene (*c*) 2,3-Dimethyl-2-pentene (*d*) 2,3-Dimethyl-1,3-butadiene (*e*) 1,4-Dibromobut-2-ene (*f*) *cis*-2-Pentene

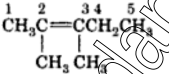
Solution: (*a*)



$$H_2\overset{1}{C}=\underset{H}{\overset{2}{C}}-\underset{C_6H_5}{\overset{\overset{Cl}{3}}{C}}-\overset{4}{CH_3}$$

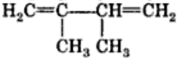
(*b*) $\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H=\overset{5}{C}H\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H_2\overset{9}{C}H_3$

(*c*)



$$\overset{1}{CH_3}\underset{CH_3}{\overset{2}{C}}=\underset{CH_3}{\overset{3}{C}}\overset{4}{CH_2}\overset{5}{CH_3}$$

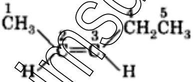
(*d*)



$$H_2\overset{1}{C}=\underset{CH_3}{\overset{2}{C}}-\underset{CH_3}{\overset{3}{C}}H=\overset{4}{C}H_2$$

(*e*) $Br\overset{1}{C}H_2\overset{2}{C}H=\overset{3}{C}H\overset{4}{C}H_2Br$

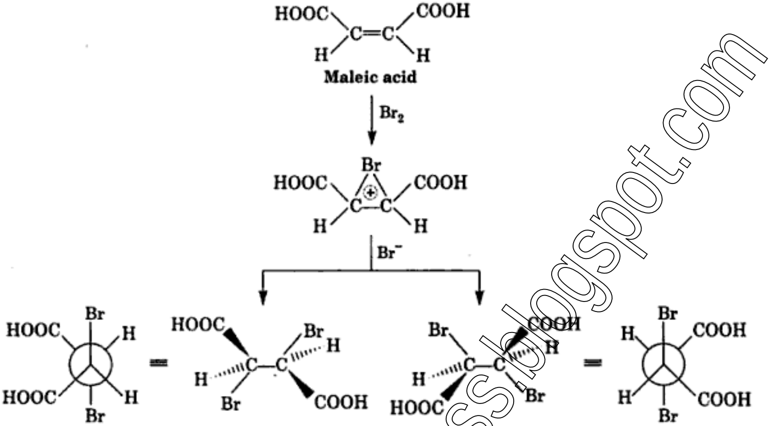
(*f*)



Problem 8.14:

When maleic acid is treated with bromine, the 2, 3-dibromosuccinic acid formed can be resolved into its enantiomers. But the addition of bromine to fumaric acids yields 2, 3-dirbromosuccinic acid which is non-resolvable. What do these observations indicate regarding the mechanism of bromine addition ?

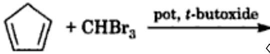
Solution: Addition of bromine to maleic acid takes place in a stereospecific *trans* manner.

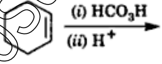


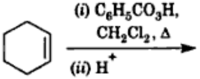
Maleic acid yields a *d*, *l* pair which can be resolved. The addition of Br_2 to fumaric acid results in a *meso* compound which is not resolvable.

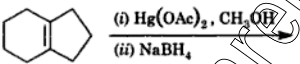
Problem 8.15:

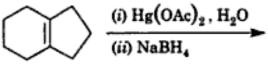
Write the major product of the following reactions :

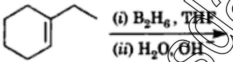
(*a*)


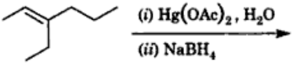
(*b*)


(*c*)


(*d*)


(*e*)


(*f*)


(*g*)


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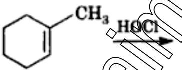
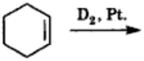
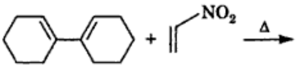
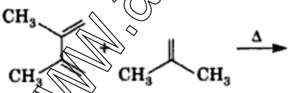
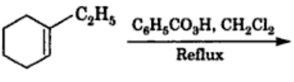
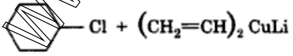


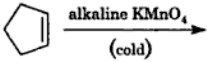
(*i*)


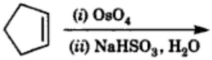
(*j*)


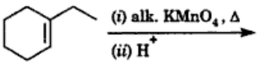
(*k*)


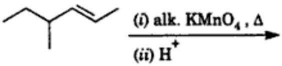
(*l*)


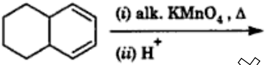
(*m*)


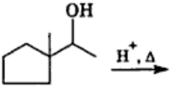
(*n*)


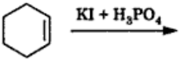
(*o*) 

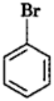
(*p*) 

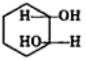
(*q*) 

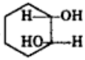
(*r*) 

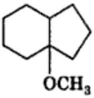
(*s*) 

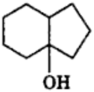
(*t*) 

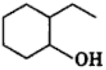
Solution: (*a*) 

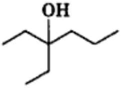
, (Product obtained by addition of carbene :CBr_2 and subsequent rearrangement) (*b*) 

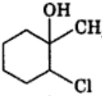
(*c*) 

(First epoxide formation, followed by ring opening by H⁺) (*d*) 

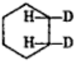
(No hydroxylic solvent is used in this reaction) (*e*) 

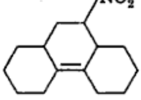
(-OH is attached to the highly substituted carbon atom of C=C bond) (*f*) 

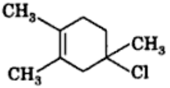
(-OH is attached to the least substituted carbon atom of C=C bond) (*g*) 

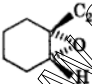
(*h*) 

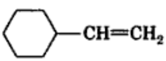
(Cl⁺ attacks the C=C bond first to give a stable cation followed by reaction with OH⁻).

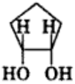
(*i*) 

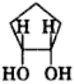
(Addition is *syn*) (*j*) 

(D.A. reaction) (*k*) 

(*l*) 

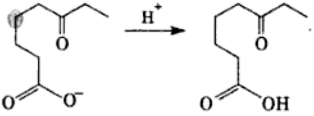
(a *cis* epoxide always results in epoxidation) (*m*) 

+ LiCl + CH_3CH_2Cu (It is the Corey-House synthesis) (*n*) 

(*o*) 

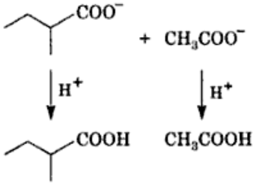
Both the reagents add from the same face of a C=C bond and give *cis*- diol. Compare with (*b*) and (*c*).

(*p*)

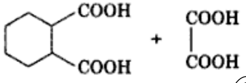


Hot KMnO$_4$ cleaves ethylene to carboxylic acids.

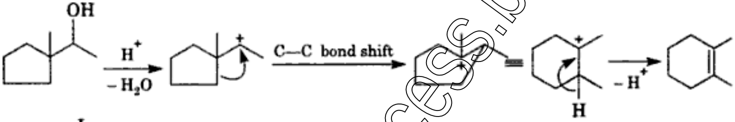
(*q*)



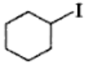
(*r*)



(*s*)



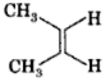
(*t*)



Problem 8.16:

Write the product(s) of the following reactions and discuss :

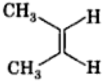
(*a*) (*i*)



cis-2-Butene

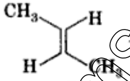
+ Br_2 →

(*ii*)



+ HCO_2H (with C=O) →

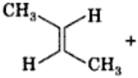
(*iii*)



trans-2- Butene

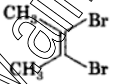
+ Br_2 →

(*iv*)



+ HCO_2H (with C=O) →

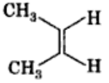
(*b*) (*i*)



cis-2,3-Dibromo-2-butene

+ H_2 →

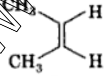
(*ii*)



cis-2-Butene

+ $KMnO_4$ →

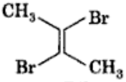
(*iii*)



cis-2-Butene

+ OsO_4 →

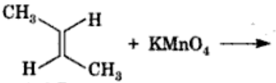
(*iv*)



trans-2,3-Dibromo-2-butene

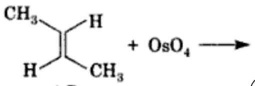
+ H_2 →

(*v*)



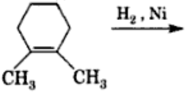
cis-2-Butene

(*vi*)

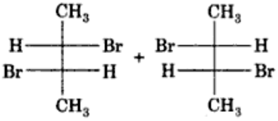


trans-2-Butene

(*c*)

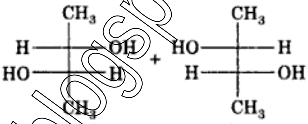


Solution: (*a*) (*i*)



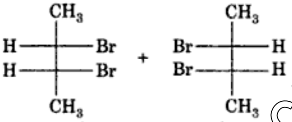
(racemic mixture)

(*ii*)



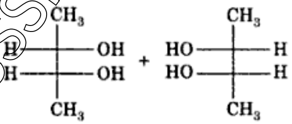
(racemic mixture)

(*iii*)



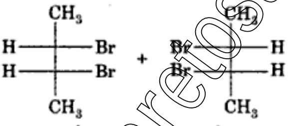
(*meso* compounds)

(*iv*)



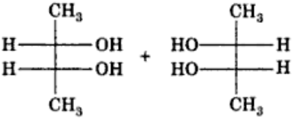
(*meso* compounds)

(*b*) (*i*)

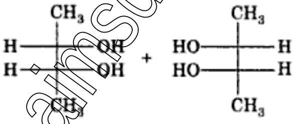


(*meso* compounds)

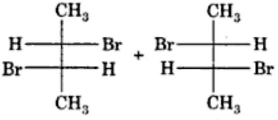
(*ii*)



(*iii*)

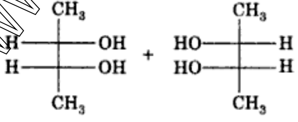


(*iv*)

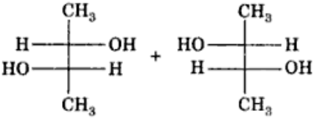


(racemic mixture)

(*v*)



(*vi*)



The above results can be summarized as follows :

For *cis*-2-Butene and maleic acid

All the reagents such as Br_2 and HCO_3H add in an *anti* manner and give a *racemic mixture.*

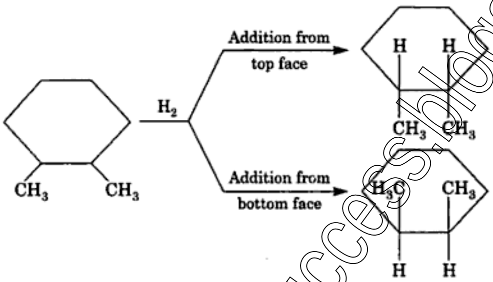
All the reagents such as H_2 , $KMnO_4$ and OsO_4 add in a *syn* manner and give *meso compound.*

For *trans*-2-Butene and fumaric acid

All the reagents such as Br_2 and HCO_3 add in *anti* manner and give *meso compound.*

All the reagents such as H_2 , $KMnO_4$, OsO_4 add in a *syn* manner and give a *racemic mixture*.

(c)



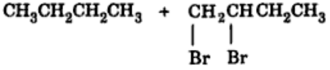
meso- Product

Problem 8.17:

A 10 g mixture containing butane and 2-butene reacts with 8.0 g of bromine dissolved in carbon tetrachloride. Calculate the percentage of butane in the mixture.

Solution: $CH_3CH_2CH_2CH_3 + CH_3CH{=}CHCH_3 + Br_2 \longrightarrow$

Molecular weight **58** **56** **160**



$$CH_3CH_2CH_2CH_3 + \underset{Br}{\underset{|}{CH_2}}\underset{Br}{\underset{|}{CH}}CH_2CH_3$$

A 10 g mixture of butane and 2-butene was treated with Br_2. According to the above reaction only 2-butene reacts with bromine.

$$160 \text{ g } Br_2 \equiv 56 \text{ g 2-butene}$$

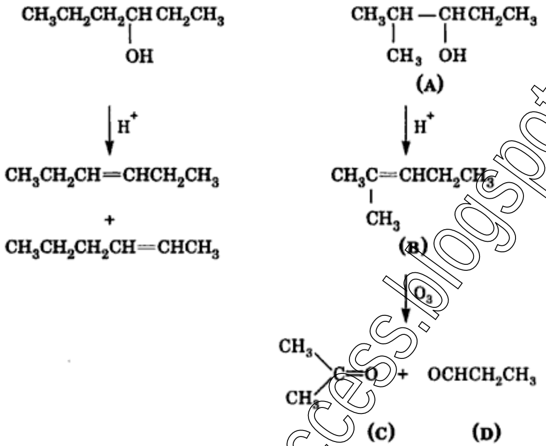
$$8 \text{ g } Br_2 = \frac{56 \times 8}{160} = \frac{14}{5} = 2.8$$

Therefore out of 10 g mixture, butene is 2.8 g and butane is 10 – 2.8 = 7.2 g or 72%.

Problem 8.18:

Compound (A), $C_6H_{14}O$, on treatment with hot sulfuric acid yields an unsaturated compound (B), C_6H_{12} which on ozonolysis gives a mixture of carbonyl compounds (C), C_3H_6O and (D), C_3H_6O. Deduce the structures of A, B, C and D.

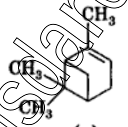
Solution: Since H_2SO_4 on treatment with $C_6H_{14}O$ removes a molecule of water to give a molecule of alkene B, there are two possibilities of writing the two isomeric alcohols :



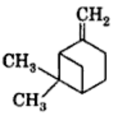
The first alcohol will yield two isomeric alkenes but second alcohol will form only one alkene ; it being the most substituted. Subsequent ozonolysis of (B) will yield (C) as ketone and (D) as aldehyde which are isomeric.

Problem 8.19:

How will you distinguish between (A) and (B) using ozonolysis.



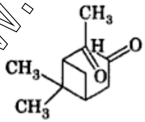
(A)



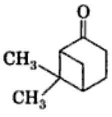
(B)

Solution: The two alkenes would yield different carbonyl compounds on ozonolysis and subsequent reduction (Zn/H_2O).

From A



, From B



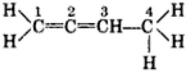
+ HCHO

Problem 8.20:

Which of the hybridized carbon atoms are present in 1, 2-butadiene:

(*a*) Only *sp* hybridized carbon atoms (*b*) *sp*, sp^2 and sp^3 hybridized carbon atoms (*c*) Only sp^2 hybridized carbon atoms (*d*) Both *sp* and sp^2 hybridized carbon atoms.

Solution:



$$\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H-\overset{4}{C}H_3$$

The answer is (*b*).

Problem 8.21:

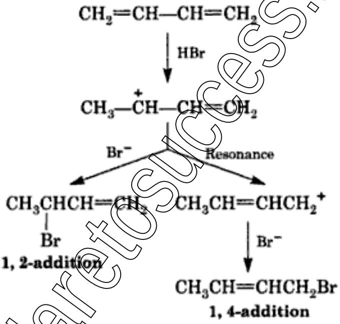
Explain why HCN does not add to an alkene as does HBr.

Solution: Because HCN is a weak acid and is not adequately ionized.

Problem 8.22:

Why does HBr add to 1, 3-butadiene to give both 1, 2- and 1, 4-addition products.

Solution: Resonance in the intermediate cation takes place after proton is added to one of the double bonds of 1, 3-butadiene to give 1, 4-addition product.

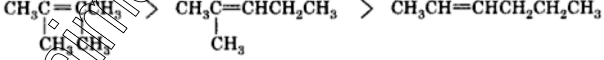


Problem 8.23:

Arrange the following alkenes in order of decreasing stability:

2, 3-Dimethyl-2-butene, 2-metyl-2-pentene, 2-hexene

Solution:



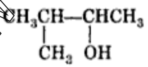
$$CH_3\underset{CH_3}{C}=\underset{CH_3}{C}CH_3 > CH_3\underset{CH_3}{C}=CHCH_2CH_3 > CH_3CH=CHCH_2CH_2CH_3$$

The order is determined on the basis of substitution around the carbon-carbon double bond.

Problem 8.24:

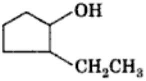
Arrange the following in the order of ease of dehydration:

(*a*)

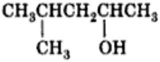


$$CH_3\underset{CH_3}{CH}-\underset{OH}{CH}CH_3$$

(*b*)



(*c*)



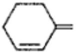
$$CH_3\underset{CH_3}{CH}CH_2\underset{OH}{CH}CH_3$$

Solution: (*c*) > (*a*) > (*b*)

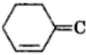
Alcohol (*c*) gives the most stable alkene.

Problem 8.25:

Would you expect the following compounds to undergo Diels-Alder reaction with maleic anhydride ?



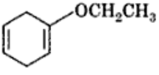
, $CH\equiv C—CH=CH_2$

Solution: Neither would undergo the Diels-alder reaction because $HC\equiv C—CH=CH_2$ is linear while  $=CH_2$ is locked in a *s-trans* conformation.

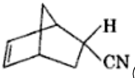
Problem 8.26:

Write the structure of the starting materials that would yield the following products in the Diels-Alder reaction:

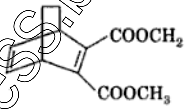
(*a*)



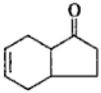
(*b*)



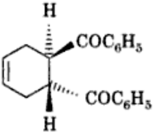
(*c*)



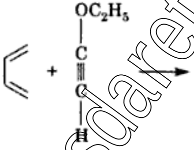
(*d*)



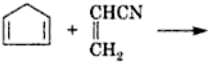
(*e*)



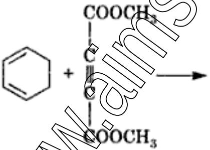
Solution: (*a*)



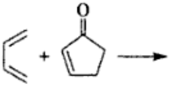
(*b*)



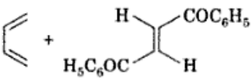
(*c*)



(*d*)



(*e*)

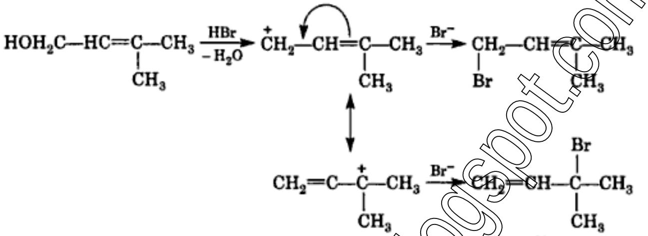


Problem 8.27:

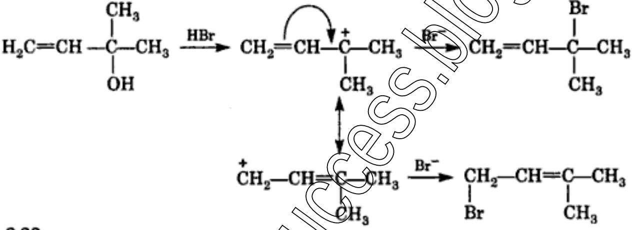
Suggest a detailed mechanism in each case to account the formation of the products:

(*a*) 3-Methyl-2-butene-1-*ol* $\xrightarrow{\text{HBr}}$ 1-bromo-2-methyl-2-butene and 3-bromo-3-methyl-1-butene (*b*) 3-Methyl-1-butene-3-*ol* $\xrightarrow{HBr}$ 1-bromo-2-methyl-2-butene and 3-Bromo-3-methyl-1-butene

Solution: (*a*)



(*b*)

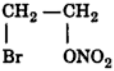


Problem 8.28:

Do alkenes react with nucleophiles or electrophiles ? Would $AlCl_3$ catalyze the polymerization of alkenes. What is the effect of adding $NaNO_3$ on the composition of products from ethylene and Br_2 ? Explain.

Solution: Electrophiles add to alkenes. No, $AlCl_3$ cannot catalyze the polymerization of alkenes.

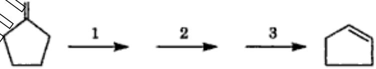
The formation of following product is also possible.



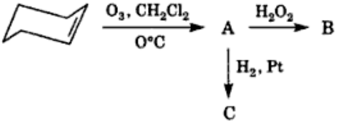
$$\underset{Br}{CH_2}—\underset{ONO_2}{CH_2}$$

Problem 8.29:

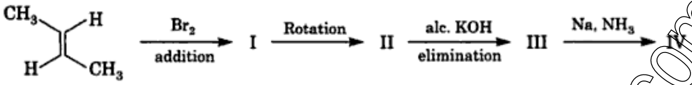
(*a*) Complete the following sequences with appropriate reagents:



(*b*) Suggest appropriate structures of the missing compounds:



(*c*) Supply the missing structures in the following sequence:

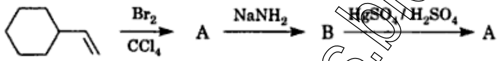


(*d*) Identify X, Y, Z in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde $(H_2{}^*CO)$ as one of the product when compound Z is treated with HBr and subsequently ozonolyzed. Mark the C* carbon in the entire scheme.

$$BaCO_3 + H_2SO_4 \longrightarrow X(gas)$$

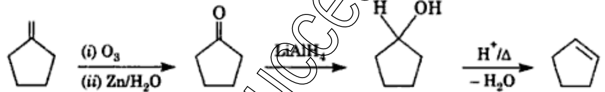
$$CH_2{=}CH{-}Br \xrightarrow[(iii)\ H_3O]{(i)\ Mg/ether\quad (ii)\ X} Y \xrightarrow{LiAlH_4} Z$$

(*e*) Identify A to E in the following schemes and write their structures:

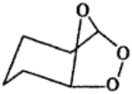


$$C \xrightarrow{H_2NNHCONH_2} D\ ,\quad C \xrightarrow{NaOD/D_2O(exces)} E$$

Solution: (*a*)

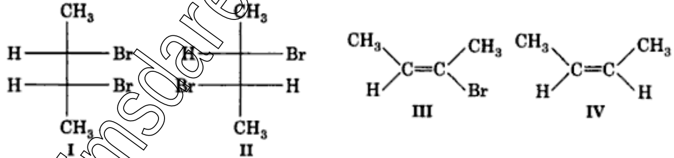


(*b*) A



B $\begin{array}{l} CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \end{array}$ C $\begin{array}{l} CH_2CH_2CHO \\ | \\ CH_2CH_2CHO \end{array}$

(*c*)



I (*Meso* compound) II (Racemic compound) III IV

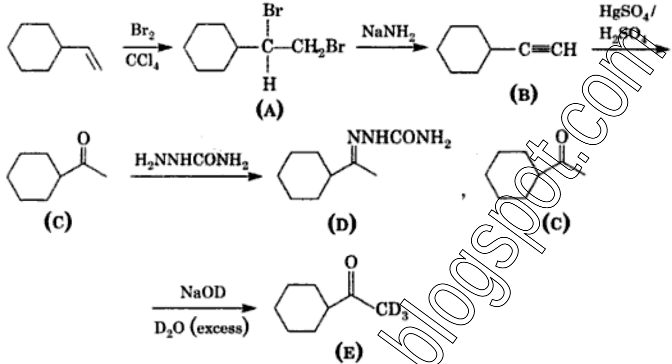
(*d*) $Ba\dot{C}O_3 + H_2SO_4 \longrightarrow \dot{C}O_2 + BaSO_4 + H_2O$

$$CH_2{=}CHBr \xrightarrow{Mg/ether} CH_2{=}CHMgBr \xrightarrow{{}^*CO_2} CH_2{=}CH\dot{C}OOMgBr \xrightarrow{H_3O^+}$$

$$CH_2{=}CH\dot{C}OOH \xrightarrow{LiAlH_4} CH_2{=}CH\dot{C}H_2OH \xrightarrow{H^+Br^-} \underset{\text{(Allylic cation)}}{CH_2{=}CH{-}\dot{C}H_2^+}$$

$$\longleftrightarrow \overset{+}{C}H_2{-}CH{=}\dot{C}H_2 \xrightarrow{Br^-} BrCH_2{-}CH{=}\dot{C}H_2 \xrightarrow{O_3} BrCH_2CHO + H\underset{\substack{|\\ H}}{\dot{C}}{=}O$$

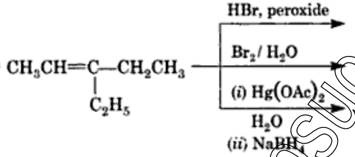
(*e*)



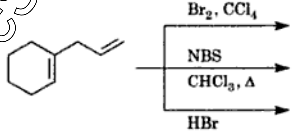
Problem 8.32:

Give the structure of the major organic product:

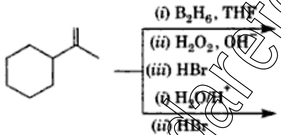
(*a*)



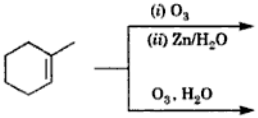
(*b*)



(*c*)

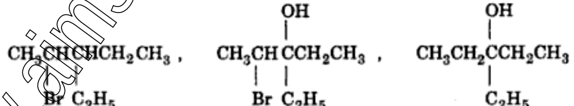


(*d*)



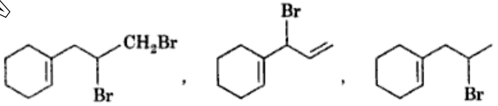
Solution: Note the attachment of Br and OH groups in these reactions.

(*a*)

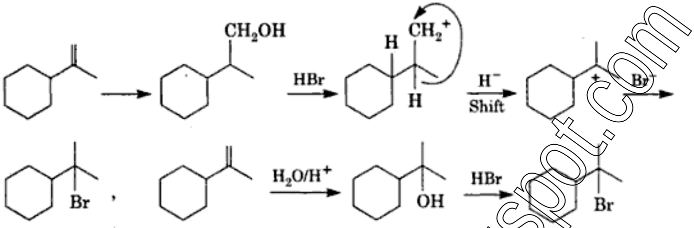


$CH_3\underset{Br}{CH}\underset{C_2H_5}{CH}CH_2CH_3$, $CH_3\underset{Br}{CH}\overset{OH}{\underset{C_2H_5}{C}}CH_2CH_3$, $CH_3CH_2\overset{OH}{\underset{C_2H_5}{C}}CH_2CH_3$

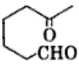
(*b*)



(c)



(d)



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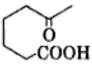


Problem 8.33:

Why do isomeric 1- and 2-butenes provide better evidence for the stabilizing effect of alkyl substituents on C—C double bond than a comparison of ethylene and 2-methylpropene ?

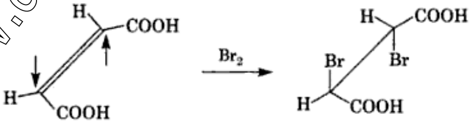
Solution: The two isomeric 1- and 2-butenes have a common hydrogenation product (*n*-butane). They are, therefore, thermodynamically linked to a fixed reference point on a potential energy scale. In case of other two alkenes, the hydrogenation products are different, namely, ethane and 2-methylpropane respectively. It is thus not possible to attribute differences in heats of hydrogenation specifically to alkene substituent effects.

Problem 8.34:

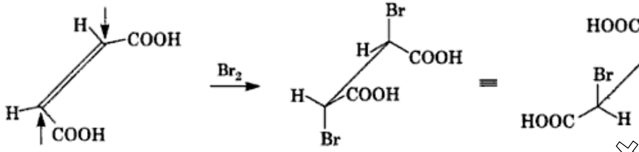
Describe the following terms with suitable examples :

(*a*) Stereospecific reaction (*b*) Stereoselective reaction (*c*) Regioselective reaction (*d*) Chemoselective reaction (*e*) Enantioselective reaction (*f*) Diastereoselective reaction.

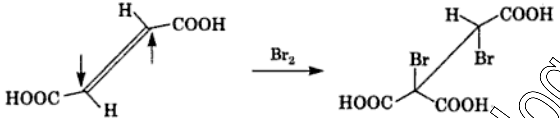
Solution: (*a*) **Stereospecific Reaction.** A *stereospecific reaction* is defined as one in which a given isomer leads to one product while another stereoisomer leads to the opposite product. Alternatively a stereospecific reaction may be defined as one in which stereochemically different reactants give stereochemically different products. All stereospecific reactions are necessarily stereoselective but the reverse is not true. Thus if bromine is added to maleic acid and fumaric acid respectively, the addition takes place in an *anti*-manner. Maleic acids yields *d, l* pair of 2, 3-dibromosuccinic acid (or racemic product). If we start with fumaric acid the only product obtained is *meso* 2, 3-dibromosuccinic acid.



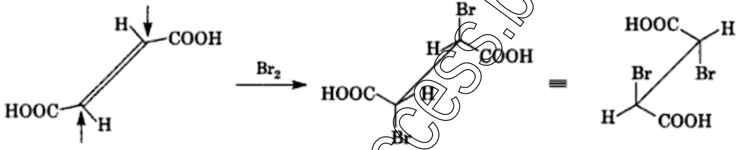
Maleic acid



Maleic acid **d,*l* pair of 2, 3-Dibromosuccinic acid**



Fumaric acid



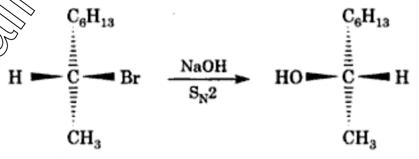
Fumaric acid ***meso* 2, 3-Dibromosuccinic acid**

The reaction is thus stereospecific as well as stereoselective because the opposite isomers give two opposite products.

The reaction of an alkene with a preacid (epoxidation) and the Diels-Alder reactions are *cis*-stereospecific reactions.

The term stereospecific is used in a much broader sense to indicate any kind of discrimination on a stereochemical basis between different reactant molecules. A stereospecific reaction may be defined as one in which stereochemically different molecules react differently. The Beckmann rearrangement is a good example.

(*b*) **Stereoselective Reaction.** A *stereoselective reaction* is one is which a reaction yields exclusively (or predominantly) one enantiomer of a possible pair or one diastereoisomer (or one enantiomeric pair) of the several possible diastereoisomers. When (–)-2-bromoctane is treated with aqueous sodium hydroxide under conditions where second order kinetics is followed there is obtained (+)-2-octanol.



(–)-2-Bromoctane **(+)-2-Octanol**

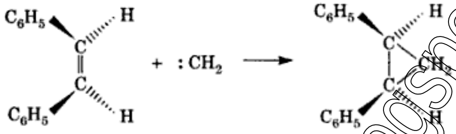
$[\alpha]^\circ = -39.6^\circ$ **$[\alpha]^\circ = +10.3^\circ$**

Although, two enantiomeric 2-octanols are possible, only one of them is obtained here. This is a stereoselective reaction.

Stereoelective reaction can be of two types : enantioselective and diastereoselective.

The Darzens condensation in non-stereoselective because both the *cis*- and *trans*-glycidic esters are formed randomly.

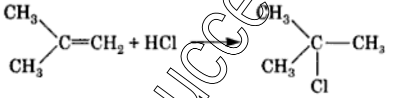
Addition of singlet methylene to an alkene is a stereoselective as well as stereospecific.



***cis*-Stilbene** ***cis*-1, 2-Diphenyl cyclopropane**

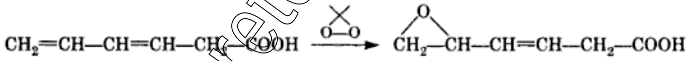
(*c*) **Regioselective Reaction.** A reaction that can potentially yield two or more structural isomers, actually produces only one (or predominance of one), is called a *regioselective reaction* (the reagent attacks a particular region of the molecule).

A familiar example is the polar addition of HCl to an unsymmetrical alkene in the Markownikoff addition. For example HCl adds to isobutylene to give *tert* butyl chloride.



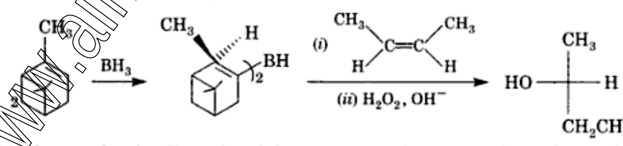
$$(CH_3)_2C{=}CH_2 + HCl \longrightarrow (CH_3)_2C(Cl){-}CH_3$$

Epoxidation of sorbic acid by dimethyldioxirane (a powerful oxidizing agent) is regioselective. The distal carbon-carbon double bond is exclusively epoxidized. This carbon-carbon double bond is more nucleophilic.



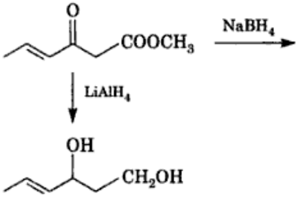
The addition of disiamylborane to an alkyne is also regioselective as the reagent adds to the less hindered carbon atom.

(*d*) **Enantioselective Reaction.** A reaction in which an inactive substrate is converted selectively to one of two enantiomers is called an *enantioelective reaction*. Use of the reagent diisopinocampheylborane results in enantioselective hydroboration oxidation of an alkene. Alcohols with optical purity as high as 98% have been obtained in this manner.



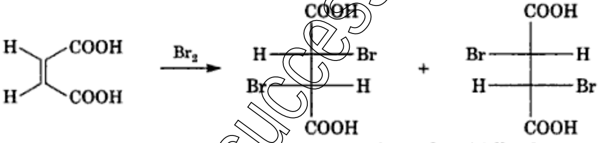
(*e*) **Chemoselective Reaction.** When a functional group is selectively attacked in the presence of two different functional groups, the reaction is said to be *chemoselective*.

Thus a keto group can be chemoselectively reduced in the presence of an ester function using sodium borohydride.



Lithium aluminum hydride, on the other hand, reduces both the functional groups and is thus non-chemoselective.

(*f*) **Diastereoselective Reaction.** If maleic acid is treated with bromine it gives only racemic 2, 3-dibromomaleic acid and none of the *meso* compound. Since the reaction yields only one enantiomeric pair of several possible diastereomers, it is *stereoselective*. Since the selectivity is between diastereomeric products, the reaction is *diastereoselective*.

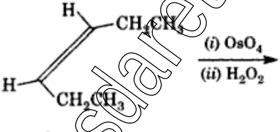


racemic product (±)dl pair

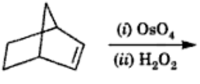
Problem 8.35:

Predict the product(s) and stereochemistry of the following reactions:

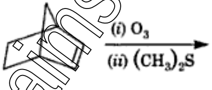
(*a*)



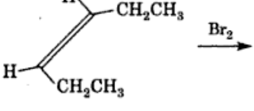
(*b*)



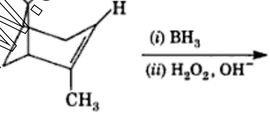
(*c*)



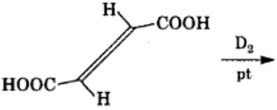
(*d*)



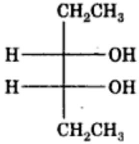
(*e*)



(*f*)

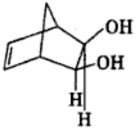


Solution: (*a*)



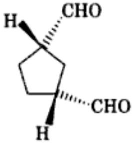
meso (∵ hydroxylation is *syn*)

(*b*)



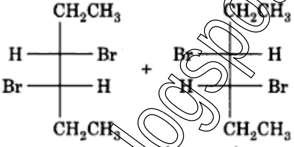
exo-cis

(*c*)



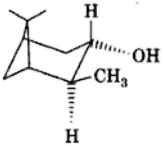
cis (∵ bromine adds *anti*)

(*d*)



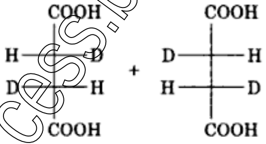
d, *l* pair (racemic)

(*e*)



cis Alcohol

(*f*)



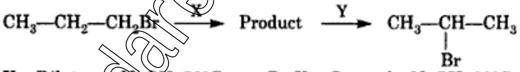
(*d, l*) pair racemic

(∵ deuterium addition is *syn*)

Problem 8.36:

Select the correct answer from the following:

(*a*) Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations



$$CH_3—CH_2—CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3—\underset{\displaystyle Br}{\underset{|}{C}H}—CH_3$$

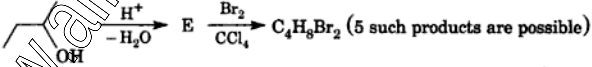
A. X = Dilute aq. NaOH, 20°C
Y = HBr/acetic acid, 20°C

B. X = Conc. alc. NaOH, 80°C
Y = HBr/acetic acid, 20°C

C. X = Dilute aq. NaOH, 20°C
Y = $Br_2/CHCl_3$, 0°C

D. X = Conc. alc NaOH, 80°C
Y = $Br_2/CHCl_3$, 0°C

(*b*)

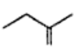


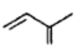
(5 such products are possible)

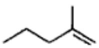
How many structures of E are possible ?

A. 2 B. 5 C. 6 D. 3

(*c*) Which will react fastest in HBr addition ?

A. 

B. 

C. 

D. 

(*d*) Electrolysis of cold conc. aqueous solution of potassium succinate yields.

A. Ethane B. Ethene C. Ethyne D. Ethan-1, 2-diol

(*e*) Addition of one equivalent of Br_2 to 1,3-pentadiene produces

A. 4,5-Dibromo-2-pentene B. 3,4-Dibromo-1-pentene

C. 3.4-Dibromo-2-pentene D. 1,4-Dibromo-2-pentene

(*f*) The nodal plane in the *p*-bond of ethene is located in

A. The molecular plane B. A plane parallel to the molecular plane

C. A plane perpendicular to the molecular plane

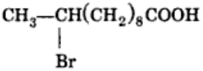
D. A plane perpendicular to the plane which contains the C—C σ bond.

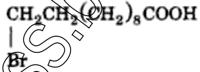
(*g*) During debromination of *meso*-2, 3-dibromobutane, the major product is

A. *n*-Butane B. *cis*-2-Butene C. 1-Butene D. *trans*-2-Butene

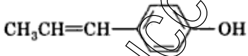
(*h*) The principal product formed in the reaction of

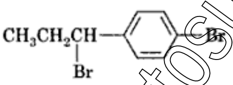
$$CH_2{=}CH(CH_2)_8COOH + HBr \xrightarrow{\text{Peroxide}} \text{ is,}$$

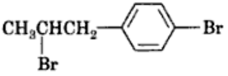
A. 
$CH_3{-}\underset{\underset{Br}{|}}{C}H(CH_2)_8COOH$

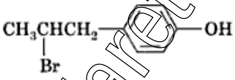
B. 
$CH_2\underset{\underset{Br}{|}}{C}H_2(CH_2)_8COOH$

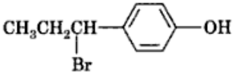
C. $CH_2{=}CH(CH_2)_7CHBrCOOH$ D. $CH_2{=}CH(CH_2)_8COBr$

(*i*) The reaction of  with HBr gives:

A. 

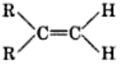
B. 

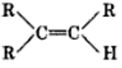
C. 

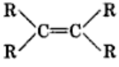
D. 

(*j*) Which of the following alkenes will react slowest with H_2 under catalytic conditions ?

A. 

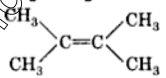
B. 

C. 

D. 

(*k*) Which of the following alkene would have the highest heat of hydrogenation ?

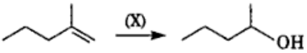
A. $CH_2{=}CH_2$ B. $CH_3CH_2CH{=}CH_2$ C. $CH_3CH{=}CHCH_3$

D. 

(*l*) Hydroboration-oxidation of 1-methylcyclopentene will give

A. *trans*-1-Methycyclopentan-2-*ol* B. *cis*-1-Methylcyclopentan-2-*ol*

C. 1-Methylcyclopentan-1-*ol* D. Mixture of A and B (*m*) In the following reaction:



the reagent 'X' is

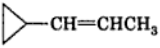
A. H_2O/H^+ B. $KMnO_4$

C. B_2H_6 ; H_2O_2/OH^- D. $Hg(OAc)_2/H_2O$; $NaBH_4$

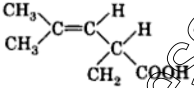
(*n*) Which of the following alkene will have the highest rate of hydration ?

A. *cis*-$CH_2CH{=}CHCH_3$ B. *trans*-$CH_3CH{=}CHCH_3$ C.

D.



(*o*) The following compound can exhibit



A. Geometric isomerism B. Tautomerism

C. Geometric and optical isomerism D. Optical isomerism

(*p*) The number of isomers for the compound with the formula $C_2BrClFI$ is

A. 3 B. 4 C. 5 D. 6

(*q*) In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give *anti* Markownikoff addition to alkenes because :

A. One of the steps is endothermic in both the cases

B. All the steps are exothermic in both the cases

C. Both are highly ionic

D. One is oxidizing agent and the other is reducing

(*r*) Which is the most reactive alkene toward electrophilic addition :

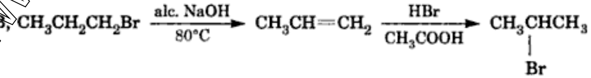
A. $(CH_3)_2C{=}CH_2$ B. $CH_2{=}CHCl$ C. $ClCH_2CH{=}CH_2$ D. $CH_3CH{=}CH_2$

(*s*) Which of the following resonating structure of 1-methoxy-1,3-butadiene is most stable ?

A. $CH_2{=}CH{-}\overset{-}{C}H{-}CH{=}\overset{+}{O}CH_3$ B. $CH_2{=}CH{-}\overset{-}{C}H{-}\overset{+}{C}H{=}OCH_3$

C. $\overset{-}{C}H_2{-}CH{=}CH{-}CH{=}\overset{+}{O}CH_3$ D. $\overset{-}{C}H_2{=}\overset{+}{C}H{-}CH{=}CH{-}OCH_3$

Solution: (*a*) B,

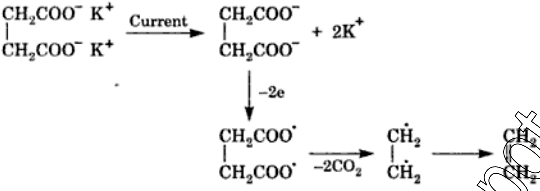


$$CH_3CH_2CH_2Br \xrightarrow[80°C]{\text{alc. NaOH}} CH_3CH{=}CH_2 \xrightarrow[CH_3COOH]{HBr} CH_3\underset{\underset{Br}{|}}{C}HCH_3$$

For elimination alc. KOH or alc. NaOH is always used.

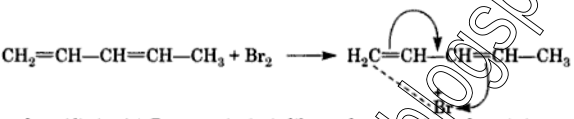
(*b*) D, 1-Butene, *cis*-2-Butene, *trans*-2-Butene (*c*) B, a tertiary carbocation is formed which is stabilized by neighbouring C=C bond.

(*d*) B,



$$\begin{matrix}CH_2COO^- K^+\\ |\\ CH_2COO^- K^+\end{matrix} \xrightarrow{\text{Current}} \begin{matrix}CH_2COO^-\\ |\\ CH_2COO^-\end{matrix} + 2K^+ \xrightarrow{-2e} \begin{matrix}CH_2CO\dot{O}\\ |\\ CH_2CO\dot{O}\end{matrix} \xrightarrow[-2CO_2]{} \begin{matrix}\dot{C}H_2\\ |\\ \dot{C}H_2\end{matrix} \longrightarrow \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}$$

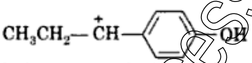
(*e*) D,



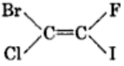
$$CH_2{=}CH{-}CH{=}CH{-}CH_3 + Br_2 \longrightarrow H_2C{=}CH{-}CH{=}CH{-}CH_3 \quad \overset{+}{Br}$$

a cyclic addition takes place (*f*) A (*g*) D, racemic 2, 3-dibromobutane gives the *cis*-isomer. (*h*) B, *anti* Markownikoff addition.

(*i*) D, By the addition of H⁺, following stable carbocation is formed

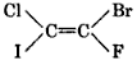


(*j*) D, steric hindrance. (*k*) A, most unsubstituted alkene. (*l*) B, *syn* addition of diborane takes place. (*m*) C, hydroboration, oxidation. (*n*) C, least steric hindrance to addition of H_2O. (*o*) C, also contains a chiral carbon. (*p*) D



cis* and *trans

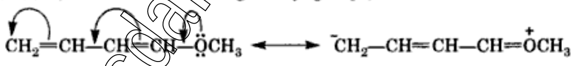
cis* and *trans



cis* and *trans

(*q*) A, only the reaction with HBr is affected by peroxides. For all other reactions (HCl or HI) there is at least one step in the free radical process that would be endothermic (energetically unfavorable). (*r*) A, two electron-donating methyl groups, make the alkene more reactive.

(*s*) C,

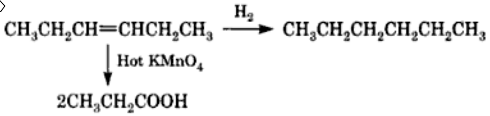


$$CH_2{=}CH{-}CH{=}CH{-}\ddot{O}CH_3 \longleftrightarrow \overset{-}{C}H_2{-}CH{=}CH{-}CH{=}\overset{+}{O}CH_3$$

Problem 8.37:

The hydrocarbon (A), adds one mole of hydrogen in the presence of Pt catalyst to form *n*-hexane. When (A), is oxidized vigorously with hot $KMnO_4$, a single carboxylic acid is formed containing three carbon atoms. Identify A.

Solution: Since A yields a single carboxylic acid containing three carbon atoms, A is a symmetrical alkene. Also the acid contains three C-atoms, the alkene will have six C-atoms.



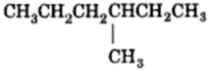
$$CH_3CH_2CH{=}CHCH_2CH_3 \xrightarrow{H_2} CH_3CH_2CH_2CH_2CH_2CH_3$$
$$CH_3CH_2CH{=}CHCH_2CH_3 \xrightarrow{\text{Hot }KMnO_4} 2CH_3CH_2COOH$$

Probem 8.38:

There are six different alkenes A to F. Each on addition of one mole of hydrogen gives G which is the lowest molecular weight hydrocarbon containing only one asymmetric carbon atom. None of the above alkenes give acetone as a product on ozonolysis. Give the structures of A to F.

Identify the alkene which is likely to give a ketone containing five carbon atoms on treatment with a warm concentrated solution of alk. $KMnO_4$.

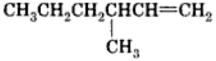
Solution: G must be a saturated hydrocarbon containing six carbon atoms in the chain and an alkyl branch so that it contains an asymmetric carbon atom. Therefore G is



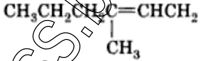
$$CH_3CH_2CH_2\underset{\underset{\textstyle CH_3}{|}}{C}HCH_2CH_3$$

(G)

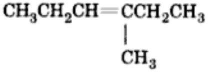
From G all other alkenes can be constructed.

A. 

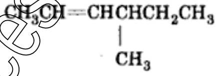
$CH_3CH_2CH_2\underset{\underset{\textstyle CH_3}{|}}{C}HCH=CH_2$

B. 

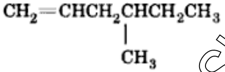
$CH_3CH_2CH_2\underset{\underset{\textstyle CH_3}{|}}{C}=CHCH_2$

C. 

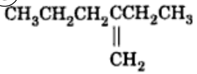
$CH_3CH_2CH=\underset{\underset{\textstyle CH_3}{|}}{C}CH_2CH_3$

D. 

$CH_3CH=CH\underset{\underset{\textstyle CH_3}{|}}{C}HCH_2CH_3$

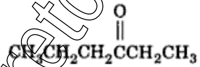
E. 

$CH_2=CHCH_2\underset{\underset{\textstyle CH_3}{|}}{C}HCH_2CH_3$

F. 

$CH_3CH_2CH_2\underset{\underset{\textstyle CH_2}{\|}}{C}CH_2CH_3$

Alkene F will give the ketone



$$CH_3CH_2CH_2\overset{\overset{\textstyle O}{\|}}{C}CH_2CH_3$$

Problem 8.39:

One mole of compound A, C_8H_{12} incapable of showing stereoisomerism, reacts with one mole of hydrogen on hydrogenation Over Pd. Compound A, undergoes ozonolysis to give a symmetrical diketone B, $C_8H_{12}O_2$. Assign structures to A and B.

Solution: Since the alkene does not exhibit stereoisomerism, it is not an open-chain compound. It cannot be a single ring with a C=C bond because it will have 14 H atoms also then the required 12. It is, therefore a bicycle ring containing a C=C bond. The alkene on ozonolysis also gives a symmetrical diketone, therefore A is

(A) (B)

Problem 8.40:

An organic compound A, C_6H_{10} on reduction first gives B, C_6H_{12} and finally C, C_6H_{14}. Compound 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 compounds A to F.

Solution: Ozonolysis of A gives two aldehydes D and E, the compound A contains C=C bond. Since the molecule A is successively reduced to C_6H_{12} and C_6H_{14} apparently it contains two C=C bonds and not one.

Structure of A can be constructed from D and E as follows :

$$CH_3CHO + OHC{-}CHO + OHCCH_3$$

$$\downarrow$$

$$CH_3{-}CH{=}CH{-}CH{=}CH{-}CH_3$$

2,4-Haxadiene

(A)

$$\downarrow H_2$$

$$CH_3CH_2CH_2CH{=}CHCH_3$$

(B)

$$\downarrow H_2$$

$$CH_3CH_2CH_2CH_2CH_2CH_3$$

(c)

CHAPTER

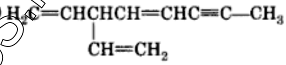
9

Alkynes

Problem 9.1:

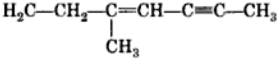
Suggest IUPAC name for reach of the following structures :

(*a*) $HC\equiv C-CH=CHCH=CH_2$ (*b*) $CH_3CH=CHC\equiv CH$ (*c*)



$H_2C=CH\underset{\displaystyle CH=CH_2}{CH}CH=CHC\equiv C-CH_3$

(*d*)



$H_2C-CH_2-\underset{\displaystyle CH_3}{C}=CH-C\equiv C-CH_3$

(*e*) $H_2C=CH-CH_2-C\equiv C-CH_2-CH_2-CH_3$

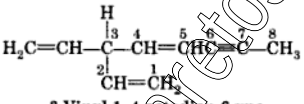
Solution: (*a*) $\overset{6}{HC}\equiv\overset{5}{C}-\overset{4}{CH}=\overset{3}{CH}-\overset{2}{CH}=\overset{1}{CH_2}$

1, 3-Hexadien-5 yne

(*b*) $\overset{5}{CH_3}-\overset{4}{CH}=\overset{3}{CH}-\overset{2}{C}\equiv\overset{1}{CH}$

3-Penten-1-yne

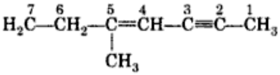
(*c*)



$H_2C=CH-\overset{\displaystyle H}{\underset{\displaystyle \overset{2}{CH}=\overset{1}{CH_2}}{\overset{3}{C}}}-\overset{4}{CH}=\overset{5}{C}\overset{6}{HC}\equiv\overset{7}{C}-\overset{8}{CH_3}$

3-Vinyl-1, 4-octadien-6-yne

(*d*)



$\overset{7}{H_2C}-\overset{6}{CH_2}-\underset{\displaystyle CH_3}{\overset{5}{C}}=\overset{4}{CH}-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{CH_3}$

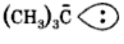
5-Methyl-4-hepten-2-yne

(*e*) $\overset{8}{H_2C}=\overset{7}{CH}-\overset{6}{CH_2}-\overset{5}{C}\equiv\overset{4}{C}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_3}$

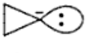
7-Octen-4-yne

Problem 9.2:

Which of the following is a weaker base ? Why ?



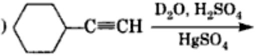
or

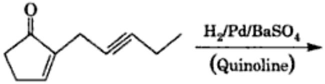


Solution: The base  is weaker because the electron pair is in an sp^2 orbital as in ethylene A cydoprapane ring behaves like a C═C bond and attracts electrons.

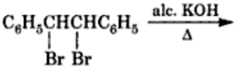
Problem 9.3:

Write the major product for each of the following reactions :

(*a*) 

(*b*) 

(*c*) $CH_3C\equiv C\,CH_3 \xrightarrow{Br_2}$

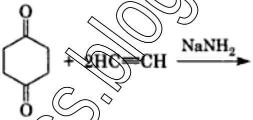
(*d*) 

$C_6H_5\underset{Br}{CH}\underset{Br}{CH}C_6H_5 \xrightarrow[\Delta]{\text{alc. KOH}}$

(*e*) 

(*f*) $CH_3C\equiv CH \xrightarrow[(ii)\ H_2O/H^+]{(i)\ O_3}$ (*g*) $CH_3C\equiv CH \xrightarrow{HI}$ (*h*) $CH_3\,CH_2\,CH_2C\equiv C\,CH_3 \xrightarrow{Li,\ NH_3}$

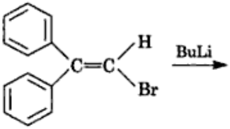
(*i*) $CH_3C\equiv CCH_2CH_3 \xrightarrow[\text{one equivalent}]{HBr}$

(*j*) 

(*k*) $HC\equiv CH \xrightarrow[(ii)\ \text{alk. } KMnO_4\text{, cold}]{(i)\ Br_2\ (\text{one equivalent})}$ (*l*) $CH_2{=}CHCH_2C\equiv CH + HBr \longrightarrow$

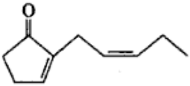
(*m*) $CH_3CH_2C\equiv CCH_2CH_3 \xrightarrow[\text{neutral}]{KMnO_4}$ (*n*) $CH_3C\equiv CHCH_3 \xrightarrow[Pt]{H_2\ (\text{one equivalent})}$

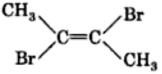
(*o*) $CH_3CH_2CH_2C\equiv CH_3 \xrightarrow{Na,\ NH_3}$ (*p*) $C_6H_5C\equiv CC_6H_5 + CHCl_3 \xrightarrow{(CH_3)_3CO^-K^+}$

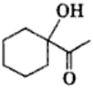
(*q*) $CH_3C=CCH_3 \xrightarrow[(ii)\ H_2O]{(i)\ NaNH_2\ \text{in inert solvent}}$ (*r*) 

(*s*) $CH_3C\equiv CCH_3 \xrightarrow{D_2\text{, Lindlar catalyst}}$ (*t*) $CH_3C\equiv CCH_3 \xrightarrow[(ii)\ CH_3COOH]{(i)\ BD_3\text{, THF}}$

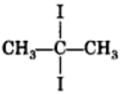
Solution: (*a*) 

(*b*) 

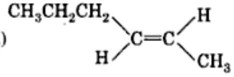
(*c*) 

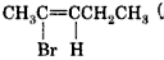
(*d*) $C_6H_5C\equiv CC_6H_5$ (*e*) 

(*f*) $CH_3COOH + HCOOH$

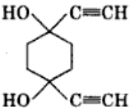
(*g*) 

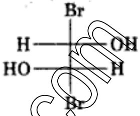
$CH_3{-}\overset{I}{\underset{I}{C}}{-}CH_3$

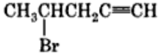
(*h*) 

(*i*) 

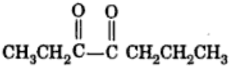
$CH_3\underset{Br}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}CH_2CH_3$

(*j*) 

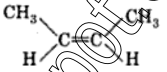
(*k*) 

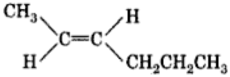
(*l*) 

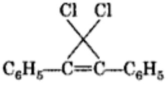
$CH_3\underset{Br}{\underset{|}{C}}HCH_2C\equiv CH$

(*m*) 

$CH_3CH_2\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}\ CH_2CH_2CH_3$

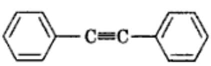
(*n*) 

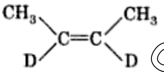
(*o*) 

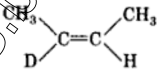
(*p*) 

(*q*) $CH_3CH_2C\equiv CH$

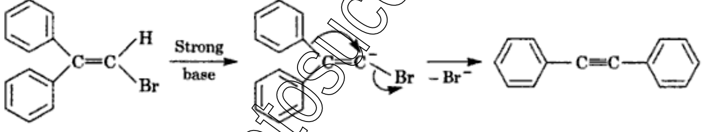
(It is an isomerization reaction)

(*r*) 

(*s*) 

(*t*) 

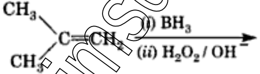
This reaction is called the *Fritsch rearrangement*. The reaction proceeds in the following sequence:

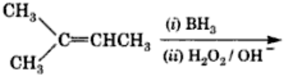


A vinyl anion is initially formed. This is followed by phenyl group migration and simultaneous expulsion of Br ion.

Problem 9.4:

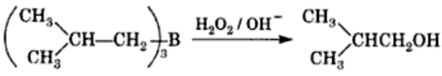
Write the product of the following hydroboration–oxidation reactions:

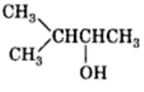
(*a*) 

(*b*) 

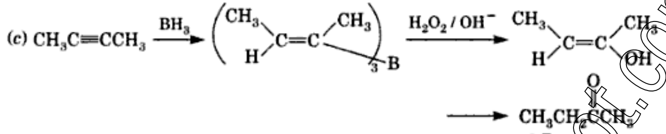
(*c*) $CH_3C\equiv CCH_3 \xrightarrow[(ii)\ H_2O_2\,/\,OH^-]{(i)\ BH_3}$ (*d*) $CH_3C\equiv CH \xrightarrow[(ii)\ H_2O_2\,/\,OH^-]{(i)\ BH_3}$

(*e*) $CH_3C\equiv CH \xrightarrow[(ii)\ H_2O_2\,/\,OH^-]{(i)\ Sia_2BH}$

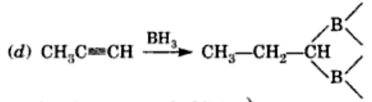
Solution: (*a*) 

(*b*) 

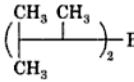
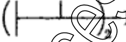
Both terminal and internal alkenes give alcohol and the addition is anti MarkowniKoff, *i.e.* -OH ataches to the least substituted carbon atom.

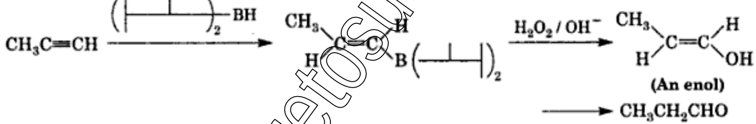


2-Butanone



(because it is not possible to stop the reaction after first stage of addition)

(*e*) Hydroboration of 1–alkynes cannot be stopped after a single addition, a second addition also takes place to give a *gem*. dibora compound. However, hydroboration of 1–alkynes after single addition can be stopped using an organoborane containing highly branched groups such as disiamyl-borane  BH or  BH and formation of undesired products can be prevented.



(An enol)

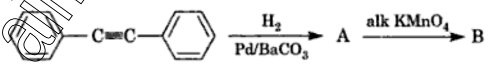
Problem 9.5:

(*a*) Identify X, Y and Z in the following sequence and write their structures.

$$CH_3CH_2C\equiv CH \xrightarrow[(ii)\ CH_3CH_2Br]{(i)\ NaNH_2} X \xrightarrow{H_2/Pd/BaSO_4} Y \xrightarrow{alk\ KMnO_4} Z$$

Is the compound Z optically active ?

(*b*) Identify A and B in the following synthetic scheme :



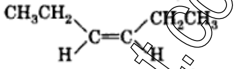
(*c*) Identify the reagents.

$$\begin{tikzcd} CH\equiv CH \arrow[r, "A"] & CH\equiv C^-\ Na^+ \arrow[r, "B"] & CH\equiv CCH_2CH_2CH_3CH_3 \arrow[dl, "C"'] \arrow[d, "D"] \\ & CH_3CH_2CH_2CH_2CH_2CHO & CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3 \end{tikzcd}$$

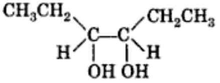
(*d*) Identify A, B and C

$$CH_3CH{=}CHCH_2CH_3 \xrightarrow[CCl_4]{Br_2} A \xrightarrow[\Delta]{\text{alc. KOH}} B \xrightarrow[\text{Lindlar catalyst}]{H_2} C$$

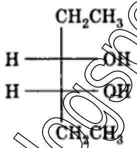
Solution: (*a*) X = $CH_3CH_2C{\equiv}CCH_2CH_3$ Y =



Z =

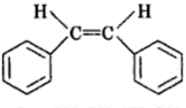


or

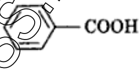


The resulting diol is not optically active. It is *meso*.

(*b*) A

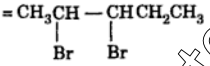


B



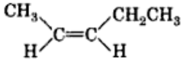
(*c*) A = $NaNH_2$ B = $CH_3CH_2CH_2CH_2Br$ C = (*i*) Sia_2BH (*ii*) H_2O_2/OH^- D = $HgSO_4/H_2SO_4/H_2O$

(*d*) A =



$$CH_3\underset{\displaystyle Br}{CH}-\underset{\displaystyle Br}{CH}CH_2CH_3$$

B = $CH_3C{\equiv}CCH_2CH_3$ C =



Lindlar catalyst yields a *cis*-alkene and no further reaction occurs.

Problem 9.6:

Write structures for the following compounds:

(*a*) But-2-yn-1, 4-diol (*b*) Vinylacetylene (*c*) 1, 4-Dichlorobut-2yne (*d*) 3-Benzyl-1-bromo-1-pentyne (*e*) 1-Sodiopropyne (*f*) 5-Dodecyne (*g*) *trans*-2-Hexen-4-yne (*h*) 3, 3-Dimethyl-1-butyne (*i*) Ethylnylcyclohexane (*j*) 5-Cyclohexyl-4-pentyn-2-*ol*

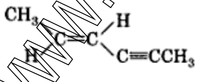
Solution: (*a*) $HOCH_2C{\equiv}CCH_2OH$ (*b*) $H_2C{=}CHC{\equiv}CH$ (*c*) $ClCH_2C{\equiv}CCH_2Cl$

(*d*)

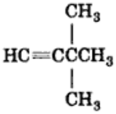
$$BrC{\equiv}C\underset{\displaystyle CH_2C_6H_5}{CH}CH_2CH_3$$

(*e*) $CH_3C{\equiv}C^-Na^+$ (*f*) $CH_3CH_2CH_2CH_2C{\equiv}CCH_2CH_2CH_2CH_2CH_3$

(*g*)

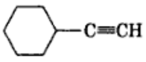


(*h*)

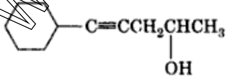


$$HC{\equiv}C\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_3$$

(*i*)



(*j*)



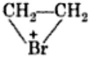
Problem 9.7:

Offer explanation :

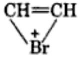
(*a*) Alkynes are less reactive than alkenes toward addition of Br_2.

(*b*) Why is terminal alkyne acidic but internal alkyne is not ? (*c*) Hydrogenation of an alkyne cannot be stopped at the alkene stage.

Solution: (*a*) The addition of Br_2 across a C=C bond occurs via a cyclic bromonium ion.



(Intermediate obtained from an alkene)



(Intermediate obtained from an alkyne)

The bromonium ion from alkyne is more strained than that formed from alkenes and thus less stable. Alkynes are thus less reactive. Remember, a product is always formed from a stable intermediate.

(*b*) An internal alkyne has hydrogens on the *sp* carbon atom in contrast to a terminal alkyne. Its acidity is similar to that of an alkane.

(*c*) Step 1 of alkyne hydrogenation to alkene is more exothermic than step 2 of alkene hydrogenation. Therefore, most of the alkyne reacts before alkene has a chance to react.

Problem 9.8:

A hydrocarbon has the formula corresponding to that of an alkyne C_nH_{2n-2} but it adds only one molecule of bromine per mole of the hydrocarbon. What type of structure does the hydrocarbon have ?

Solution: It is a cyclic alkene because a straight chain alkyne would add two moles of bromine.

Problem 9.9:

A cylinder contains one of the following gases: propane, propene or propyne. What chemical tests would you apply to identify the gases ?

Solutions: $CH_3C{\equiv}CH$, $CH_2CH{=}CH_2$, $CH_3CH_2CH_3$

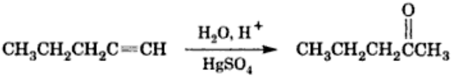
Propyne **Propene** **Propane**

Propyne forms the red colored Cu-acetylide with Cu_2Cl_2 and NH_4OH. Propene decolorizes bromine water while propane does not respond to any of these reactions.

Problem 9.10:

Hydration of an alkyne gave methyl proplyl ketone. What formula would you assign to the alkyne ?

Solution: The alkyne could be either 1-butyne or 2-butyne



$$CH_3CH_2CH_2C{\equiv}CH \xrightarrow[HgSO_4]{H_2O,\ H^+} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$$

Problem 9.11:

Write the formula for each of the isomeric hydrocarbon, C_5H_8 which contains a triple bond. Suggest names according to IUPAC system of nomenclauture.

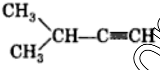
Solution: C_5H_8 has three isomers

$HC\equiv C-CH_2-CH_2-CH_3$

1-Pentyne

$CH_3-C\equiv C-CH_2-CH_3$

2-Pentyne

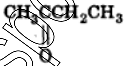


3-Methyl-1-butyne

Problem 9.12:

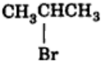
Starting from acetylene and any other reagent show how would you obtain the following ?

(a) $CH_3CH_2\equiv CH$ (b) CH_3CH_2COOH (c) $CH_3CH_2CH_2CH_3$ (d)



$CH_3\underset{\underset{\displaystyle O}{\|}}{C}CH_2CH_3$

(e)

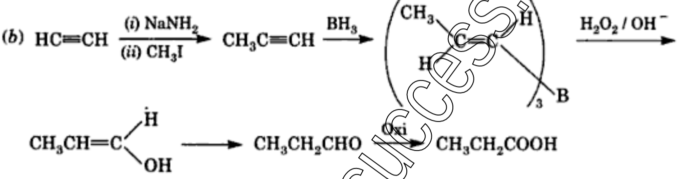


$CH_3\underset{\underset{\displaystyle Br}{|}}{C}HCH_3$

(f) $CH_2=CHCH_3$

Solution: (a) $HC\equiv CH \xrightarrow{NaNH_2} HC\equiv C^-Na^+ \xrightarrow{C_2H_5I} HC\equiv CC_2H_5$

(b)



$HC\equiv CH \xrightarrow[(ii)\ CH_3I]{(i)\ NaNH_2} CH_3C\equiv CH \xrightarrow{BH_3}$ … $\xrightarrow{H_2O_2/OH^-}$

… $\longrightarrow CH_3CH_2CHO \xrightarrow{Oxi} CH_3CH_2COOH$

(c) $HC\equiv CH \xrightarrow[liq.\ NH_3]{NaNH_2} HC\equiv C^-Na^+ \xrightarrow{C_2H_5I} HC\equiv CC_2H_5 \xrightarrow{H_2/Ni} CH_3CH_2CH_2CH_3$

(d) $HC\equiv CH \xrightarrow[(ii)\ CH_3I]{(i)\ NaNH_2} HC\equiv CCH_3 \xrightarrow[CH_3I]{NaNH_2} CH_3C\equiv CCH_3 \xrightarrow{BH_3} \xrightarrow{H_2O_2/OH^-} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3$

(e) $HC\equiv CH \xrightarrow[(ii)\ CH_3I]{(i)\ NaNH_2} HC\equiv CCH_3 \xrightarrow[H_2]{Lindlar\ Catalyst} CH_2=CHCH_3 \xrightarrow{HBr} H_3C\underset{\underset{\displaystyle Br}{|}}{C}HCH_3$

(f) $HC\equiv CH \xrightarrow[(ii)\ CH_3I]{(i)\ NaNH_2} HC\equiv CCH_3 \xrightarrow[H_2]{Lindlar\ Catalyst} CH_2=CHCH_3$

Problem 9.13:

Would $CH_3C\equiv CCH_3$ react with $NaNH_2$?

Solution: No, because no acidic terminal hydrogen is present.

Problem 9.14:

Rank the following in order of increasing acidity

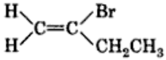
$n\text{-}C_3H_7\text{—}CH{=}CH_2$, $n\text{-}C_3H_7\text{—}C{\equiv}CH$, $n\text{-}C_4H_9CH_3$

Solution: $n\text{-}C_4H_9CH_3 < n\text{-}C_3H_7CH{=}CH_2 < n\text{-}C_3H_7C{\equiv}CH$

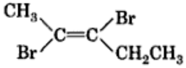
Problem 9.15:

What reaction of an appropriate alkyne would lead to the following product ?

(a)

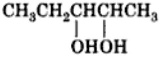


(b)



(c) CH_3CH_2COOH

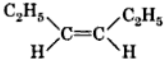
(d)



$CH_3CH_2\underset{OH}{CH}\underset{OH}{CH}CH_3$

(e) $CH_3(CH_2)_4CHO$ (f) $CH_3CH_2C{\equiv}CCH_2OH$

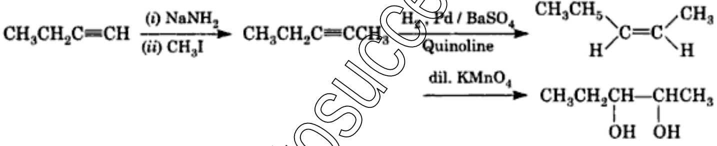
(g)



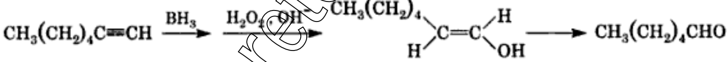
Solution:

(a) $CH_3CH_2{\equiv}CH + HBr$ (b) $CH_2CH_2C{\equiv}CCH_3 + Br_2$ (c) $CH_3CH_2C{\equiv}CCH_2CH_3 + O_3$

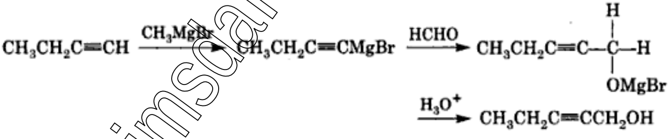
(d)



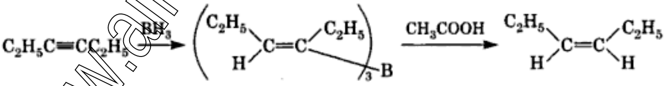
(e)



(f)



(g)



Problem 9.16:

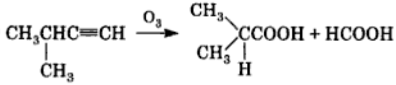
Write the product of ozonolysis O_3/H_2O of following unsaturated hydrocarbons :

(a) 2-Pentyne (b) 1-Pentyne (c) 1, 4-Pentadiene (d) 3-Methyl-1-butyne

Solution: (a) $CH_3CH_2C{\equiv}CCH_3 \xrightarrow{O_3} CH_3CH_2COOH + CH_3COOH$

(*b*) $CH_3CH_2CH_2C \equiv CH \xrightarrow{O_3} CH_3CH_2CH_2COOH + HCOOH$

(*c*) $CH_2{=}CHCH_2CH{=}CH_2 \xrightarrow{O_3} HCHO + HOOCCH_2COOH + HCHO$

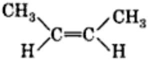
(*d*) 

$$CH_3\underset{\underset{CH_3}{|}}{C}HC \equiv CH \xrightarrow{O_3} (CH_3)(CH_3)\underset{\underset{H}{|}}{C}COOH + HCOOH$$

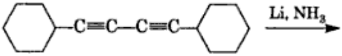
Problem 9.17:

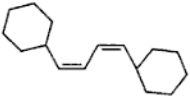
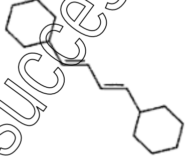
Select the correct answer.

(*a*) Which of the following has the lowest dipole moment ?

A.  B. $CH_3C \equiv CCH_3$ C. $CH_3CH_2C \equiv CH$

D. $CH_2{=}CH{-}C \equiv CH$

(*b*)  A, A is

A.  B.  C. None D. Both

(*c*) Which of the following hydrocarbon will react with CH_3MgBr ?

A. $CH_3CH_2CH_2CH_2CH_3$ B. $CH_3C \equiv C{-}CH{=}CH_2$

C. $CH_3C \equiv CCH_2CH_3$ D. $CH_3CH_2CH_2C \equiv CH$

(*d*) Which reagent can easily distinguish between 1-butyne and 2-butyne ?

A. Amm. Cu_2Cl_2 solution B. Dil $H_2SO_4/HgSO_4$

C. Br_2/CCl_4 D. H_2, Lindlar Catalyst

(*e*) 1-Butyne reacts with hot alk. $KMnO_4$ to produce.

A. $CH_3CH_2CH_2COOH$ B. CH_3CH_2COOH

C. $CH_3CH_2COOH + CO_2$ D. $CH_3CH_2COOH + HCOOH$

(*f*) Which of the following represents the given mode of hybridization ?

sp^2–*sp*^{2}–*sp*–*sp* from left to right.

A. $CH_2{=}CH{-}C \equiv N$ B. $CH \equiv C{-}C \equiv CH$ C. $CH_2{=}CH{-}CH{=}CH_2$

D. $CH{=}CH{=}C{=}CH$

(*g*) The following two reactions

(*i*) $CH_3C \equiv CCH_3 \xrightarrow[(ii)\ H_2O_2\ /\ OH^-]{(i)\ B_2H_6}$ (*ii*) $CH_3C \equiv CCH_3 \xrightarrow{H^+/\ H_2O\ /\ HgSO_4}$

Yield

A. Same aldehyde B. Different aldehydes C. Same ketons

D. Different ketones

(*h*) Select the incorrect statement :

A. Trivinylborons on protonation with CH_3COOH give a *cis*-alkene.

B. $CH_3C{\equiv}CH$ turns red litmus blue.

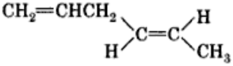
C. $CH_3C{\equiv}CH_3$ on reduction with Li/NH_3 gives a *trans* alkene.

D. Primary alkyl halides do not respond to Wurtz reaction.

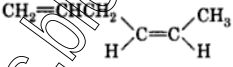
(*i*) The following reduction

$$CH_2{=}CH{-}CH_2{-}C{\equiv}C{-}CH_3 \xrightarrow[\text{Lindlar Catalyst}]{H_2\text{ , Pd/BaSO}_4}$$

gives.

A. 

$CH_2{=}CHCH_2(H)C{=}C(H)CH_3$

B. 

$CH_2{=}CHCH_2(H)C{=}C(CH_3)H$

C. $CH_3CH_2CH_2CH_2CH_2CH_3$ D. $CH_3CH_2CH_2C{\equiv}CCH_3$

(*j*) Which of the following compound in most acidic ?

A. $CH_2{=}CH_2$ B. $CH{\equiv}CH$ C. CH_3OH D. CH_3Cl

(*k*) What is the decreasing order of base strength of the following bases;

$$OH^-,\ NH_2^-,\ HC{\equiv}C^-,\ \text{and}\ CH_3CH_2^-$$

A. $CH_3CH_2^- > NH_2^- > HC{\equiv}C^- > OH^-$

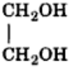
B. $NH_2^- > HC{\equiv}C^- > OH^- > CH_3CH_2^-$

C. $HC{\equiv}C^- > CH_3CH_2^- > NH_2^- > OH^-$

D. $OH^- > NH_2^- > HC{\equiv}C^- > CH_3CH_2^-$

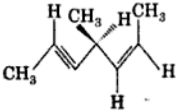
(*l*) Identify compound B in the following scheme

$$HC{\equiv}CH \xrightarrow{O_3\text{ , }OH^-} A \xrightarrow{Zn\ /\ CH_3COOH} B$$

A. CH_3OH B. CH_3CH_2OH C.  D. CH_3COOH

$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$

(*m*) Hydrogenation of the following compound in the presence of H_2 and poisoned



palladium catalyst gives

A. An optically active compound B. An optically inactive compound

C. A racemic mixture D. A diastereoisomeric mixture

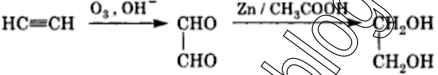
Solution: (*a*) B, because this molecule is symmetrical and linear. (*b*) B, Li-NH_3 reuduce an alkyne to give a *trans* alkene. No further reaction takes place. (*c*) D, It is a terminal alkyne and thus contains an acidic hydrogen.

(*d*) A, $2CH_3CH_2C{\equiv}CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow 2RC{\equiv}Cu + 2NH_4Cl + 2H_2O$

2-Butyne does not react (Red ppt.)

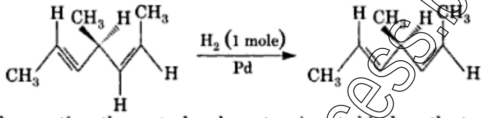
(*e*) C, $CH_3CH_2C{\equiv}CH \xrightarrow[\Delta]{\text{alk. } KMnO_4} CH_3CH_2COOH + CO_2$ (*f*) A , $\overset{sp^2}{CH_2}{=}\overset{sp^2}{CH}{-}\overset{sp}{C}{\equiv}\overset{sp}{N}$ (*g*) C

(*h*) B, the terminal alkynes are weakly acidic. (*i*) B, a *cis* alkene. (*j*) B, the $CH{\equiv}C^-$ is only slightly basic. (*k*) A (*l*)



$$HC{\equiv}CH \xrightarrow{O_3,\ OH^-} \begin{array}{c} CHO \\ | \\ CHO \end{array} \xrightarrow{Zn\,/\,CH_3COOH} \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

(*m*) B,



On hydrogenation, the central carbon atom is not chiral, as the two groups become equal.

Problem 9.18:

A compound contains C = 90% and H = 10% and its molecular weight is 54. One mole of the compound absorbs two moles of bromine and when it is shaken with Cu_2Cl_2 in ammonia, the compound produces a white precipitate containing copper. Draw the structure of the compound.

Solution: Empirical Formula

Element	*Percentage composition*	*Atomic weight*	*Relative number of atoms*	*Simplest ratio*	
C	90	12	7.5	1	2
H	10	1	10	1.5	3

The empirical formula is C_2H_3 and empirical formula weight = 27

Molecular formula is $(C_2H_3)_n$ where $n = \frac{54}{27} = 2$

$$= (C_2H_3)_2$$

$$= C_4H_6$$

As one mole of the compound absorbs two moles of bromine, the molecular formula corresponds to butyne. The butyne must be terminal since it produces a precipitate with Cu_2Cl_2 in NH_3. The structure of the compound is

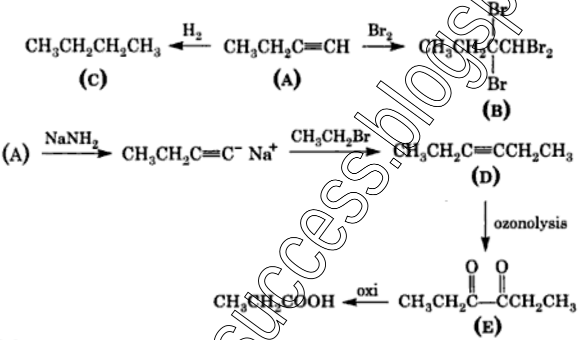
$$CH_3CH_2C{\equiv}CH$$

1-Butyne

Problem 9.19:

A hydrocarbon A, of molecular weight 54 reacts with an excess of Br_2 in CCl_4 to give a compound B, whose molecular weight is 593% more than that of A. However, on catalytic hydrogenation with excess of H_2, A forms C, whose molecular weight is only 7.4% more that that of A. A reacts with CH_3CH_2Br in the presence of $NaNH_2$ to give another hydrocarbon D which on ozonolysis yields a diketone E. Compound E, on oxidation gives propanoic acid Assign structures A to E.

Solution: Since A reacts with $NaNH_2$ and also gives propanoic acid at the end, therefore its structure is :



$$\underset{(C)}{CH_3CH_2CH_2CH_3} \xleftarrow{H_2} \underset{(A)}{CH_3CH_2C{\equiv}CH} \xrightarrow{Br_2} \underset{(B)}{CH_3CH_2\overset{Br}{\underset{Br}{C}}CHBr_2}$$

$$(A) \xrightarrow{NaNH_2} CH_3CH_2C{\equiv}C^- \, Na^+ \xrightarrow{CH_3CH_2Br} \underset{(D)}{CH_3CH_2C{\equiv}CCH_2CH_3}$$

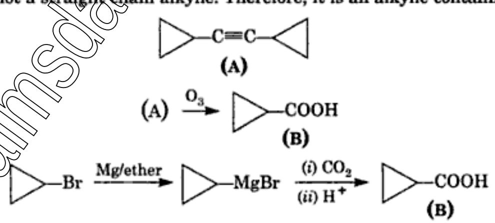
$$\downarrow \text{ozonolysis}$$

$$CH_3CH_2COOH \xleftarrow{oxi} \underset{(E)}{CH_3CH_2\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_2CH_3}$$

Problem 9.20:

A hydrocarbon A, C_6H_{10} on ozonolysis gives compound B, $C_6H_6H_2$ only. The compound B can also be obtained from the alkyl bromide C_3H_5Br on treatment with magnesium in dry ether followed by reaction with CO_2 and acidfication. Identify A, B and C

Solution: Since A on ozonolysis gives only $C_4H_6O_2$ a carboxylic acid, it is a symmetrical alkyne. Moreover, it is not a straight chain alkyne. Therefore, it is an alkyne containing two rings.



Problem 9.21:

A hydrocarbon A, was found to contain 85.7% carbon and 14.3% hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon B. One gram of hydrocarbon A, just decolorizes 38.05 of a 5% solution (by weight) of Br_2 in CCl_4. Compound A, on oxidation with conc $KMnO_4$ gave compound C, C_4H_8O and compound C could easily be prepared by the action of acidic aqueous mercuric sulfate on 2-butyne. Determine the molecular formula of A and identify structures A, B and C

Solution:

Element	*Percentage Composition*	*Atomic Weight*	*Rel. No. of Atoms*	*Simplest Ratio*
C	85.7	12	7.14	1
H	14.3	1	14.3	2

Empirical formula of A is CH_2

Since compound A consumes 1 mole of H_2, it contains only one C = C bond.

1 g of A consumes 38.05 g of 5% Br_2 solution.

$$\therefore \ 1 \text{ g of A consumes} = 38.05 \times \frac{5}{100}$$

$$= 1.9 \text{ g of } Br_2 \, (100\%)$$

1.9 g of Br_2 is absorbed by 1 g of A

$$16 \text{ g of } Br_2 \text{ is absorbed by } \frac{160}{109}$$

$$= 84.1 \text{ g}$$

Therefore, molecular weight of A is = 84.1

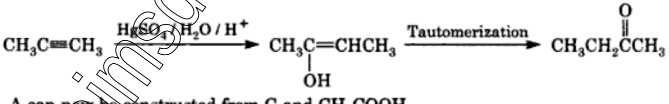
$$\text{Mol. formula} = \frac{84.1}{14} = 6$$

$$= (CH_2)_6$$

$$= C_6H_{12}$$

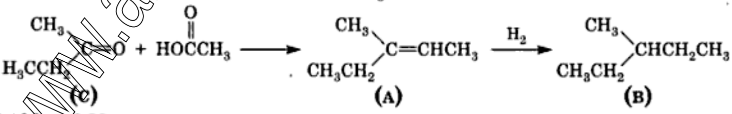
$$\underset{}{(A)} \xrightarrow{\text{Conc. } KMnO_4} \underset{(C)}{C_4H_8O} + CH_3COOH$$

To identify C, let us prepare it from 2-Butyne.



$$CH_3C{\equiv}CH_3 \xrightarrow{HgSO_4/H_2O/H^+} CH_3\underset{\displaystyle OH}{\underset{|}{C}}{=}CHCH_3 \xrightarrow{\text{Tautomerization}} CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_3$$

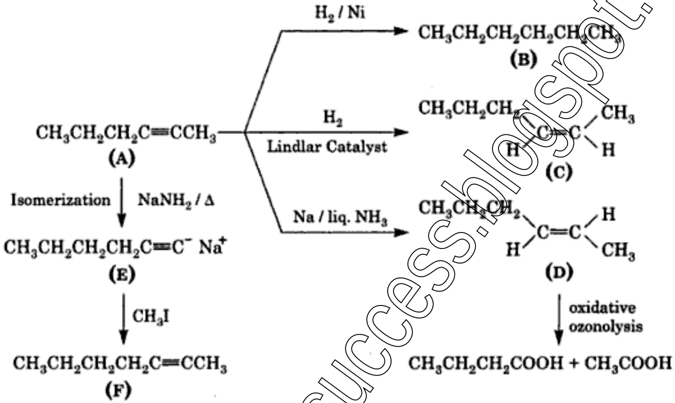
A can now be constructed from C and CH_3COOH



Problem 9.22:

Hydrocarbon A, C_6H_{10} on treatment with H_2/Ni, H_2/Lindlar catalyst and Na/liq NH_3 forms three different reduction products B, C and D respectively. A, does not form any salt with ammonical $AgNO_3$ 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 A to E with proper reasoning.

Solution: Reduction of A containing six carbon atoms with different reducing agents gives different geometrical isomers. Therefore, it cannot be a symmetrical alkyne such as 3-hexyne. It is rather 2-hexyne.



CHAPTER
10
Polymers

Problem 10.1:

Describe briefly the following with a suitable example:

A polymers, functionality, elastomers, thermoplastic polymers, thermosetting polymers.

Plastics, copolymerization, radical inhibitor, monomer, degree of polymerization, branched polymer and a polyamide.

Solution: A Polymer. A Polymer may be described as a large or giant molecule formed by linking together smaller molecules.

Functionality. The number of reactive sites present in a monomer is referred to as its functionality. Ethylene monomer, for instance, has a functionality of two.

Elastomers. Elastomers are those polymers which on vulcanization convert into rubber—like products and have elastic properties.

Thermoplastic Polymers. A thermoplastic is one which on heating becomes soft and can be moulded to any shape. On cooling they become hard and rigid. During this process no chemical change takes place. A thermoplastic polymer can assume a linear or branched structure. Polyethylene, polystyrene, polyprophylene, are examples.

Thermosetting Polymers. A thermosetting polymer is one which on heating results in a three-dimensional cross-linked structure. The change is irreversible. The resulting polymer is hard, rigid and insoluble. Bakelite and epoxy resins are some such polymers.

Plastics. When a polymer is molded into hard and tough utility articles by the application of heat or pressure it is called a *plastic.* Polyethylene PVC, polystyrene etc. are examples of plastics.

Copolymerization. The process by which two monomers of different chemical structures are polymerized is called *copolymerization*. Saran wrap and Buna rubbers are examples.

Radical Inhibitor. Those compounds which are capable of inhibiting or stopping the chain growth process in a free radical polymerization are called *inhibitors.* A representative example is 2, 6-*di* *t*-butyl-4-methylphenol.

Monomer. The individual small molecules from which a polymer is formed is called a *monomer.*

Degree of Polymerization. The length of the polymer chain is specified by the number of repeat units. This is called the *degree of polymerization.*

Branched Polymers. Those polymers which contain branches along the main chain of the polymer are called *branched polymers.*

Polyamides. Polyamides are made from a chemical reaction between diacids and diamines and contain amide linkages. The most common polyamide is nylon 6, 6.

Problem 10.2:

Atmospheric oxygen is a good inhibitor. Show its inhibiting action with a growing polymer chain ($P^{\bullet}$)

Solution: Oxygen is biradical and since $P^{\bullet}$ is the growing polymer chain the following reaction takes place.

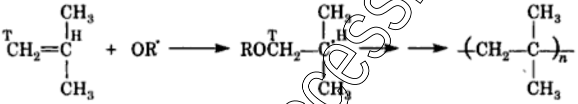
$$P^{\bullet} + {}^{\bullet}O{-}O^{\bullet} \longrightarrow P{-}O{-}O^{\bullet}$$
$$P{-}O{-}O^{\bullet} + P^{\bullet} \longrightarrow P{-}O{-}O{-}P$$

The chain is thus terminated and no more growing polymer chain is observed.

Problem 10.3:

Show the head to tail free radical polymerization of the alkene $CH_2{=}C(CH_3)_2$.

Solution:



$$\overset{T}{C}H_2{=}\underset{CH_3}{\overset{CH_3}{C}}{}^{H} + OR^{\bullet} \longrightarrow RO\overset{T}{C}H_2{-}\underset{CH_3}{\overset{CH_3}{C}}{}^{\bullet H} \longrightarrow \longrightarrow \left(CH_2{-}\underset{CH_3}{\overset{CH_3}{C}} \right)_n$$

The $OR^{\bullet}$ radical first attacks the tail end of the alkene forming a stable cation. This cation attacks the tail end of second alkene molecule leading to head and tail polymerization.

Problem 10.4:

Which of the following monomers will react faster in cationic polymerization? Why?

$$CH_2{=}CHCH_3, \quad CH_2{=}C(CH_3)_2, \quad CH_2{=}CHCH(CH_3)_2$$

Solution: $CH_2{=}C(CH_3)_2$ will react faster than the other two alkenes because of the formation of a stable tertiary carbocation during polymerization.

Problem 10.5:

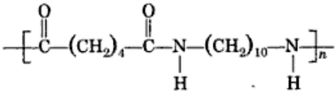
Describe coordination polymerization.

Solution: Polymerization reaction especially of alkenes and dienes catalyzed by organometallic compounds is called *coordination polymerization*. These catalyst, are prepared by the interaction of alkyls of metals of groups I to III of the periodic table with halides of transition metals of groups IV to VIII. A combination of triethyl aluminium with titanium chloride is the typical Ziegler-Natta catalyst $[(C_2H_5)_3Al.\ TiCl_4]$. The first step in this polymerization is the formation of an alkene monomer- catalyst complex. Polymerization occurs due to the insertion of an alkene monomer unit between the Ti—C bond. In this process branching of polyethylene is virtually avoided and a high density polyethylene is obtained.

Problem 10.6:

Write a general formula for Nylon 6, 10.

Solution: General formula for Nylon 6, 10 is:



$$-\!\!\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_{10}-\underset{H}{\underset{|}{N}}\right]_n\!\!-$$

This means one monomer has six while the other has ten carbon atoms.

Problem 10.7:

Describe the following terms:

Chain polymerization and step-growth polymerization.

Solution: Chain Polymerization. It is a process in which molecules of monomer are simply added together. It is generally initiated by free radicals. No by-product is formed. The product has the same elemental composition as that of the monomer.

Step-growth Polymerization. In this the polymer is formed through a reaction between functional groups of two monomers with the elimination of a small molecule like water in a stepwise manner. Condensation polymers are now a day called step-growth polymers because they grow in a stepwise manner. Dacron polyester is an example.

Problem 10.8:

Describe the following with a suitable example:

Butyl rubber, gum rubber, soft rubber, synthetic rubber and thiokol rubber.

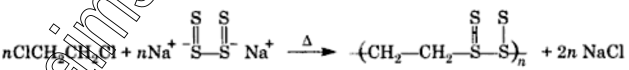
Solution: Butyl Rubber. A copolymer of isobutylene with 2-5% isoprene is marketed under the commercial name *butyl rubber.*

Gum Rubber. This rubber is obtained by coagulating the latex, a colloidal solution of rubber with 1% acetic acid.

Soft Rubber. Gum rubber on vulcanization in the presence of 1-2% of sulfur is referred to as *soft rubber.*

Synthetic Rubber. Synthetic rubbers are man-made rubbers and there are different types of synthetic rubbers. The simplest is polybutadiene obtained by the polymerization of 1, 3-butadiene. Another example is polychloroprene (neoprene).

Thiokol Rubber. It is a polymer of 1, 2-dichloroethane and sodium polysulfide.



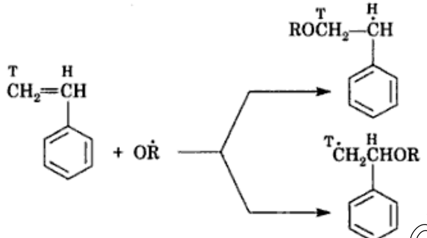
$$n\,ClCH_2CH_2Cl + n\,Na^+\ {}^-\overset{S}{\overset{\|}{S}}-\overset{S}{\overset{\|}{S}}{}^-\ Na^+ \xrightarrow{\Delta} -\!\!\left(CH_2-CH_2-\overset{S}{\overset{\|}{S}}-\overset{S}{\overset{|}{S}}\right)_n + 2n\,NaCl$$

Thiokol has poor strength. It is used for making containers for transporting solvents and for making hoses and gaskets.

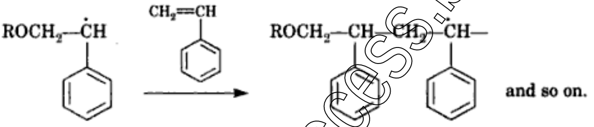
Problem 10.9:

Account for the face that radical polymerization of styrene occurs in a head-to-tail manner.

Solution: Two radicals are formed depending on the attack of $O\dot{R}$ (initiator) at the two carbon atoms linked by a double bond in styrene.



Out of these two radicals the former is more stable being secondary and also stabilized by the phenyl ring, therefore this will control the chain propagation step. The formation of this radical is also favored by the fact that attack of $O\dot{R}$ at the internal carbon atom will be sterically hindered. The stable radical will now attack another styrene molecule at the tail end generating a new radical.

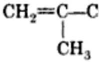
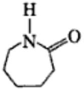


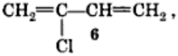
The process will continue. The growing polymer chain would thus be finally joined in a head-to-tail manner.

Problem 10.10:

Give the structure of the monomer/monomers from which each of the following is likely to be made.

Plexiglass, orlon, teflon, nylon-6, saran wrap, neoprene, tedlar, styrofoam and Buna-*S*.
1 2 3 4 5 6 7 8 9

Solution: 
$CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}COOCH_3$, $CH_2{=}CHCN$, $CF_2{=}CF_2$,  , $CH_2{=}CHC_6H_5$
1 2 3 4

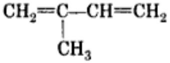
$CH_2{=}CCl_2 + CH_2{=}CHCl$, 
$CH_2{=}\underset{Cl}{\underset{|}{C}}{-}CH{=}CH_2$, $CH_2{=}CHF$,
5 6 7

$CH_2{=}CHC_6H_5$ and $CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CHC_6H_5$
8 9

Problem 10.11:

Describe natural rubber. What type of polymer is it?

Solution: Natural rubber is a mixture of hydrocarbons having the empirical formula C_5H_8. Natural rubber is highly unsaturated. A careful ozonolysis confirms that it is a linear chain polymer of isoprene :



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2$$

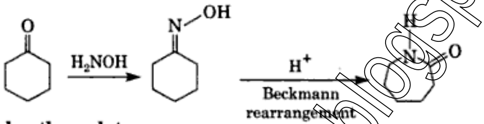
Isoprene on polymerization gives natural rubber. It is a chain polymer.

Problem 10.12:

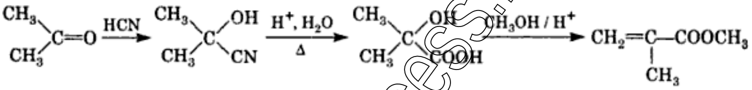
Suggest a synthesis of the monomers used for the formation of the following polymers:

Nylon-6, polymethylmethacrylate, polytetrafluoroethylene, polyacrylonitrile, neoprene and polystyrene.

Solution: Nylon-6



Polymethylmethacrylate



Methylmethacrylate

Polytetrafluoroethylene

$$CHCl_3 + 2HF \longrightarrow CHClF_2 + 2HCl$$

$$2CHClF_2 \xrightarrow{\text{Heat}} CF_2{=}CF_2 + 2HCl$$

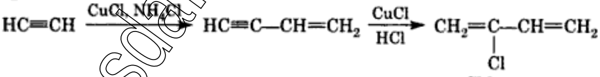
Tetrafluoroethylene

Polyacrylonitrile

$$HC{\equiv}CH + HCN \xrightarrow{\text{CuCl in HCl}} CH_2{=}CHCN$$

Acrylonitrile

Neoprene



$$HC{\equiv}CH \xrightarrow{\text{CuCl, }NH_4Cl} HC{\equiv}C{-}CH{=}CH_2 \xrightarrow[\text{HCl}]{\text{CuCl}} CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2$$

Chloroprene

Polystyrene

$$C_6H_6 + CH_2{=}CH_2 \xrightarrow[\Delta]{AlCl_3} C_6H_5CH_2CH_3 \xrightarrow[600°C]{ZnO} C_6H_5CH{=}CH_2$$

Styrene

Problem 10.15:

Describe the purpose of the following compounds in polymer chemistry: benzoyl peroxide, hydroquinone, carbon tetrachloride, ethanethiol, hydrogen peroxide.

Solution: Benzoyl peroxide – free radical initiator
Hydroquinone – antioxidant
Carbon tetrachloride – chain transfer agent

Ethanthiol	–	chain transfer agent
Hydrogen peroxide	–	free radical initiator

Problem 10.14:

List three methods of terminating a growing polymer chain with suitable examples in free radical polymerization.

Solution: Three methods for terminating a growing polymer chain are:

(*i*) Coupling (*ii*) Disproportionation (*iii*) Addition of free radical inhibitors

Problem 10.15:

Answer the following and give reasons:

(*a*) Can ethylene be polymerized by the cationic process ? (*b*) Is polyvinyl alcohol soluble in water ? (*c*) Is natural rubber flexible ? (*d*) Can neoprene be used for making delivery hoses for petrol ?

Solution: (*a*) No, a stable carbocation is not formed by the addition of H^+ to ethylene. (*b*) Yes, makes H-bond with water. (*c*) Yes, because there is free rotation about the C—C bond. (*d*) Yes, because it is non-inflammable.

Problem 10.16:

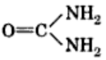
What is a crosslinked polymer ? What are the uses of crosslinked polymers ?

Solution: A cross-linked or thermosetting polymer is one which on heating gives rise to a three-dimensional cross-linked structure. It undergoes a permanent change on heating which is irreversible. The resulting polymer is hard, rigid and insoluble in organic solvents. Some familiar examples are bakelite, epoxy resins and urea-formaldehyde polymers. These polymers are used for making radio and telephone equipments, electric iron and fry pan handles and in adhesive industry.

Problem 10.17:

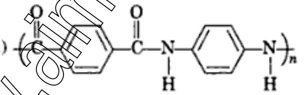
Write the repeat unit of the polymers that would be obtained in the following cases:

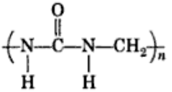
(*a*)

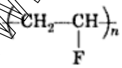

(*b*)


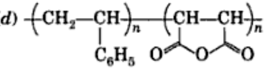
+ HCHO

(*c*) $CH_2{=}CHF$ (*d*) $CH_2{=}CHC_6H_5$ +


Solution: (*a*)


(*b*)


(*c*)


(*d*)


Problem 10.18:

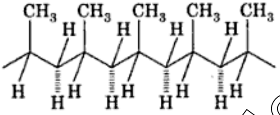
(*a*) Describe the term tacticity.

(*b*) Name and write structures of the modes of orientation of groups in polypropylene. Which of them is prepared by the Ziegler-Natta catalyst ?

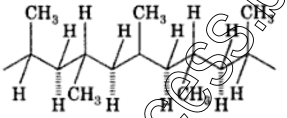
Solution: (*a*) Orientation of monomeric units about the polymer chain is called *tacticity*. It can be either regular or irregular

(*b*) There are three modes of orientation namely. Isotactic, syndiotactic and stactic.

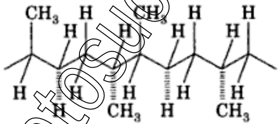
Isotactic. All the -CH_3 groups in case of propylene are arranged regularly on the same side of the C—C chain.



Syndiotactic. The groups and the hydrogen atoms fall alternatively above and below the C—C chain.



Atactic. The groups are arranged irregularly above and below the C—C chain.



The isotactic mode of polypropylene is prepared by using the Ziegler—Natta catalyst.

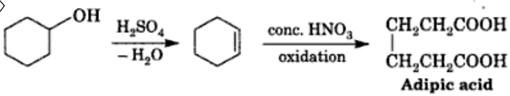
Problem 10.19:

What are step growth polymers ? Describe the synthesis of monomers used for the preparation of Nylon-6, 6. List its industrial applications.

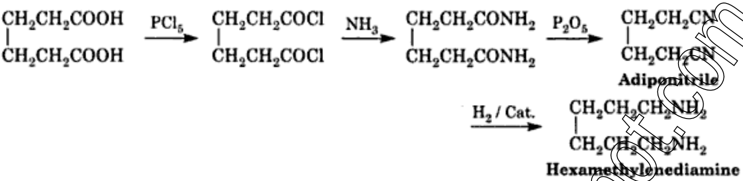
Solution: Step growth polymers are those in which two organic monomers combine with the elimination of a small molecule. In these polymers the polymeric molecules contain a structural identity repeating itself several time but less number of atoms are present than in the monomers of the repeat unit.

Nylon 6, 6 (a polyamide) uses two monomers.

(*i*) Adipic acid



(*ii*) Hexamethylenediamine

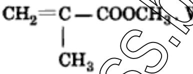


$$\begin{array}{l}CH_2CH_2COOH\\|\\CH_2CH_2COOH\end{array}\xrightarrow{PCl_5}\begin{array}{l}CH_2CH_2COCl\\|\\CH_2CH_2COCl\end{array}\xrightarrow{NH_3}\begin{array}{l}CH_2CH_2CONH_2\\|\\CH_2CH_2CONH_2\end{array}\xrightarrow{P_2O_5}\underset{\textbf{Adiponitrile}}{\begin{array}{l}CH_2CH_2CN\\|\\CH_2CH_2CN\end{array}}$$

$$\xrightarrow{H_2\,/\,Cat.}\underset{\textbf{Hexamethylenediamine}}{\begin{array}{l}CH_2CH_2CH_2NH_2\\|\\CH_2CH_2CH_2NH_2\end{array}}$$

Industrial applications. Nylon 6, 6 is used as a plastic. It is very hard and also has good tensile strength. It does not absorb moisture and it is not attacked by moth. It is used in making tyre cord, fishing nets, strings for musical instruments, in textile industry and in nearly invisible women's stockings called "*nylon*".

Problem 10.20:



Lucite is a polymer of the monomer $CH_2{=}\underset{\underset{CH_3}{|}}{C}-COOCH_3$. Would you expect Lucite to show typical properties of an alkene ?

Solution: Yes, because the C=C bond can take part in all the addition reactions.

Problem 10.21:

Which of the following polymers would you expect to exhibit stereochemical features (*i.e.* isotactic or atactic) ?

(*a*) Polyethylene (*b*) Teflon (*c*) PVC (*d*) Polystyrene (*e*) Poly (methylmethacrylate)

Solution: (*a*) No chiral center is present in the polymer (*b*) No chiral center is present in the polymer (*c*) Possible (*d*) Possible (*e*) Possible

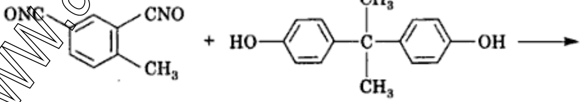
Problem 10.22:

Why are only high-boiling solvents used as plasticizers ?

Solution: In order for a plasticizer to function efficiently, it must not evaporate during the functional life time of the polymer or the commercial product for which it is used. Therefore, a high boiling solvent is most suitable.

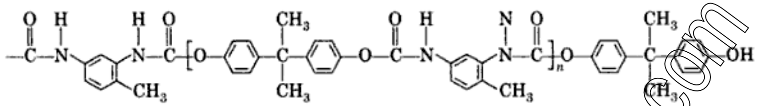
Problem 10.23:

Give the structure of the polyurethane formed in the following reaction.



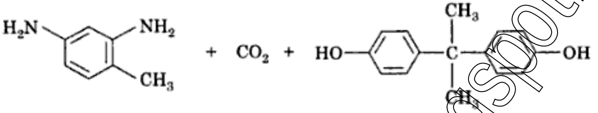
(*a*) Is this a chain polymer or a step growth polymer ? (*b*) Draw this structure of the products that would be formed on complete hydrolysis of the polymer.

Solution:



(*a*) It is a step growth polymer.

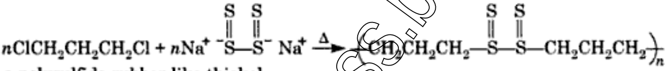
(*b*)



Problem 10.24:

Write the structure of the elastomer obtained by treating 1, 3-dichloropropane and sodium polysulfide.

Solution:

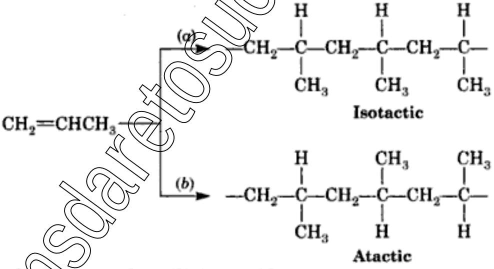


$$n\mathrm{ClCH_2CH_2CH_2Cl} + n\mathrm{Na^+}\ {}^-\overset{\overset{S}{\|}}{S}-\overset{\overset{S}{\|}}{S}{}^-\ \mathrm{Na^+} \xrightarrow{\Delta} \left(\mathrm{CH_2CH_2CH_2}-\overset{\overset{S}{\|}}{S}-\overset{\overset{S}{\|}}{S}-\mathrm{CH_2CH_2CH_2}\right)_n$$

It is a polysulfide rubber like thiokol.

Problem 10.25:

On polymerizing propylene using different catalyst, the following polymers are obtained. Give the name of the pertinent catalyst.



Solution: (*a*) Ziegler-Natta catalyst (*b*) A peroxide.

Problem 10.26:

What is synthetic rubber ? Name some compounds used for producing synthetic rubbers.

Solution: *Synthetic rubber* is the term used for synthetic rubber-like materials or elastoplastics which can complete with natural rubber in many uses especially for the manufacture of automobile tyres, the single largest users of rubber.

The following compounds are those most frequently used to produce synthetic rubber: butadiene, chloroprene, styrene, ethylene dichloride, isobutylene and acrylonitrile. Butadiene is by far the most important of these compounds. It can be used to react with itself or with other compounds such as styrene or acrylonitrile to produce synthetic rubber formulations.

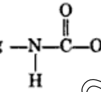
Some common examples of synthetic rubbers are :

Buna-S, polybutadiene, neoprene and thiokol.

Problem 10.27:

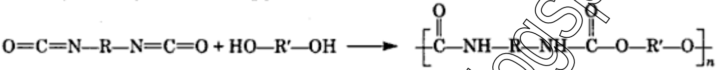
What are polyurethanes ? Describe their uses.

Solution: Polyurethanes are polymers containing the grouping



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

They are formed by treating a diisocyanate with a glycol.



$$\mathrm{O{=}C{=}N{-}R{-}N{=}C{=}O + HO{-}R'{-}OH} \longrightarrow \left[\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{C}}-\mathrm{NH}-\mathrm{R}-\mathrm{NH}-\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{C}}-\mathrm{O}-\mathrm{R'}-\mathrm{O}\right]_n$$

The glycol HO—R—OH is usually not a simple glycol but is a low molecular weight (1000-2000) glycol with -OH end groups. The diisocyanate most frequently used is 2, 4-diisocyanotoluene.

Polyurethanes are used to make flexible foam products, *i.e.*, pillows and furnishing, cushions, mattresses and elastomers and in coating.

Problem 10.28:

Discuss molecular weights of polymers.

Solution: Molecular weight in general, represents the sum of the atomic weight of each kind of atom in a molecule. In polymerization some chains grow longer than others. Therefore, the product of a polymerization process is a mixture of chains of different lengths and hence of different molecular weights. The molecular weight of a polymer for this reason are thus taken as averages.

The molecular weight of a polymer can be determined by using :

(*i*) Colligative property method (*ii*) Light scattering measurements (*iii*) Viscosity measurement.

A colligative method depends on the number of molecules present in solution and the molecular weight thus obtained is called the *number average molecular weight* denoted by $\bar{M}_n$.

$$\bar{M}_n = \frac{\text{Total molecular weight of the polymer}}{\text{Total number of molecules present}} = \frac{n_1M_1 + n_2M_2 + n_3M_3 + \ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots}$$

where n_1, n_2, n_3 are the numbers of molecular species

and M_1, M_2, M_3 are the corresponding molecular weights.

When the molecular weight is averaged according to the weight of the molecule of each type, them *weight average molecular weight* $\bar{M}_w$ is obtained.

$$\bar{M}_w = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2 + \ldots\ldots}{n_1M_1 + n_2M_2 + n_3M_3 + \ldots\ldots}$$

where n_1, n_2, n_3 and M_1, M_2, M_3 have the same meaning as above. The value of $\bar{M}_w$ is often higher than $\bar{M}_n$.

Problem 10.29:

Select the correct answer.

(*a*) Buna-N is a polymer of

A. Vinyl chloride and styrene B. Vinyl chloride and 1, 2-butadiene

C. Vinyl chloride and 1, 3-butadiene D. 1, 3-Butadiene and styrene

(*b*) Monomer of neoprene is

A. Chloroprene B. Isoprene C. Vinyl chloride D. Vinylacetylene

(*c*) Monomer for the preparation of teflon is

A. $CHCl_2—CHF_2$ B. $Cl_2C=CF_2$ C. F_2CHCHF_2 D. $F_2C=CF_2$

(*d*) Polyacrylonitrile is called

A. Teflon B. Lucite C. Acrilam D. Styrofoam

(*e*) Adipic acid is one of the monomers for

A. Nylon-6 B. Nylon 6, 6 C. Bakelite D. Polyethyleneterephthalate

(*f*) Non-sticking frying pans are coated with

A. Polyethylene B. Polystyrene C. Polytetrafluoroethylene

D. Chlorofluoromethane

(*g*) Phenol is used in the manufacture of

A. Nylon B. PVC C. Polystyrene D. Bakelite

Solution: (*a*) C (*b*) A (*c*) D (*d*) C (*e*) B (*f*) C (*g*) D

CHAPTER

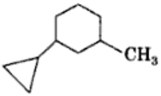
11

Cycloalkanes

Problem 11.1:

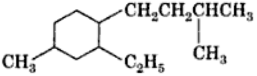
Name the following compounds:

(*a*)

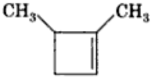


(*b*)

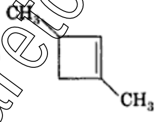
(*c*)



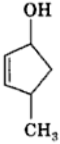
(*d*)



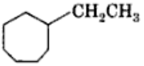
(*e*)



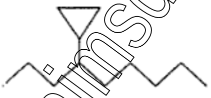
(*f*)



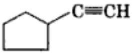
(*g*)



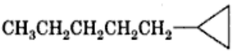
(*h*)



(*i*)



(*j*)



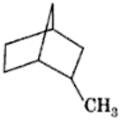
(*k*)

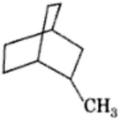
(*l*)

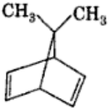
Solution: (*a*) 1-Cyclopropyl-3-methylcyclohexane (*b*) Propylcyclobutane (*c*) 2-Ethyl-4-methyl-1-sec. butylcyclohexane (*d*) 2, 3-Dimethylcyclobutene (*e*) 1, 3-Dimethylcyclobutene (*f*) 4-Methylcyclopent-2-en-1-ol (*g*) Ethylcycloheptane (*h*) 4-Cyclopropylnonane (*i*) Ethynylcyclopentane (*j*) 1-Cyclopropylpentane (*k*) *trans*-1, 2-Dimethylcyclobutane (*l*) *cis*-1, 2-Dimethylcyclopropane

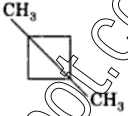
Problem 11.2:

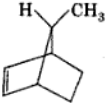
Suggest a name for the following bridgehead compounds:

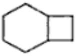
(*a*)


(*b*)


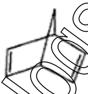
(*c*)


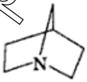
(*d*)


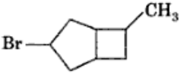
(*e*)


(*f*)


(*g*)


(*h*)


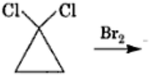
(*i*)


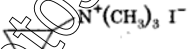
(*j*)


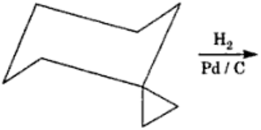
Solution: (*a*) 2-Methylbicyclo [2.2.1] heptane (*b*) 2-Methylbicyclo [2.2.2] octane (*c*) 7, 7-Dimethylbicyclo [2.2.1] hepta-2, 5-diene (*d*) 1, 3-Dimethylbicyclo [1.1.0] butane (*e*) 7-Methylbicyclo [2.2.1] hept-2-ene (*f*) Bicyclo [4.2.0] octane (*g*) Spiro [5.2] octane (*h*) Bicyclo [2.2.1] hepta-2, 5-diene (*i*) 1-Azabicyclo [2.2.1] heptane (*j*) 6-Bromo-2-methylbicyclo [3.2.0] heptane

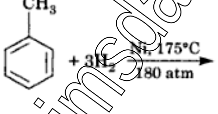
Problem 11.3:

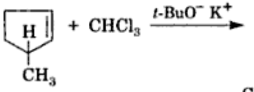
Predict the product for each of the following reactions:

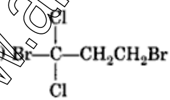
(*a*)


(*b*)


(*c*)


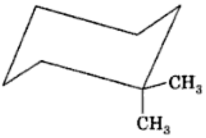
(*d*)


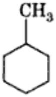
(*e*)


Solution: (*a*)


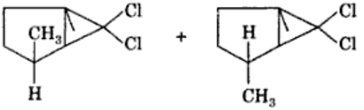
$Br-C(Cl)_2-CH_2CH_2Br$

(*b*)


(*c*)


(*d*)


(*e*)



The cyclopropane ring is either *cis* or *trans* to the methyl group.

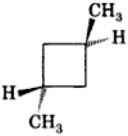
Problem 11.4:

Draw structures for the following compounds:

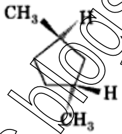
(*a*) *meso*-1,2-Dicarboxycyclobutane (*b*) *trans*-1, 3-Dimethylcyclobutane (*c*) *trans*-1, 3-Dimethylcyclopentane

Solution: (*a*)

(*b*)



(*c*)



Problem 11.5:

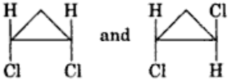
Describe the relationship between each pair of structures:

(*i*) Constitutional isomers
(isomers differing in the manner bonded together)

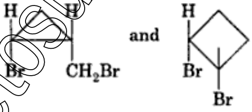
(*ii*) Stereoisomers (*cis* and *trans* isomers)

(*iii*) Different compounds :

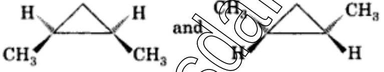
(*a*)



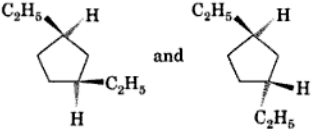
(*b*)



(*c*)

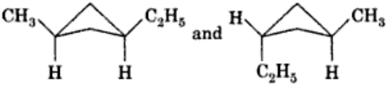


(*d*)

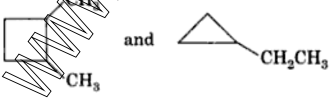


(*e*)

(*f*)



(*g*)

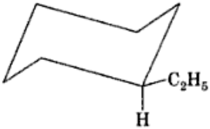


Solution: (*a*) Stereoisomers (*b*) Constitutional isomers (C_3 *vs* C_4) (*c*) Same (both are *cis*) (*d*) Stereoisomers (*e*) Constitutional isomers (C_5 *vs* C_6) (*f*) Stereoisomers (*g*) Different compounds

Problem 11.6:

Which form of ethylcyclohexane would be present in a large amount at equilibrium ?

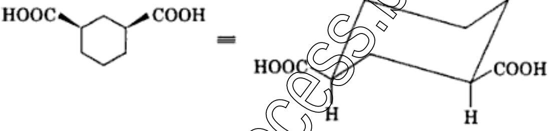
Solution: One in which the ethyl group is in the equatorial position.

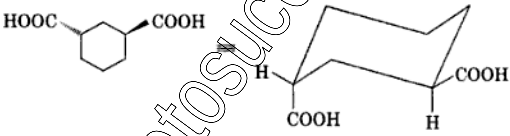


Problem 11.7:

Draw the optically active and *meso* forms of 1, 3-cyclohexanedicarboxylic acid.

Solution:



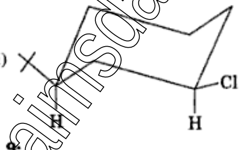


Problem 11.8:

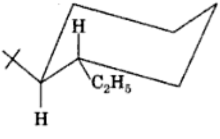
Draw the most stable conformation of

(*a*) *cis*-1-*t*-Butyl-3-chlorocyclohexane (*b*) *trans*-1-*t*-Butyl-2-ethylcyclohexane.

Solution: (*a*)



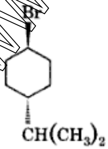
(*b*)



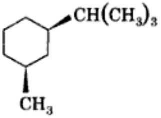
Problem 11.9:

Draw the most stable conformation of each of the following structures:

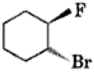
(*a*)



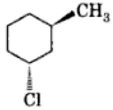
(*b*)



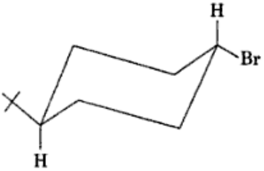
(*c*)



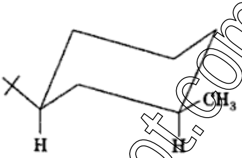
(*d*)



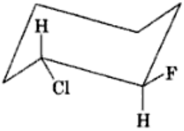
Solution: (*a*)



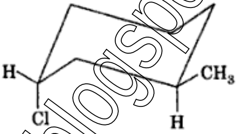
(*b*)



(*c*)



(*d*)



Problem 11.10:

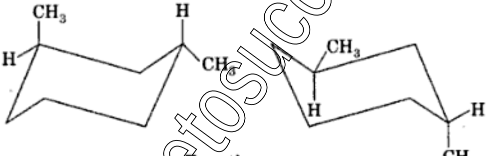
For each of the following compounds indicate whether the two chair forms are:

(*i*) Identical molecules (*ii*) Enantiomers or (*iii*) Diastereoisomers

(*a*) *trans*-1, 3-Dimethylcyclohexane (*b*) *cis*-1, 4-Dimethylcyclohexane

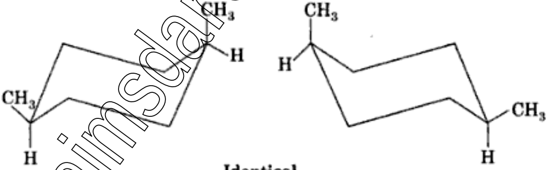
(*c*) *cis*-1, 3-Dimethylcyclohexane.

Solution: (*a*)



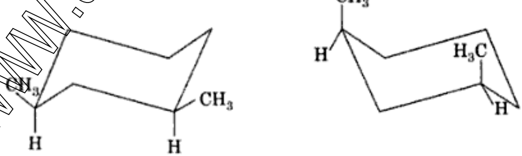
Enantiomers

(*b*)



Identical

(*c*)

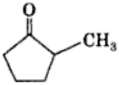


Diastereoisomers

Problem 11.11:

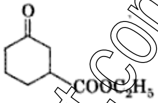
Suggest IUPAC name for each of the following structures:

(*a*)

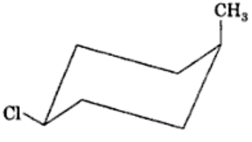


(*b*)

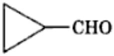
(*c*)



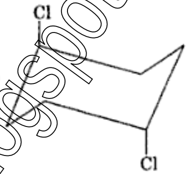
(*d*)



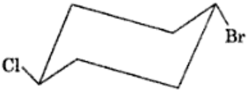
(*e*)



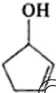
(*f*)



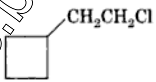
(*g*)



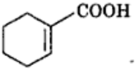
(*h*)



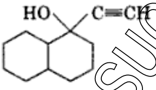
(*i*)



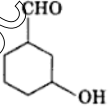
(*j*)



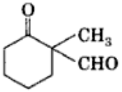
(*k*)



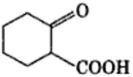
(*l*)



(*m*)



(*n*)

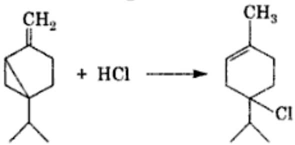


(*o*)

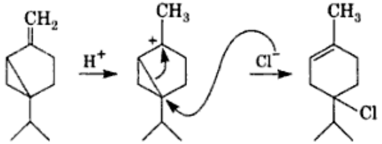
Solution: (*a*) 2-Methylcyclopentanone (*b*) *cis*-1, 3-Dichlorocyclobutane (*c*) 3-Oxocarboethoxycyclohexane (*d*) *cis*-1-Chloro-4-methylcyclohexane (*e*) Cyclopropane carbaldehyde (*f*) *trans*-1, 4-Dichlorocyclohexane (*g*) *trans*-1-Bromo-4-Chlorocyclohexane (*h*) Cyclopent-2-en-1-ol (*i*) 2-Cyclobutyl-1-chloroethane (*j*) 1-Cyclohexanecarboxylic acid (*k*) 1-Ethnyl-1-decalol (*l*) 3-Hydroxycyclohexane-carbaldehyde (*m*) 2-Formyl-2-methylcyclohexanone (*n*) 2-Oxocyclohexanecarboxylic acid (*o*) 1-Vinyl-1-cyclohexanol

Problem 11.12:

Suggest a mechanism for the following reaction:



Solution:



Problem 11.13:

Describe simple chemical tests to distinguish between the following pairs:

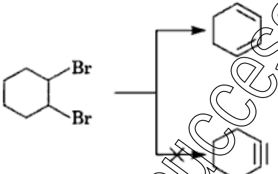
(*a*) Cyclobutane and 1-butene (*b*) Cyclopentane and cyclopentene (*c*) Cyclopropane and propane (*d*) Cyclopentane and 1-pentene (*e*) Cyclohexane and benzene

Solution: (*a*) Addition of bromine or Bayer's test (*b*) Same as in (*a*) (*c*) Bromination of cyclopropane (*d*) Same as in (*a*) (*e*) Bromination $(Br_2 + Fe)$ of benzene

Problem 11.14:

Comment on the fact that 1, 2-dibromocyclohexane on treatment with base yields 1, 3-cyclohexadiene and not cyclohexyne.

Solution:



Putting a triple bond in a small ring is energetically unfavorable.

Problem 11.15:

Why is cyclohexane more resistant to ring opening than cyclopropane ?

Solution: Because of the presence of low bond angle strain in cyclohexane as compared to cyclopropane.

Problem 11.16:

Describe briefly the following terms:

(*a*) Ring strain (*b*) Conformational analysis (*c*) Chair and boat conformations (*d*) Heat of combustion (*e*) 1, 3-Diaxial interaction (*f*) Torsional strain.

Solution: (*a*) **Ring Strain:** *Ring strain* is the sum of angle strain caused by the compression of the internal bond angles because of departure from the normal angle of 109.5° and torsional strain because of non-bonded interaction of atoms or groups.

(*b*) **Conformational analysis:** The analysis of molecular conformations and their relative energies is called *conformational analysis.*

(*c*) The most stable chair conformation of cyclohexane consists of one part puckered upwards and the other part puckered downward.

The less stable conformation of cyclohexane is the boat form with both parts puckered upwards.

(*d*) **Heat of combustion:** It is the amount of heat evolved when a compound is burned in a sealed container.

(*e*) **1, 3-Diaxial interaction:** The strong steric interaction between two axial groups on cyclohexane carbons with one carbon between them is termed as the 1, 3-*diaxial interaction.*

(*f*) **Torsional strain:** The higher energy associated with the eclipsing of bonds is called *torsional energy* a *torsional strain.* If an ethane molecule is rotated toward the eclipsed conformation, its potential energy increases and there is resistance to the rotation. Therefore, the eclipsed ethane is torsionally strained by 2.9 KCal/mole relative to staggered ethane.

Problem 11.17:

Knowing the two conformations of decalin, predict which isomer is more stable, why ?

Solution: The *trans*-isomer is more stable because both the bonds to the second cyclohexane ring are in equatorial positions.

Problem 11.18:

Which member of each of the following pairs of isomers is more stable and why ?

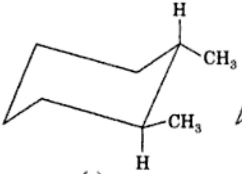
(*a*) *cis-or trans*-1, 2-Dimethylcyclohexane (*b*) *cis-or* trans-1, 3-Dimethylcyclohexane

(*c*) *cis-or trans-1, 4-Dimethylcyclohexane*

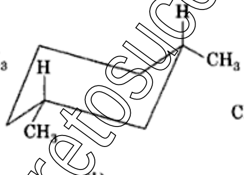
Solution: (*a*) The *trans*-isomer is more stable because both methyl groups are equational.

(*b*) The *cis*-isomer is more stable because both methyl groups are equational.

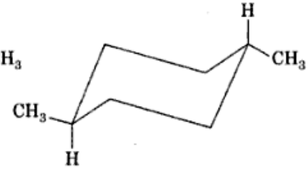
(*c*) The *trans*-isomer is more stable for the same reason as in (*a*)



(*a*)



(*b*)

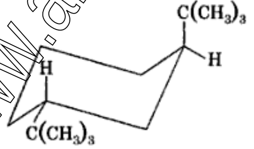


(*c*)

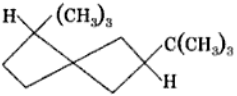
Problem 11.19

It has been observed that while *cis*-1, 3-*di*-*t*-butylcyclohexane exists predominantly in a chair conformation, the *trans*-isomer adopts a twist conformation. Explain.

Solution: In the *cis*-isomer the two *t*-butyl substituents are both equational but in the *trans*-isomer, one *t*-butyl group must occupy an axial position. The instability of a chair conformation with a large group in an axial position forces the molecule into a less strained form.



trans-Isomer



cis-Isomer

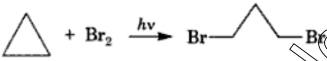
Problem 11.20:

Cyclic anhydride can be formed from only the *cis*-1, 2-cyclopentanedicarboxylic acid but equally from both the *cis*- and *trans*-1, 2-cyclohexanedicarboxylic acids. Account for this observation.

Solution: The two carboxyl groups are at very nearly the same distance apart in the *cis*- and *trans*-1, 2 cyclohexanedicarboxylic acids and the anhydride can form easily from either. In *trans*-1, 2-cyclopentanedicarboxylic acid, formation of the anhydride will put strain in the resulting molecule.

Problem 11.21:

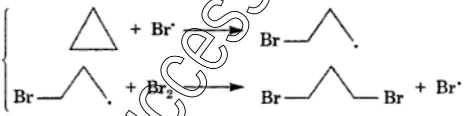
Write a mechanism for following reaction:



Solution: It is a free radical reaction and would thus proceed in the following three usual steps:

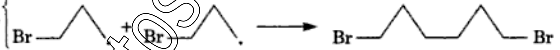
Chain initiating step $Br_2 \xrightarrow{h\nu} 2Br^{\cdot}$

Chain propagating step



Chain terminating step

$Br^{\cdot} + Br^{\cdot} \longrightarrow Br_2$



Problem 11.22:

Make sketches for the most stable of the following compounds indicating whether the substituents are axial or equatorial. Also indicate whether each can be optically active.

(*a*) *cis*-1, 2-Dichlorocyclohexane (*b*) *cis*-1, 3-Dichlorocyclohexane (*c*) *cis*-1, 4-Dichlorocyclohexane

Solution:

(*a*)

Optically inactive
(a plane of symmetry)

(*b*)

Optically inactive
(a plane of symmetry)

(*c*)

Optically inactive
(a plane of symmetry)

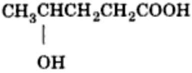
Problem 11.23:

Cyclopentane is non-planar molecule inspite of the fact that a regular pentagon has internal angles of 108° very close to the tetrahedral angle. Comment.

Solution: Planar cyclopentane would require C—C and C—H bonds to be eclipsed. The molecule thus distorts from planarity to avoid this eclipsing of bonds occurs.

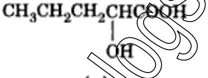
Problem 11.24:

A major difference between isomeric hydroxy acids (A and B) is that (A) loses water spontaneously to form a cyclic ester while (B) is recovered unchanged under identical experimental conditions. Explain.



$CH_3\underset{\substack{|\\ OH}}{CH}CH_2CH_2COOH$

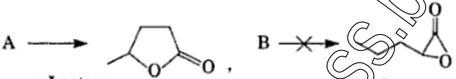
(A)



$CH_3CH_2CH_2\underset{\substack{|\\ OH}}{CH}COOH$

(B)

Solution:



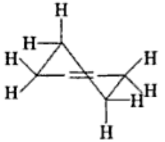
γ-Lactone, α-Lactone

α-Lactone, if formed from B, would suffer badly from angle strain (a 3-membered ring) and so would be the activated complex leading to its formation. Thus (B) would not react.

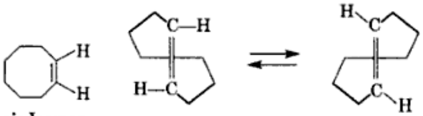
Problem 11.25:

Discuss the conformation of cyclohexene. Name and comment on the smallest cycloalkene in which both the *cis*- and *trans*-isomers are possible.

Solution: The four groups attached to an alkene lie in a plane because sp^2 hybridization of the carbon atoms. Similarly in cyclohexene, two hydrogen atoms and the two methylene groups must be coplanar in order to provide an effective overlap from the π-bond. It is a sort of half-chair structure and thus accounts for effective staggering of the methylene groups.



The smallest cycloalkene for which *trans*-isomer is possible is cyclooctene. Molecular models of the *trans*-isomer show that it assumes a twisted (chiral) conformation. It is less stable than the *cis*-compound. *trans*-Cyclooctene exists in enantiomeric forms.

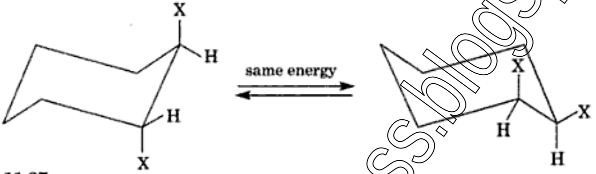


cis-Isomer *trans*-Isomer

Problem 11.26:

cis-1, 2-Disubstituted cyclohexanes are non resolvable although the molecule is chiral in nature.

Solution: When *cis*-1, 2-disubstituted cyclohexane flips from one chair form to the other, the groups that are in the equatorial position become axial while groups that are axial become equatorial. In both conformations, the number and type of axial and equatorial substituents remain the same and the two conformers are equal in energy and are present in equal amounts. The second conformer is, in fact, the enantiomer of the first one. The two enantiomeric forms of *cis*-1, 2-disubstituted cyclohexane interconvert rapidly with the practical consequence that the compound cannot be separated into optically active mirror image isomers. In effect, molecules with identical substituents behave like a *meso* compound having a plane of symmetry.

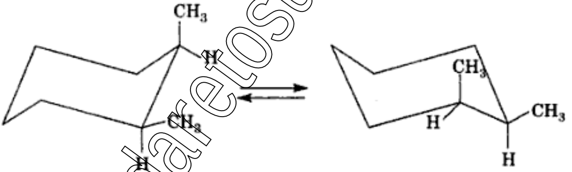


Problem 11.27:

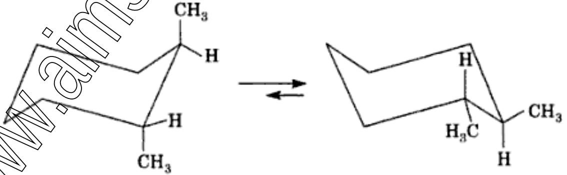
(*a*) Predict the most stable chair conformation of isomeric *cis* and *trans*-1, 2-dimethylcyclohexanes.

(*b*) Predict the major chair conformation of *trans*-tert. butyl-3-methylcyclohexane.

Solution: (*a*) The two *cis* conformations are

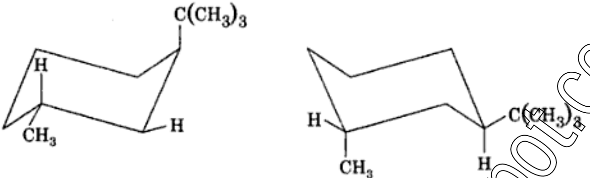


These two are of equal energy because each has one axial and one equatorial -CH_3 groups. The *trans*-conformations are:



The *trans*-isomer with both equatorial -CH_3 groups is stable. This conformation is more stable by 1.7 kcal/mole than the *cis*-isomer.

(*b*) The two *trans*-conformations may be written as follows:



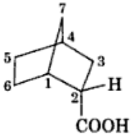
***trans*-1-*t*-Butyl-3-methylcyclohexane**

Of these the second is more stable because the bulky *t*-butyl group (referred to as the anchoring group) is in the equatorial position.

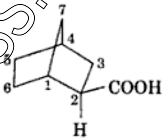
Problem 11.28:

Describe the *exo* and *endo* nomenclature of bridghead compounds.

Solution: The nomenclature may be explained by taking the following acids as examples:



***endo*-Bicyclo (2.2.1) heptan-2-carboxylic acid**



***exo*-Bicyclo (2.2.1) heptan-2-carboxylic acid**

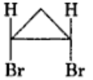
In the *exo*-isomer the -COOH group is 'up' or *cis* with respect to carbon-7 of the bicyclic system. On the other, hand in *endo* the -COOH group is 'down' or *trans* with respect to this carbon.

Problem 11.29:

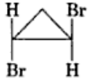
Write all the stereoisomers of 1, 2-dibromocyclopropane.

Solution: 1, 2-Dibromocyclopropane has four stereoisomers:

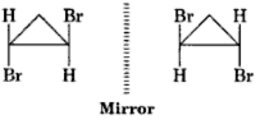
cis- and *trans*-1, 2-Dibromocyclopropane



and



enantiomeric *trans*-1, 2-Dibromocyclopropane.



Problem 11.30:

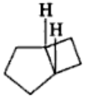
The heat of formation for cyclopentane is higher than for cyclohexane. Why ?

Solution: The higher energy of cyclopentane is due to both the angle strain and to eclipsing between the hydrogen atoms.

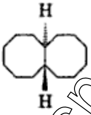
Problem 11.31:

Would you expect the following cyclic compounds isolable ?

(A)



(B)



(C)

Solution: (A) No, because a six and a three-membered ring cannot be fused *trans*. (B) Yes, because any sized rings can be fused *cis*. (C) Yes, large rings can be fused *trans*.

(Two five-membered and larger rings can be *trans* fused.

Problem 11.32:

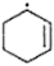
Why is cyclobutane less strained than cyclopropane ?

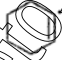
Solution: If cyclobutane were perfectly square and planar, it would have 90° bond angles. The deviation from 109.5° is considerably less. Thus it has less angle strain. Further to diminish this angle strain, cyclobutane assumes a slightly puckered geometry.

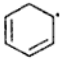
Problem 11.33:

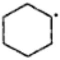
Select the correct answer.

(*a*) Which of the following is the most stable radical

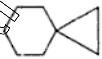
A. 

B. 

C. 

D. 

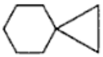
(*b*) The following compound on reduction gives



$+ H_2 \xrightarrow{Ni}$ A is

A. 

B. 

C. 

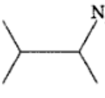
D. None of these.

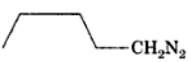
(*c*) The product of the following reaction

$+ CH_2N_2 \xrightarrow{A}$ is

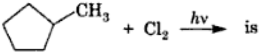
A. 

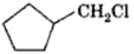
B. 

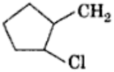
C. 

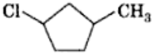
D. 

(*d*) The major production of monochlorination of



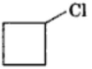
A.


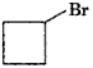
B.


C.


D.


(*e*) What would be the product obtained when 1-bromo-1-chlorocyclobutane reacts with two equivalents of metallic sodium in ether ?

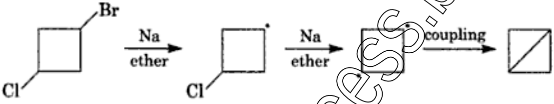
A.


B.


C.


D.


Solution: (*a*) C, resonance stabilized radical. (*b*) A (*c*) B, a *syn*-addition always takes place. (*d*) D, this will involve a tertiary free radical intermediate.



It is similar to the Wurtz reaction.

CHAPTER

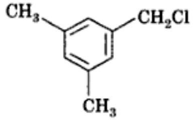
12

Aromatic Hydrocarbons

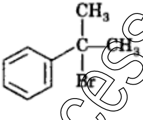
Problem 12.1:

Suggest a name for each of the following compounds:

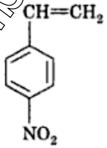
(a)



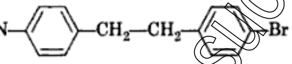
(b)



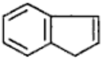
(c)



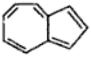
(d)



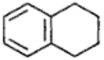
(e)



(f)



(g)



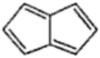
Solution: (a) 1-Chloromethyl-3, 5-dimethylbenzene (b) 1-Bromo-1-methylethylbenzene (c) p-Nitrostyrene (d) 1-(4-Bromophenyl), 2-(4-nitrophenyl) ethane (e) Benzocyclopentadiene (Indene) (f) Azulene (g) 1, 2, 3, 4-Tetrahydronaphthalene (Tetralin)

Problem 12.2:

Define Hückel rule and anti-aromatic compounds. Indicate whether the following compounds are aromatic, non-aromatic or antiaromatic.

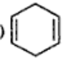
(a)

(b)

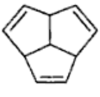


(c)

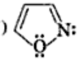
(d)



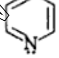
(e)



(f)

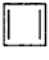


(g)

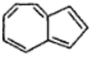


(h)

(i)



(j)



Solution: Hückel's rule. Benzene and many benzene derivation are aromatic. The extra stability is conferred upon them due to a unique property called aromaticity. Using Hückel rule one can define aromaticity more precisely. To predict whether a compound is aromatic or not, the Hückel's rule states that a planar, conjugated and cyclic compound containing $(4n + 2)\pi$ electrons should be aromatic where n is a positive integer (0, 1, 2..... etc.).

What do we mean when we say that these compounds are aromatic ? This means that π electrons are delocalized over the entire ring and the compounds have less energy and more stable.

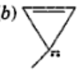
Anti-aromatic compounds. Compounds that are planar, conjugated and cyclic and contain instead $4n\pi$ electrons are unstable and are called anti-aromatic. Such compounds have greater π-electron energy than the open-chain counterparts.

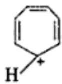
(*a*) Non-aromatic, the double bonds are not conjugated. (*b*) Non-aromatic, does not obey Hückel's rule. (*c*) Non-aromatic, not planar and also does not comply with the Hückel's rule. (It is also not anti-aromatic though it contains $4n\pi$ electrons). (*d*) Non-aromatic, not conjugated (π electrons cannot be delocalized). (*e*) Non-aromatic, not conjugated. (*f*) Anti-aromatic, contains $4n\pi$ electrons. (*g*) Aromatic (*h*) Aromatic, the two electrons on the nitrogen atoms are counted and it thus obeys Hückel rule. It is a non-benzenoid aromatic compound. (*i*) Anti-aromatic, contains $4n\pi$ electrons. (*j*) Aromatic, contains 10π electrons. This compound is aromatic but does not contain a benzene ring. Therefore, this compound is also classified as non-benzenoid aromatic.

Problem 12.3:

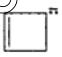
Indicate whether the following ions are aromatic or non-aromatic and why?

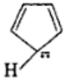
(*a*)


(*b*)


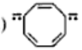
(*c*)


(*d*)


(*e*)


(*f*)


(*g*)


(*h*)


Solution: (*a*) Anti-aromatic, contains $4n\pi$ electrons (*b*) Antiaromatic, contains $4n\pi$ electrons (*c*) Aromatic, obeys Hückel's rule (It is known as the tropylium ion) (*d*) Aromatic, contains 6π electrons (*e*) Antiaromatic (*f*) Aromatic (*g*) Aromatic, contains 2π electrons (*h*) Aromatic, contains 10π electrons (The dianion is planar).

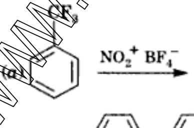
Problem 12.4:

Which of the two would you expect to possess a high boiling point, nitrobenzene or *n*-propylbenzene?

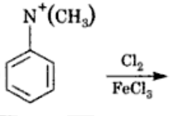
Solution: Nitrobenzene because it has a higher dipole moment.

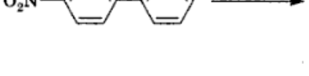
Problem 12.5:

Predict the product of monosubstitution in the following reactions:

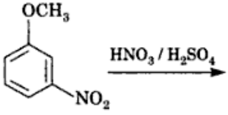
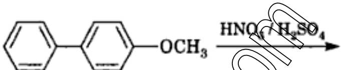
(*a*)


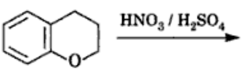
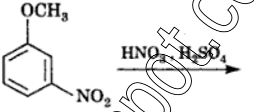
(*b*)

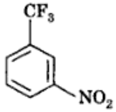

(*c*)


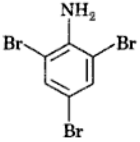
(*d*)


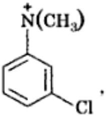
(*e*)

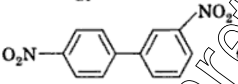

(*f*)  A + B (*g*) 

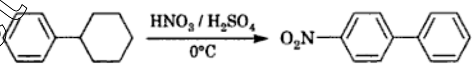
(*h*)  A + B (*i*) 

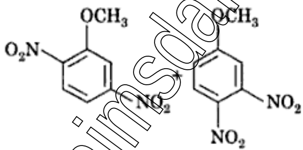
Solution: (*a*)  , (CF$_3$ is an electron-withdrawing group inductively.)

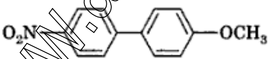
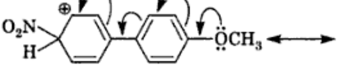
(*b*)  , (-NH$_2$ is a powerful electron-donating group like the -OH group.)

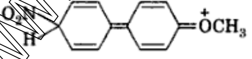
(*c*)  , (-$\overset{+}{N}$(CH$_3$)$_3$ is electron-withdrawing group inductively.)

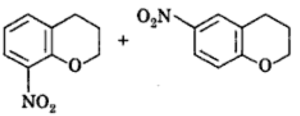
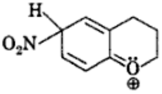
(*d*) 

(*e*) 

(*f*)  (electron-donating group controls orientation)

(*g*)  because 

 is a stable intermediate.

(*h*)  because  is a stable intermediate.

Problem 12.6:

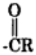
Arrange the following compounds in order of decreasing reactivity towards electrophilic substitution :

$C_6H_5OH, C_6H_5OCH_3, C_6H_6, C_6H_5NO_2, C_6H_5CH_3$

Solution: $C_6H_5OCH_3 > C_6H_5OH > C_6H_5CH_3 > C_6H_6 > C_6H_5NO_2$

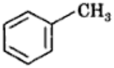
Problem 12.7:

Why is acylation and not alkylation of naphthalene practical ?

Solution: Acylation introduces a  $-\overset{O}{\overset{\|}{C}}R$ group and prevents further acylation. Introduction of R group induces alkylation, an electron-donating group.

Problem 12.8:

If the rings of each of the following compounds were nitrated where would you expect the nitro group to enter (there may be more than one positions).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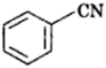
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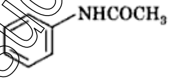
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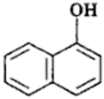

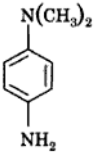
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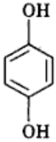
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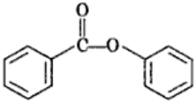
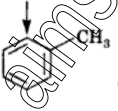


Solution: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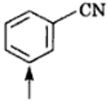
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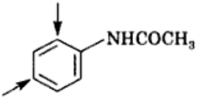
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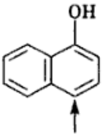

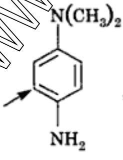
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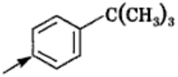
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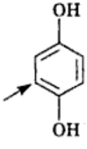
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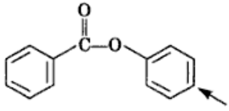
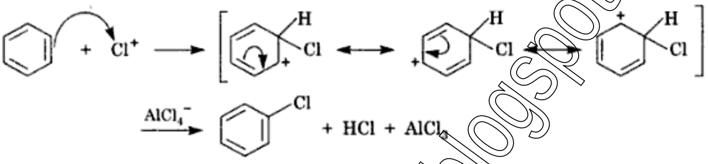


Problem 12.9:

Write a mechanism for the chlorination of benzene in the presence of $AlCl_3$ catalyst.

Solution: The mechanism starts with the formation of a *chloronium ion*, Cl^+ which attacks the benzene ring to form a *benzenechloronium ion* which is stabilized by resonance. In the final step a proton is lost with the help of $AlCl_3^-$ forming chlorobenzene and hydrogen chloride.

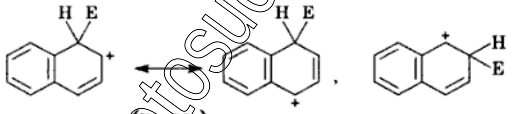
$$Cl{-}Cl + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$$



Problem 12.10:

Explain why sulfonation of naphthalene under different conditions leads to different products.

Solution: Sulfonation of naphthalene under mild conditions yields 1-naphthalenesulfonic acid. However, under more vigorous conditions, sulfonation yields 2-naphthalenesulfonic acid. Also the attack at the 1-position is rapid than at position-2. This is so because the arenium ion formed by attack at position-1 is more stable than when the attack takes place at the 2-position.



$(E = SO_3)$

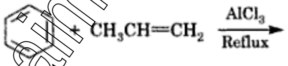
Attack at position-1 **Attack at position-2**

At higher temperature, the more thermodynamically controlled 2-naphthalenesulfonic acid is formed.

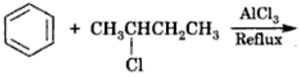
Problem 12.11:

Complete the following reactions:

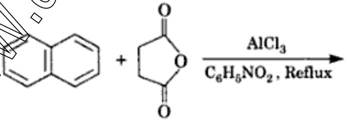
(*a*)



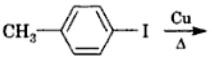
(*b*)

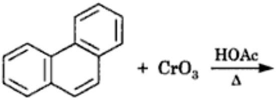


(*c*)



(*d*)



(*e*)


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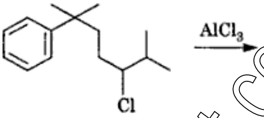

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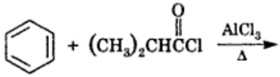
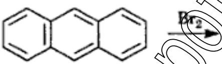
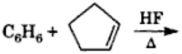
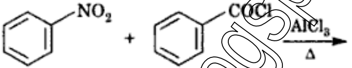
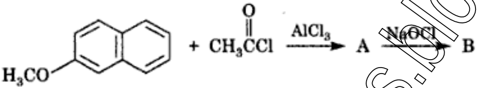
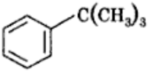


(*h*)


(*i*)


(*j*)


(*k*)


Solution: (*a*)


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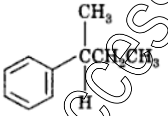

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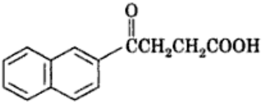

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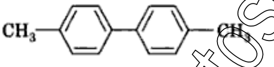

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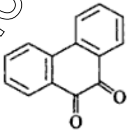

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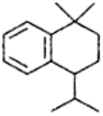
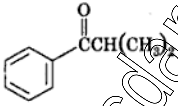
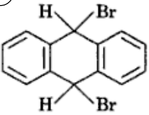
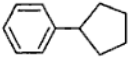
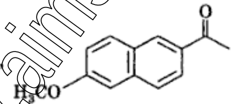


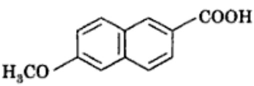
(*g*)


(*h*)


(*i*)


(*j*) No reaction

(*k*) A,


B,


Problem 12.12:

Compounds A, B and C are three isomeric derivatives of benzene. Identify which is *ortho*, *meta* or *para* from the products of nitration :

$$\text{A} \xrightarrow{\text{conc. } HNO_3\text{, } H_2SO_4} \text{two mononitro products}$$

$$B \xrightarrow{\text{conc. } HNO_3\text{ , }H_2SO_4} \text{three mononitro products}$$

$$C \xrightarrow{\text{conc. } HNO_3\text{ , }H_2SO_4} \text{one mononitro product}$$

Solution: A is *o*-xylene, B is *m*-xylene and C is *p*-xylene.

Problem 12.13:

Describe the necessary conditions and reagents required to convert benezene into the following:

(*a*) Nitrobenzne, (*b*) Ethylbenzene, (*c*) Cyclohexane (*d*) Benzaldehyde,
(*e*) Chlorobenzene, (*f*) *t*-Butylbenzene, (*g*) Acetophenone and (*h*) Benzoic acid

Solution: (*a*) $HNO_3 / H_2SO_4 / 50–55°C$ (*b*) $C_2H_5Cl/AlCl_3$ (*c*) H_2 / Ni 175°C, 180 atm (*d*) $CH_2O/HCl/2Cl_2$ followed by reaction with $C_6H_{12}N_4 / H_2O$ (*e*) $Cl_2 / FeCl_3$ (*f*) $(CH_3)_3CCl / AlCl_3$ (*g*) $CH_3COCl/AlCl_3$ (*h*) $CH_3Cl/AlCl_3$ followed by oxidation $(KMnO_4)$

Problem 12.14:

Would you expect *m*-dinitrobenzene to undergo bromination with a halogen carrier rapidly or slowly. Why ?

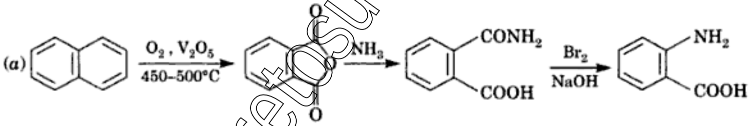
Solution: Slowly, NO_2 is a powerful deactivating group.

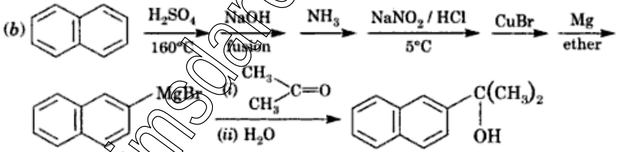
Problem 12.15:

How will you convert naphthalene into:

(*a*) Anthranilic acid and (*b*) 2-Naphthyl-2-propanol.

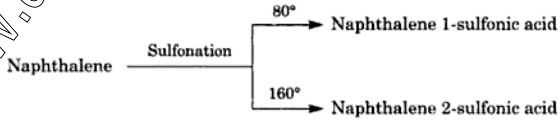
Solution:





Problem 12.16:

Comment on the formation of the following products:



Solution: Since sulfonation is reversible, the thermodynamically controlled and more stable, but more slowly formed 2-isomer is produced at 160°C.

Problem 12.17:

Nitration of toluene is easier than that of benzene. Explain.

Solution: Inductive effect of methyl group activates the ring towards the attack of nitronium ion. The methyl group in toluene activates the benzene ring toward electrophilic attack.

Problem 12.18:

(*a*) How is benzene obtained from coal tar ?

(*b*) How does benzene react with the following ?

(*i*) Conc. H_2SO_4 (*ii*) Chlorine, $AlCl_3$ (*iii*) Conc. HNO_3 , H_2SO_4 .

Solution: (*a*) Benzene is obtained by fractional distillation of coal tar. At 200°C light oil (or crude naphtha) is obtained which is the first fraction. It is washed with cold sulfuric acid to remove pyridine and other basic materials; and then with dil. sodium hydroxide to remove phenol, cresol, xylol, etc., and finally redistilled. Benzene is obtained between 90-110°C.

(*b*) (*i*) Benzene reacts at room temperature with fuming sulfuric acid, *i.e.* conc, sulfuric acid containing dissolved SO_3 forming benzenesulfonic acid. (*ii*) Chlorine reacts with benzene in the presence of $AlCl_3$ (a Lewis acid) to form chlorobenzene. (*iii*) Conc. HNO_3 , H_2SO_4 together introduce a nitro group in the benzene ring to form nitrobenzene.

Problem 12.19:

(*a*) What do you understand by electrophilic substitution in the benezene ring ?

(*b*) Discuss the influence of orientation of the following groups on substitution in aromatic compounds by electrophilic reagents: $-NH_2$, $-NO_2$, -Cl.

Solution: (*a*) Replacement of a hydrogen on the benzene ring by a strong electrophile is referred to as *electrophilic aromatic substitution*.

(*b*) $-NH_2$: A amino group is electron-donating, therefore it is *o*- and *p*- directing.

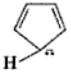
$-NO_2$: A nitro group is a strong electron-withdrawing group, it is *meta*-directing.

-Cl : A Cl group is inductively electron-withdrawing but electron-donor by resonance, therefore, it is *o*- and *p*-directing.

Problem 12.20:

What do you understand when one says that the cyclopentadiene anion is aromatic ?

Solution:



It implies that (*i*) cyclopentadiene anion is planar (*ii*) it has $(4n + 2)\pi$ electrons ($n = 2$) (*iii*) electrons are delocalised in the molecule.

Problem 12.21:

Offer explanation for the following observations:

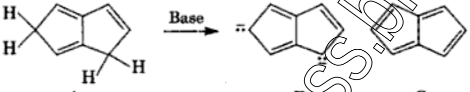
(*a*) Toluene requires lower temperature (30°) than benzene (55°) for nitration.

(*b*) Chlorobenzene is less reactive than benzene. (*c*) *t*-Butylbenzene is more reactive than toluene towards electrophilic substitution. (*d*) The $C_1—C_2$ bond distance in naphthalene is shorter than $C_2—C_3$ bond. (*e*) Nitrobenzene is used as a solvent in certain Friedel-Crafts acylations. (*f*) Aniline does not undergo the Friedel-Craft reaction though $-NH_2$ group is electron-donating. (*g*) 1, 4-Disubstituted isomers of benzene have higher mp's than the corresponding 1, 2- and 1, 3-isomers. (*h*) A hydrocarbon with 10π electrons ($n = 2$) is not aromatic. (*i*) Most electrophilic substitution reactions are irreversible.

Solution: (*a*) -CH_3 group is an activating. (*b*) -Cl withdraws electrons inductively. (*c*) *t*-Butyl is an activating group. (*d*) Naphthalene is considered as a resonance hybrid of three resonance structures in which C—C bonds are not identical. The bond distance between (1.365 Å) is shorter than C_2—C_3 (1.404 Å). In the resonance two structures have a double bond between C_1 and C_2 and only one between C_2 and C_3. Therefore C_1—C_2 bond distance is shorter. (*e*) -NO_2 group is a strong deactivating group and thus nitrobenzene does not participate in the Friedel-crafts reaction. (*f*) -NH_2 group complexes with $AlCl_3$ thus it becomes deactivating. (*g*) The 1, 4-isomers of benzene have a more symmetrical structure and thus permitting it to fit into the crystal lattice than either of the other isomeric benzene derivatives. (*h*) It cannot adopt the necessary planar conformation. (*i*) $ArH + E^+ \underset{k-1}{\overset{k_1}{\rightleftharpoons}} [ArH\ E^+] \xrightarrow[-H^+]{k_2} ArE \therefore k_2 >> k-1$

Problem 12.22:

The triene (A) can be readily deprotonated twice to give the stable dianion (B). The neutral analog of (B) *i.e.* (C) however, is unstable. Explain.

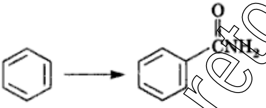


A B C

Solution: The dianion (B) is an aromatic compound containing 10π electrons but pentalene (C) has only 4*n*π electrons, it is antiaromatic. Delocalization of electrons destabilizes the molecule.

Problem 12.23:

Affect the following conversions:

(*a*)


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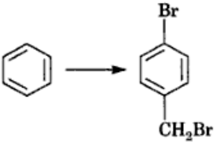

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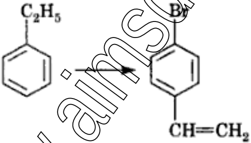

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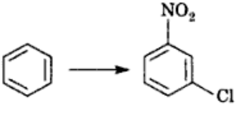

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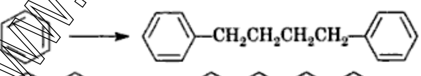

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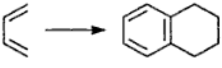

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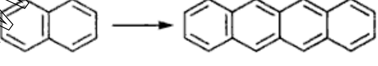
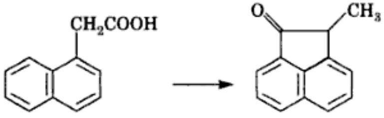
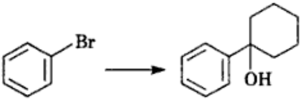


(h)



(i)



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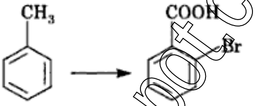


Solution: (a) $C_6H_5 \xrightarrow{CH_3Cl\ /\ AlCl_3} C_6H_5CH_3 \xrightarrow{KMnO_4} C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl$

$\xrightarrow{NH_3} C_6H_5CONH_2$

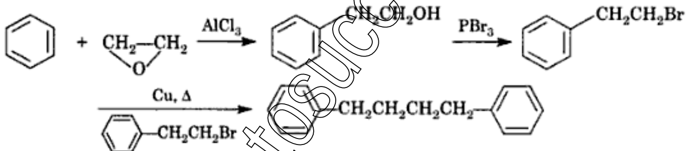
(b) $C_6H_6 \xrightarrow{CH_3Cl\ /\ AlCl_3} C_6H_5CH_3 \xrightarrow{Br_2\ /\ FeBr_3} p\text{-}BrC_6H_4CH_3 \xrightarrow{Cl_2\ ,\ h\nu} p\text{-}BrC_6H_4CH_2Cl$

(c) $C_6H_5CH_2CH_3 \xrightarrow{Br_2\ /\ FeBr_3} p\text{-}BrC_6H_4CH_2CH_3 \xrightarrow{Cl_2\ ,\ h\nu} p\text{-}BrC_6H_4CHClCH_3$

$\xrightarrow{alc.\ KOH} p\text{-}BrC_6H_4CH{=}CH_2$

(d) $C_6H_6 \xrightarrow[\Delta]{HNO_3\ /\ HSO_4} C_6H_5NO_2 \xrightarrow{Cl_2\ ,\ AlCl_3} m\text{-}ClC_6H_4NO_2 \xrightarrow{Zn/HCl} m\text{-}ClC_6H_4NH_2$

(e)



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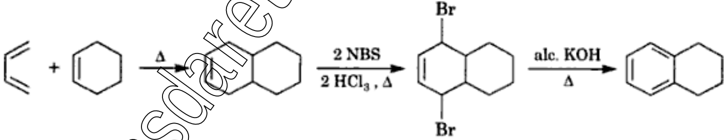

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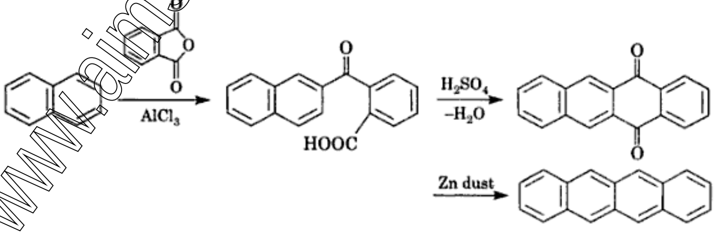
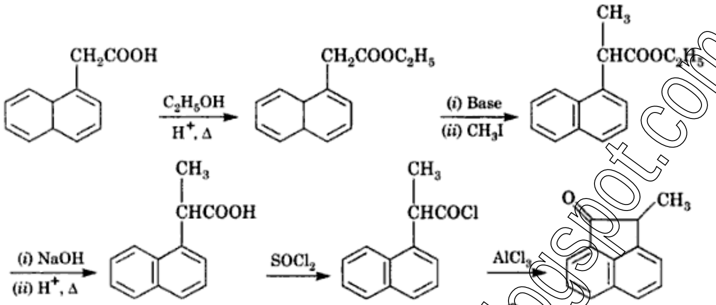
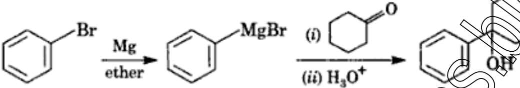


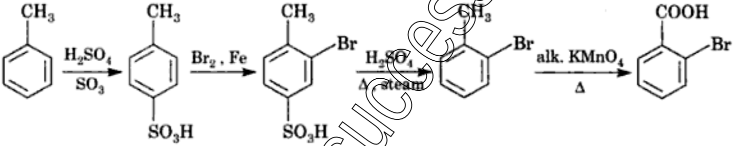
(h)



(i)



(j)

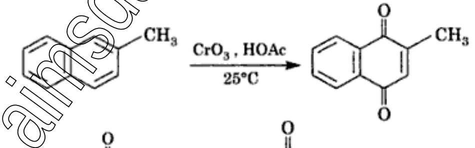


Problem 12.24:

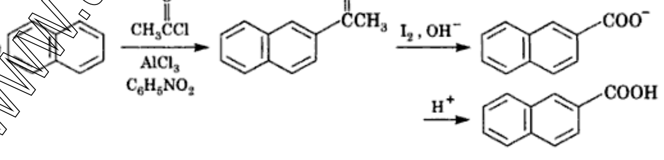
(*a*) 2-Methylnapthalene does not give 2-naphthalenecarboxylic acid on oxidation. Explain.

(*b*) Suggest a method for the preparation of 2-naphthalenecarboxylic acid.

Solution: (*a*) The oxidation of 2-methylnaphthalene does not give 2-naphthalenecarboxylic acid instead 2-methyl-1, 4-napthoquinone is obtained with the destruction of aromaticity of one aromatic benzene ring. In 2-methylnaphtalene, the α-positions are more easily oxidized than -CH_3 under these conditions.



(*b*)



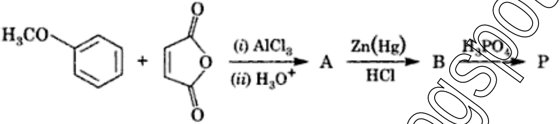
Problem 12.25:

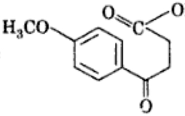
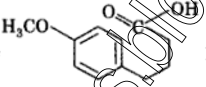
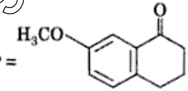
Why is naphthalene-1-sulfonic acid less stable than naphthalene-2-sulfonic acid?

Solution: Napththalene-1-sulfonic acid is sterically hindered by the hydrogen atom present in the 8-position. Thus the 2-isomer is more stable.

Problem 12.26:

Predict the structure of the intermediates and the final product in the following reaction sequence.



Solution: A =  B =  P = 

Problem 12.27:

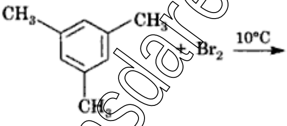
How do you account for the aromaticity of naphthalene.

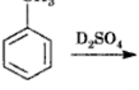
Solution: Naphthalene is aromatic because of the following reasons:

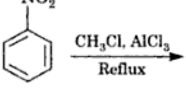
(*i*) It contain 10π electrons and obeys Huckel's rule. (*ii*) It has high resonance energy. (*iii*) It undergoes substitution rather than addition reactions. (*iv*) It is stable towards usual oxidizing agents.

Problem 12.28:

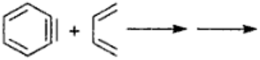
Write the products for the following reactions. If there is no reaction, write N.R.

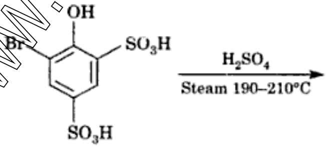
(*a*) 

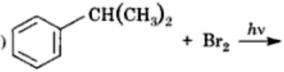
(*b*) 

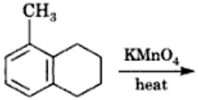
(*c*) 

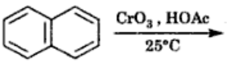
(*d*) 

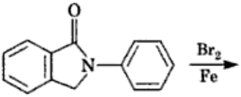
(*e*) 

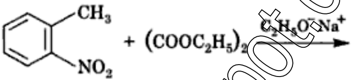
(*f*) 

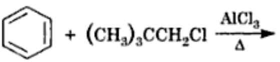
(*g*) 

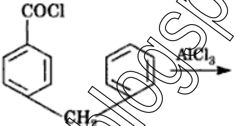
(h) 

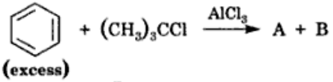
(i) 

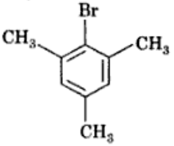
(j) 

(k) 

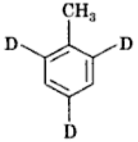
(l) 

(m) 

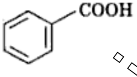
(n) 

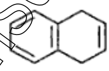
Solution: (a) 

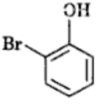
(Mesitylene undergoes electrophilic substitution easily)

(b) 

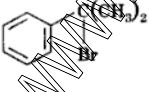
(c) N.R. (-NO$_2$ is a powerful electron-withdrawing group)

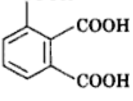
(d) 

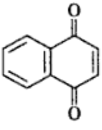
(e) 
(Diels-Alder reaction)

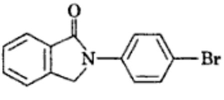
(f) 

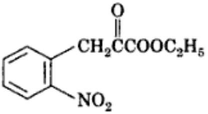
(-SO$_3$H groups are removed.)

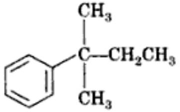
(g) 

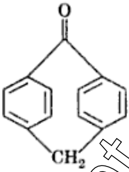
(h) 

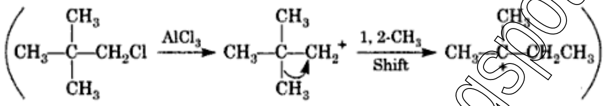
(i) 

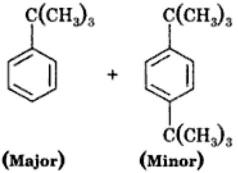
(j) 

(k) 

(l) 

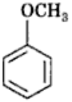
(m) 

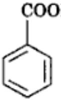
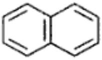


(n) 

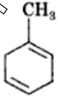
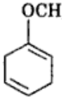
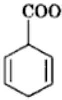
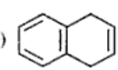
Problem 12.29:

Describe the Birch reduction. Write the product of the following reductions:

(a)  $\xrightarrow[(ii)\ C_2H_5OH]{(i)\ Li,\ liq.\ NH_3}$ (b)  $\xrightarrow[(ii)\ C_2H_5OH]{(i)\ Na,\ liq.\ NH_3}$ (c)  $\xrightarrow[(ii)\ C_2H_5OH]{(i)\ Na,\ liq.\ NH_3}$

(d)  $\xrightarrow[(ii)\ C_2H_5OH]{(i)\ Li,\ liq.\ NH_3}$ (e)  $\xrightarrow[(ii)\ C_2H_5OH]{(i)\ Na,\ liq.\ NH_3}$

Solution: The Birch reduction is particularly used for reducing aromatic hydrocarbons. The reducing agent is Na or Li in liq. NH_3 and ethanol.

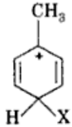
(a)  (b)  (c)  (d)  (e) 

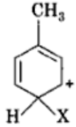
Problem 12.30:

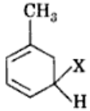
Select the correct answer.

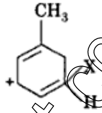
(a) The electrophile in aromatic nitration is:

A. Nitrinium ion B. Nitronium ion C. Nitrite ion D. Nitrate ion (*b*) Which of the following benzenium ions is expected to be most stable ?

A. 

B. 

C. 

D. 

(*c*) Nitrobenzene can be prepared from benezene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture, HNO_3 acts as :

A. Acid B. Base C. Catalyt D. Reducing agent

(*d*) Benzyl chloride $(C_6H_5CH_2Cl)$ can be prepared from toluene by chlorination with

A. SO_2Cl_2 B. $SOCl_2$ C. NaOCl D. Cl_2

(*e*) Among the following statements on the nitration of aromatic compounds, the false one is:

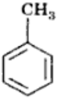
A. The rate of nitration of toluene is greater than that of benzene.

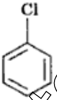
B. Nitration is an electrophilic aromatic substitution reaction.

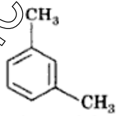
C. The rate of nitration of benzene is almost the same as that of hexadeuteriobenzene.

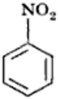
D. The rate nitration of benzene is greater than that of hexadeuteriobenzene.

(*f*) The most reactive among the following towards sulfonation is:

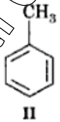
A. 

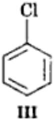
B. 

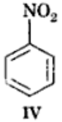
C. 

D. 

(*g*) Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:





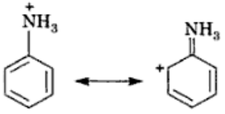


I, II, III, IV

A. I > II > III > IV B. IV > III > II > I C. II > I > III > IV

D. II > III > I > IV

(*h*) Examine the following two structures of anilinium ion and choose the correct statement from those given below:



I II

A. It is not an acceptable canonical structure because the carbocation is less stable than the ammonium ion.

B. It is not an acceptable canonical structure because it is non-aromatic.

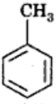
C. It is not an acceptable structure because the nitrogen has 10 valence electrons.

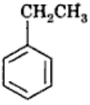
D. It is an acceptable canonical structure.

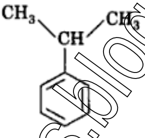
(*i*) In a reaction of C_6H_5R, the major product ($>$ 65%) is the *m*-isomer, so the group R is:

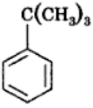
A. -Cl B. -COOH C. $-NH_2$ D. -OH

(*j*) In the nitration of the following compounds which will give the largest amount of the *p*-isomer?

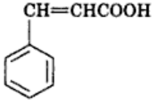
A. 

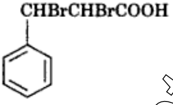
B. 

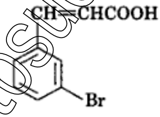
C. 

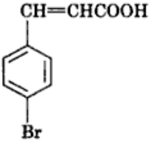
D. 

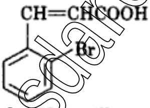
(*k*) In the following reaction:

 + $Br_2 \xrightarrow{FeCl_3}$? the product obtained is:

A. 

B. 

C. Only 

D. Both  + *para*

(*l*) The compound that will react most readily with NaOH to form methanol is :

A. $(CH_3)_3N^+I^-$ B. CH_3OCH_3 C. $(CH_3)_3S^+I^-$ D. $(CH_3)_3CCl$

(*m*) An S_N2 reaction of an asymmetric carbon of a compound always gives:

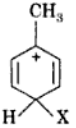
A. An enantiomer of the substrate B. A product with opposite rotation

C. A mixture of diastereoisomers D. A single stereoisomer

(*n*) How many monochloro derivatives of anthracene are possible ?

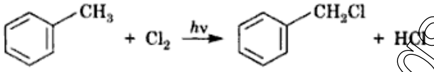
A. 2 B. 3 C. 4 D. 5

Solution: (*a*) B, nitronium ion $(O{=}\overset{+}{N}{=}O)$

(*b*) A, 

positive charge is present at the carbon atom bearing the electron-donating $-CH_3$ group.

(*c*) C, Base, nitric acid accepts a proton from sulfuric acid.

(*d*) D, Cl_2 , 

(*e*) C, the rate of nitration is almost same. This means the kinetic isotope effect is absent therefore a C—H bond is not weakened in the slow step. In simple words the mechanism of electrophilic aromatic substitution does not involve the breakage of a C—H bond in the rate-determining step.

(*f*) C, in *m*-xylene the two $-CH_3$ groups activate the ring.

(*g*) C, $-CH_3$ group is activating while $-NO_2$ group is deactivating.

(*h*) C.

(*i*) B, -COOH is electron-withdrawing and hence *meta*-directing.

(*j*) D, the $-C(CH_3)_3$ group being bulky, hinders the attack of the nitronium ion at the *ortho* position.

(*k*) D, -CH=CHCOOH is *ortho* and *para*-directing group.

(*l*) A, the $-N(CH_3)_3$ group is a better leaving group and bulky $(CH_3)_3CCl$ instead will form *tert*-butyl alcohol.

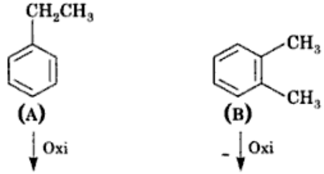
(*m*) B, An S_N2 reaction leads to inversion of configuration.

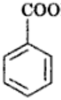
(*n*) B, (4, 5, 8) ; (3, 6, 7) and (9, 10) are same.

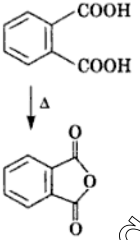
Problem 12.31:

Compounds A, and B, are isomers having the formula C_8H_{10}. On oxidation A, gives benzoic acid while B, gives phthalic acid which forms an anhydride C, on heating. Write the names and structural formulas of A, B and C. Explain the reactions involved.

Solution: Since A on oxidation gives only benzoic acid, it is a monoalkyl benzene derivative. On the other hand, compound B is a disubstituted benzene.



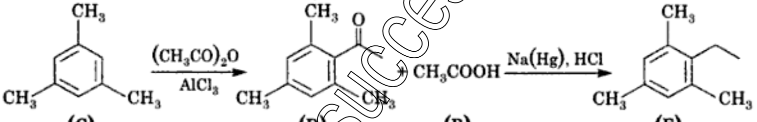




Problem 12.32:

An organic compound A on heating with $AlPO_4$ at 700°C forms B. Compound B, reacts with A to give C. Compound C, on reaction with 1, 3, 5-trimethylbenzene in the presence of $AlCl_3$ gives acetic anhydride and a ketone D and CH_3COOH. D on Clemmenson reduction gives an aromatic hydrocarbon E. Deduce the structures A to E with proper reasoning.

Solution: Since C on reaction with 1, 3, 5-trimethylbenzene in the presence of $AlCl_3$ (Friedel-crafts reaction) gives a ketone and CH_3COOH, compound C is acetic anhydride.



The first sequence of reaction is the preparation of acetic anhydride through a ketene.

$$\underset{(A)}{CH_3COOH} \xrightarrow{AlPO_4\ ,\ 700°C} \underset{\substack{\text{(A ketene)}\\ (B)}}{CH_2{=}C{=}O} + H_2O \xrightarrow{CH_3COOH} \underset{(C)}{(CH_3CO)_2O}$$

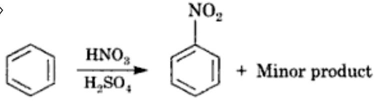
Problem 12.33:

Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with hot mixture of HNO_3 and H_2SO_4. The minor product consists of 42.86% C, 2.40% H, 16.67% N and 38.07% O.

(*i*) Determine the empirical formula of the minor product.

(*ii*) When 5.5 g of the minor product is dissolved is 45 g of benzene, the boiling point of the solution is 1.84°C higher than pure benzene. Calculate the molecular weight of the minor product and determine its molecular formula and structural formula. (K_b of benzene = 2.53 K kg/mole)

Solution:



Empirical Formula of the Minor product

Element	*% composition*	*At weight*	*Rel. no. of atoms*	*Simplest ratio*
C	42.80	12	3.56	$\frac{3.56}{1.19} = 3$
H	2.40	1	2.40	$\frac{2.40}{1.19} = 2$
N	16.67	14	1.19	$\frac{1.19}{1.19} = 1$
O	16	16	2.38	$\frac{2.38}{1.19} = 2$

Empirical formula is $C_3H_2O_2N$

Mol. wt of the minor compound.

$$\text{Mol. wt} = \frac{1000 \times K_b \times \omega}{W \times \Delta T}$$

$$= \frac{1000 \times 2.53 \times 5.5}{45 \times 1.84}$$

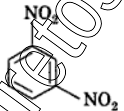
$$= 168.05/\text{mol.}$$

$$\text{MF.} = (\text{EF})_n$$

$$n = \frac{168.05}{84} = 2$$

$$\therefore \quad \text{Mol. formula} = C_6H_4O_4N_2$$

Minor compound is



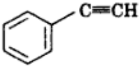
Benzene on nitration yields nitrobenzene and a small quantity of *m*-dinitrobenzene.

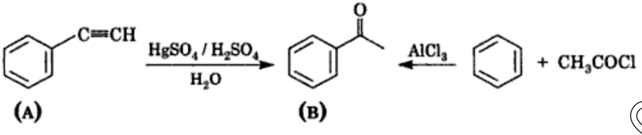
Problem 12.34:

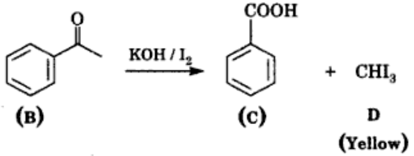
An organic compound A, C_8H_6 on treatment with dil. H_2SO_4 acid containing mercuric sulfate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminum chloride. The compound B, on treatment with iodine in aqueous KOH, yields C, and a yellow compound D. Identify A to D with justification.

Solution: Reaction of A with $HgSO_4$ / H_2SO_4 shows that it is an acetylenic derivative. Therefore

A is

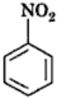


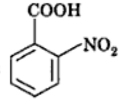




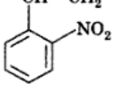
Problem 12.35:

Compound A, $C_8H_7O_2N$ by careful reduction gives B, $C_8H_9O_2N$. Further reduction with Sn/HCl gives C, $C_8H_{11}N$. Bromination of C in acid solution gives two isomeric compounds $C_8H_{10}NBr$. Oxidation of A, with hot alk. $KMnO_4$ gives D, $C_7H_5O_4N$. Compound D dissolves in $NaHCO_3$ with effervescence. D on heating with soda lime gives E, C_6H_5ON. E can be reduced to aniline with Sn/HCl. Deduce structures of the lettered compounds.

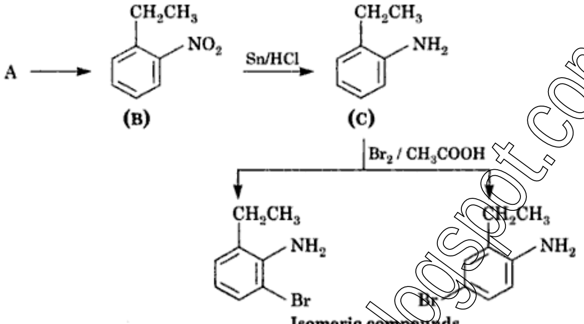
Solution: E, is  because on reduction with Sn/HCl it gives aniline.

D, is  because on heating with soda lime produces E.

A, contains a $-NO_2$ group and an unsaturation in the side-chain. Therefore it is



(A)



Isomeric compounds

Compound A has the substituents at the *ortho* position because only in that case (C) will give two isomeric products on bromination.

Problem 12.36:

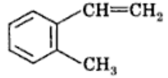
Compound A, C_9H_8 called indene is found in coal tar. It rapidly decolorizes Br_2/CCl_4 and dil. $KMnO_4$ solution. It absorbs only one mole of H_2 readily to give B, C_9H_{10}. However vigorous catalytic hydrogenation leads to a compound C, C_9H_{16}. Oxidation of A with hot alk. $KMnO_4$ yields phthalic acid. Assign structures to A, B and C.

Solution: Since oxidation of A yields phthalic acid, A contains a benzene ring. A also absorbs one mole of H_2 , therefore, there is a double bond in the side-chain.

The following two possible structures can be considered for A.

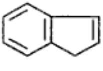
C_9H_8

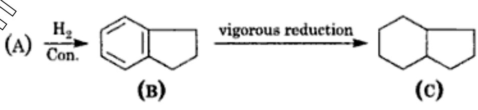
and



C_9H_{10}

Obviously the second structure can be rejected as its molecular formula is different. Therefore, indene is





CHAPTER

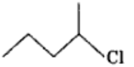
13

Organic Halogen Compounds

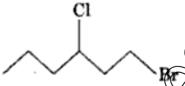
Problem 13.1:

Suggest suitable IUPAC name for each of the following compounds.

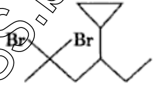
(a)



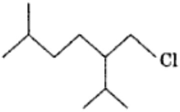
(b)



(c)

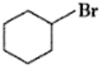


(d)

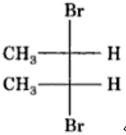


(e) $CH_3CH{=}CHCH_2CH_2I$

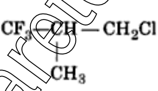
(f)



(g)

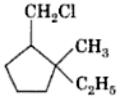


(h)



$CF_3-\underset{\underset{CH_3}{|}}{CH}-CH_2Cl$

(i)



(j) $Cl_2CHCH_2CF_2OCH_3$

Solution: (a) 2-Chloropentane (b) 1-Bromo-3-chlorohexane (c) 2, 3-Dibromo-4-cyclopropylhexane (d) 1-Chloro-4-isopropyl-5-methylhexane (e) 5-chloro-2-pentene (f) Bromocyclohexane (g) moso-2, 3-Dibromobutane (h) 1-Chloro-3, 3, 3-trifluoro-2-methylpropane (i) 1-Ethyl-1-methyl-2-chloromethylcyclopentene (j) 3, 3-Dichloro-1, 1-difluoro-1-methoxypropane.

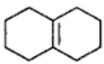
Problem 13.2:

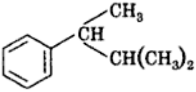
The C—Cl bond has a larger dipole moment than the C—I bond though the latter has a larger bond distance. Explain.

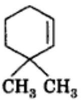
Solution: The C—Cl bond has considerably more charge separation (0.23 *e*) than the C—I bond (0.16 *e*). Dipole moment = charge × distance.

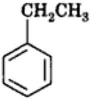
Problem 13.3:

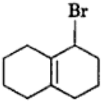
What products would be formed when each of the following compounds react with *n*-bromosuccinimide in $CHCl_4$ in the presence of light ?

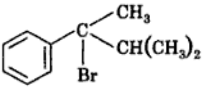
(*a*)


(*b*)


(*c*)


(*d*)


Solution: (*a*)


(*b*)


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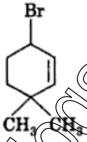

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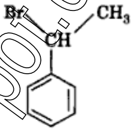


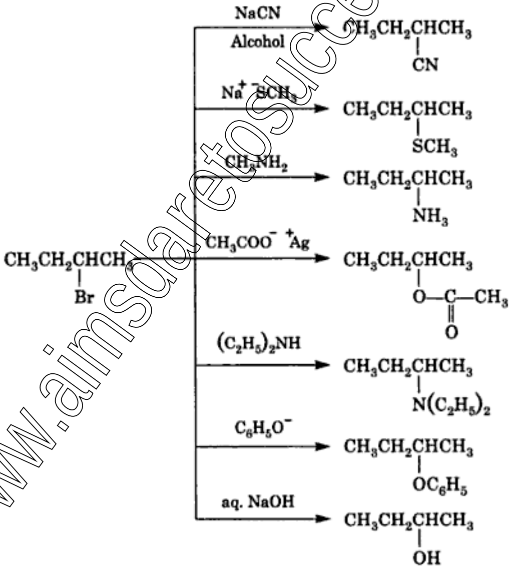
NBS brominates an allylic carbon atom.

Problem 13.4:

Give the structure of the major organic product obtained from the reaction of 2-butyl bromide with the following reagents:

(*a*) Alc. NaCN (*b*) $NaSCH_3$ (*c*) CH_3NH_2 (*d*) CH_3COOAg

(*e*) $(CH_2H_5)_2NH$ (*f*) $C_6H_5O^-$ (*g*) Aq. NaOH

Solution:


Problem 13.5:

Arrange the following compounds in order of reactivity towards S_N1 displacement.

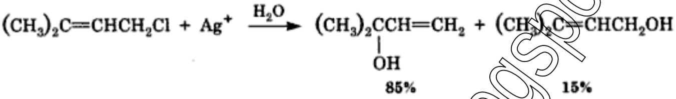
(*a*) 2-Bromo-2-methylbutane (*b*) 1-Bromopentane (*c*) 2-Bromopentane

Solution: 2-Bromo-2-methylbutane > 2-bromopentane > 1-bromopentane

More stable the carbocation, more reactive is the alkyl halide.

Problem 13.6:

Explain the formation of the products in the following reaction:



$$(CH_3)_2C{=}CHCH_2Cl + Ag^+ \xrightarrow{H_2O} \underset{\substack{|\\ OH \\ 85\%}}{(CH_3)_2CCH{=}CH_2} + \underset{15\%}{(CH_3)_2C{=}CHCH_2OH}$$

Solution: Both products are derived from the allylic cation which has two resonance forms and the product can be formed by attack of water at either electron deficient carbon. The major product (85%) is formed from the most stable tertiary cation.

Problem 13.7:

The following reaction is pH dependent:

$$R{-}Br \xrightarrow[\text{acetone}]{\text{90\% aqueous}} ROH + HBr$$

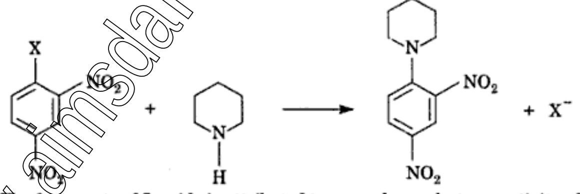
$R = -C_2H_5$, $-CH(CH_3)_2$, $-C(CH_3)_3$

It was found that an increase in hydroxide ion concentration causes a corresponding increase in the rate of the reaction when $R = -C_2H_5$ but not when $R = -C(CH_3)_3$.

Solution: This simply shows that the reaction of C_2H_5Br and $(CH_3)_3CBr$ is proceeding by two different mechanisms. The latter proceeds by the S_N2 mechanism.

Problem 13.8:

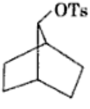
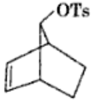
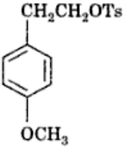
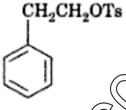
In the following reaction the relative rate is 3,300 times faster when X = F than I. Explain.

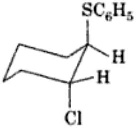
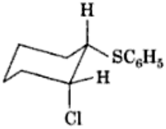


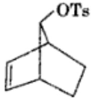
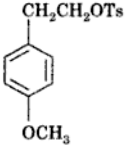
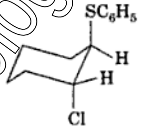
Solution: The faster rate of fluoride is attributed to a very large electronegativity of fluorine, it makes the attack of a nucleophile easier at the site of reaction.

Problem 13.9:

Which of the compound in the following pairs will hydrolyze faster in a displacement reaction:

(*a*)  or  (*b*)  or 

(*c*)  or 

Solution: (*a*)  (*b*)  (*c*) 

In these compounds, there is intramolecular nucleophilic participation.

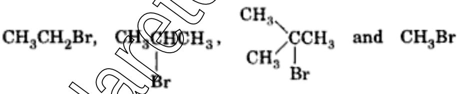
Problem 13.10:

Why is D.D.T. not stored in iron containers?

Solution: Because D.D.T. decomposes on contact with iron.

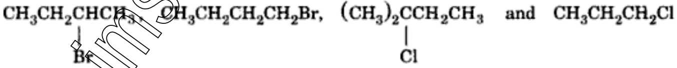
Problem 13.11:

(*a*) Arrange the following alkyl bromides in order of decreasing reactivity towards iodide ion in dry acetone.



CH_3CH_2Br, $CH_3CH(Br)CH_3$, $(CH_3)_2C(Br)CH_3$ and CH_3Br

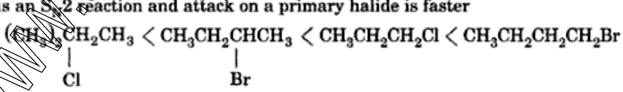
(*b*) Arrange the following alkyl halides in order of increasing reactivity towards S_N2 displacement.



$CH_3CH_2CH(Br)CH_3$, $CH_3CH_2CH_2CH_2Br$, $(CH_3)_2C(Cl)CH_2CH_3$ and $CH_3CH_2CH_2Cl$

Solution: (*a*) $CH_3Br > CH_3CH_2Br > (CH_3)_2CHBr > (CH_3)_3CBr$

It is an S_N2 reaction and attack on a primary halide is faster

(*b*) 

$(CH_3)_2C(Cl)CH_2CH_3 < CH_3CH_2CH(Br)CH_3 < CH_3CH_2CH_2Cl < CH_3CH_2CH_2CH_2Br$

The last compound is a primary halide.

Problem 13.12:

Discuss the various techniques of distinguishing between S_N1 and S_N2 reactions.

Solution: The following techniques may be used to distinguish between S_N1 and S_N2 reactions

Technique	S_N1	S_N2
(*i*) Kinetics	First order reaction	Second order reaction
(*ii*) Intermediate	A carbocation is the intermediate	A transition state is involved
(*iii*) Mechanism	Two step mechanism	Single step mechanism
(*iv*) Stereochemistry	Racemic product formation	Inversion of configuration in the products
(*v*) Reactant structure	Favored in tertiary halides	Favored in primary halides
(*vi*) Effect of adding base	No effect	Rate is accelerated

Problem 13.13:

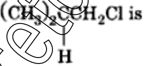
How will you distinguish among the following?

1-Chlorobutane, 1-Choloro-1-butene and 1-Chloro-2-butene

Solution: Since these are primary alkyl chlorides, their reactivities may be determined in S_N2 reaction. The reactivity of 1-chloro-2-butene > 1-cholorobutane > 1-chloro-1-butene in S_N2 displacement.

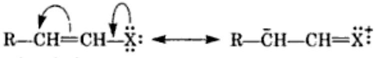
Problem 13.14:

Offer explanation for the following observations:

(*a*) Dichlorobenzene has a net dipole moment of zero. (*b*) Vinyl chloride is unreactive in nucleophilic substitution reactions. (*c*) Chlorobenzene has a lower dipole moment than methyl chloride. (*d*) Alkyl halides, though polar, are insoluble in water. (*e*) Benzyl bromide is more reactive than cyclohexyl bromomethane with aq. NaOH. (*f*) CH_3CH_2I is more reactive than CH_3CH_2Cl towards KCN. (*g*)  $(CH_3)_2\underset{H}{\underset{|}{C}}CH_2Cl$ is very unreactive toward nucleophiles. (*h*) Ethanol is a better for S_N1 reaction than acetone solvent. (*i*) $(CH_3)_3CCl$ reacts faster than $(CD_3)_3CCl$ in E2 elimination.

Solution: (*a*) In  the two individual bond dipoles are opposite and cancel each other. (*b*) Vinyl cation is not formed readily. The carbon chloride bond of vinyl chloride is shorter and stronger due to two reasons:

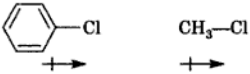
(1) The carbon bearing the halide is sp^2 hybridized and thus the electrons of carbon orbitals are closer to the nucleus than those of an sp^3 hybridized carbon. (2) Resonance of the type shown here strengthens the carbon-halogen bond by giving it a double bond character.



$$R{-}CH{=}CH{-}\ddot{\underset{..}{X}}{:} \longleftrightarrow R{-}\bar{C}H{-}CH{=}\ddot{X}^{+}{:}$$

Thus a stronger carbon-halogen bond means that bond breaking by either an S_N1 or S_N2 mechanism will require more energy.

(*c*) The value of dipole moment of chlorobenzene is lower than that of methyl chloride. The difference is attributed to two factors—first the lone-pair on the chlorine atom overlaps the *p*-orbital of the benzene ring and secondly because C—Cl bond in chlorobenzene may be represented as



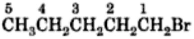
i.e. C_{sp^2}—Cl_p and C_{sp^3}—Cl_p respectively. Therefore, the higher *s* character of the benzene carbon atom makes it electron-withdrawing which lowers the dipole moment.

(*d*) Alkyl halides do not hydrogen-bond with water. (*c*) The benzyl cation is stabilized by resonance. (*f*) Iodide ion is a better leaving group. (*g*) Steric hindrance to S_N2 attack because it is a tertiary halide. (*h*) Ethanol has a higher dielectric constant than acetone and can also H-bond with X. (*i*) A β-C—H bond is broken faster than a β-C—D bond.

Problem 13.15:

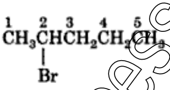
Write structural formulas for all the alkyl bromides of molecular formula $C_5H_{11}Br$. Name each isomer.

Solution:



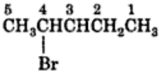
$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2Br$

1-Bromopentane



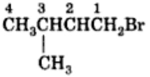
$\overset{1}{C}H_3\underset{\underset{Br}{|}}{\overset{2}{C}}H\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$

2-Bromopentane



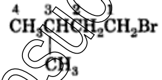
$\overset{5}{C}H_3\underset{\underset{Br}{|}}{\overset{4}{C}}H\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}H_3$

3-Bromopentane



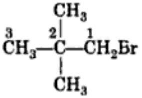
$\overset{4}{C}H_3\underset{\underset{CH_3}{|}}{\overset{3}{C}}H\overset{2}{C}H\overset{1}{C}H_2Br$

2-Methylbromobutane



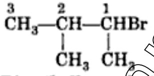
$\overset{4}{C}H_3\underset{\underset{CH_3}{|}}{\overset{3}{C}}H\overset{2}{C}H_2\overset{1}{C}H_2Br$

3-Methylbromobutane



$\overset{3}{C}H_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}—\overset{1}{C}H_2Br$

2, 2-Dimethylbromopropane

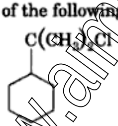


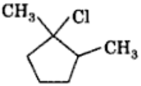
$\overset{3}{C}H_3—\underset{\underset{CH_3}{|}}{\overset{2}{C}H}—\underset{\underset{CH_3}{|}}{\overset{1}{C}HBr}$

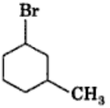
1, 2-Dimethylbromobutane

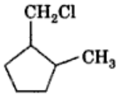
Problem 13.16:

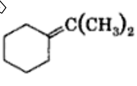
Assuming only E2 elimination, write structures for all the possible elimination products from each of the following alkyl halides :

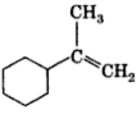
(*a*)


(*b*)


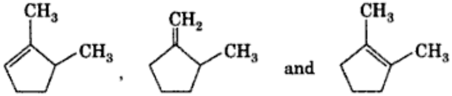
(*c*)


(*d*)


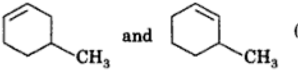
Solution: (*a*)


and


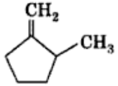
(b)



(c)



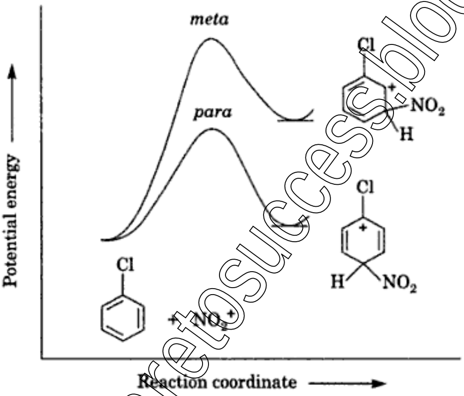
(d)



Problem 13.17:

On a potential energy diagram show the course of *meta* and *para* nitration of chlorobenzene.

Solution:

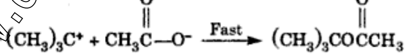


The Cl group is *ortho*- and *para*-directing. The ring is thus activated towards nitration at these positions but deactivated at the *meta*-position.

Problem 13.18:

Assume that acetolysis of *t*-butyl bromide in acetic acid involves the following mechanism:

$$(CH_3)_3CBr \overset{\text{Slow}}{\rightleftharpoons} (CH_3)_3C^+ + Br^-$$



$$(CH_3)_3C^+ + CH_3\overset{\overset{O}{\|}}{C}{-}O^- \xrightarrow{\text{Fast}} (CH_3)_3CO\overset{\overset{O}{\|}}{C}CH_3$$

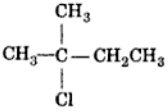
If addition of sodium acetate to the reaction mixture does not increase the rate appreciably, which step is rate-determining?

Solution: First step is rate determining because acetate ion reacts only in the second and fast step.

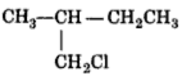
Problem 13.19:

An alkyl halid, $C_5H_{11}Cl$, by formation of Grignard reagent and subsequent hydrolysis yields 2-methylbutane. Suggest four possible formulas for the original alkyl halide which will yield this single product.

Solution: Four possible alkyl halides are the following:

(*i*) 

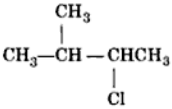
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2CH_3$

(*ii*) 

$CH_3-\underset{\underset{CH_2Cl}{|}}{CH}-CH_2CH_3$

(*iii*) 

$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_2Cl$

(*iv*) 

$CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}CH_3$

Problem 13.20:

Are S_N2 reactions stereospecific and/or stereoselective ?

Solution: S_N2 reactions are stereospecific because the stereoisomeric reactants give stereochemically different products. These reactions are also stereoselective because they form predominantly only one of a posible pair of in enantiomers or one of the possible diastereoisomers.

Problem 13.21:

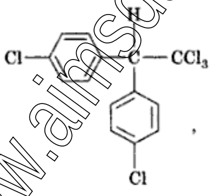
A compound with molecular formula C_5H_{10} does not react with chlorine in the dark, yields a single product, C_5H_9Cl in bright sunlight. Write the structure of the original compound.

Solution: For a hydrocarbon of formula C_5H_{10}, there is a choice between an alkane and a cycloalkane. Since chlorination yields C_5H_9Cl only, the original compound is cyclopentane.

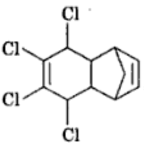
Problem 13.22:

Write the names and structures of some chlorinated hydrocarbons that are useful to crops.

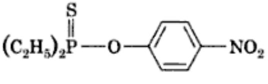
Solution:



DDT



Aldrin



Parathion

Problem 13.23:

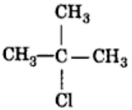
Give an example where hydrolysis of an alkyl halide may proceed according to S_N1 mechanism and one example where it may proceed through S_N2.

Solution: *t*-Butyl chloride $(CH_3)_3CCl$ hydrolysis by S_N1 and methyl chloride CH_3Cl by S_N2 mechanism.

Problem 13.24:

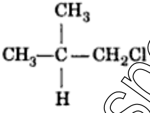
Why is S_N2 displacement more difficult with 2-methyl-2-chlorobutane than with 2-methyl-1-chlorobutane?

Solution:



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_3$$

2-Methyl-2-chlorobutane



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-CH_2Cl$$

2-Methyl-1-chlorobutane

Because 2-methyl-2-chlorobutane is a tertiary chloride.

Problem 13.25:

When CH_3Br is treated with CN^-, the major product is CH_3CN, but some CH_3NC is also formed. Explain.

Solution: The CN^- ion can be described by two resonance structures $:C^-:::N: \longleftrightarrow :C::\ddot{N}:^-$ in which case a formal negative charge is placed on either C or N atom, to give rise to a mixture of products.

Problem 13:26

The chlorine atom in *p*-nitrochlorobenzene but not in *m*-nitrochlorobenzene is replaced by -OH on treatment with aq. $NaHCO_3$. Why ?

Solution: *m*-Nitro group does not activate the ring toward nucleophilic attack.

Problem 13.27:

The rate of formation of *t*-butyl ether from the reaction of *t*-butyl bromide with ethanol does not increase if a better nucleophile ethoxide ion is added.

Solution: Because the rate depends only on the concentration of *t*-butyl bromide (S_N1 reaction).

Problem 13.28:

The following chlorides undergo solvolysis in the following order. Explain.

$$(C_6H_5)_3CCl > (C_6H_5)_2CHCl > C_6H_5CHClCH_3 > C_6H_5CH_2Cl$$

Solution: Because this is the order of the stability of carbocations formed after the cleavage of the C—Cl bond in each compound.

Problem 13.29:

The following reaction proceeds by an S_N2 pathway.

$$C_6H_5CH_2Br + NaN_3 \longrightarrow C_6H_5N_3 + NaBr$$

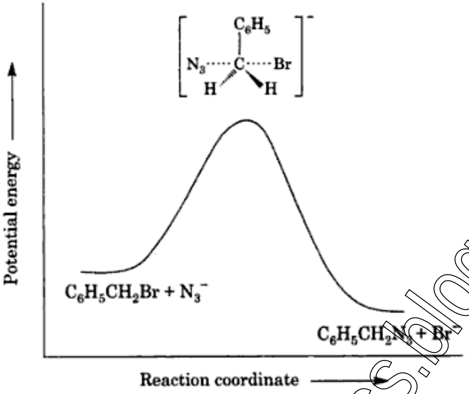
(*a*) Write an equation for the expected rate constant.

(*b*) Draw a potential energy diagram for the reaction.

(*c*) How would the rate of the reaction change if concentration of sodium azide is doubled ?

Solution: (*a*) rate = $k[C_6H_5CH_2Br]\,[NaN_3]$

(*b*)

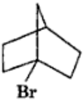


(*c*) The rate will be doubled.

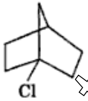
Problem 13.30:

Rank the following halides in order of increasing rates of S_N1 solvolysis. Explain your answer.

(*a*)

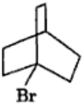


(*b*)



(*c*) $(CH_3CH_2CH_2)_3CBr$

(*d*)



Solution: *c* > *d* > *a* > *b*, because

(*c*) Forms a stable carbocation.

(*d*) Flexible structure, thus can support a carbocation.

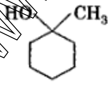
(*a*) An alkyl bromide reacts faster than a chloride (*b*).

(*a*) and (*b*) are less reactive because the three carbon atoms attached to the electron deficient carbon are tied back units the bicyclic ring structure. They cannot become coplanar without introducing a great deal of strain into the molecule.

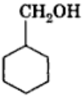
Problem 13.31:

Show how 1-(bromomethyl) cyclohexane might be transformed into each of the following compounds. The products should be free of isomers.

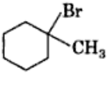
(*a*)



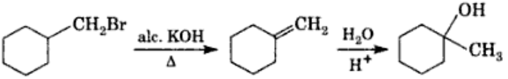
(*b*)



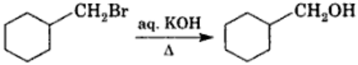
(*c*)



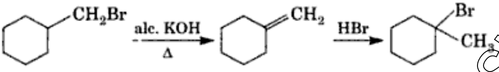
Solution: (*a*)



(*b*)



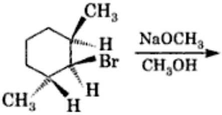
(*c*)



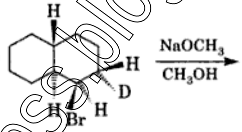
Problem 13.32:

Give the expected products of E2 elimination for each of the following reactions:

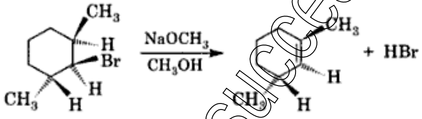
(*a*)



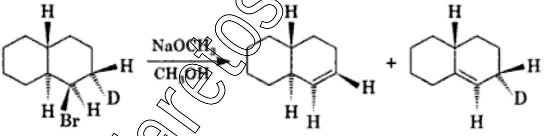
(*b*)



Solution: (*a*)



(*b*)



Problem 13.33:

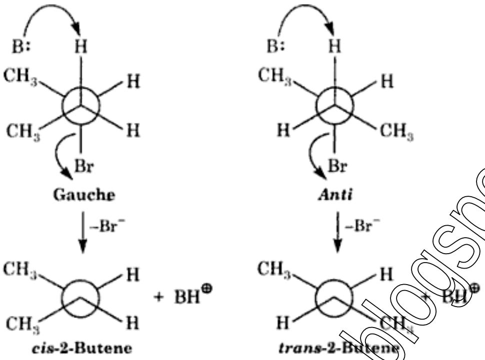
A concentrated aqueous solution of HBr reacts with C_2H_5OH but a concentrated aq. solution of NaBr does not do so.

Solution: In the initial step, the alcohol is protonated by HBr to form protonated alcohol. In this step a poor leaving group (OH^-) is converted to a good leaving group (H_2O). In the next step Br^- attack by S_N2 mechanism takes place to form ethyl bromide. NaBr solution does not have H^+ to protonate the alcohol thereby prohibiting the formation of good leaving group (H_2O).

Problem 13.34:

Trans-2-butene is obtained as the major product on dehydrobromination of 2-bromobutane.

Solution: The β-hydrogen and the leaving group in 2-bromobutane can assume an *anti*-periplanar conformation in two ways:



The *gauche* conformation of 2-bromobutane has more energy (hence less stable) than *anti* conformation due to torsional strain. Therefore, the major product is obtained from *anti*-conformation as *trans*-2 butene.

Problem 13.35:

Iodide ion acts as a good entering as well as a good leaving group in nucleophilic substitution reactions. Explain.

Soluton: The C—I bond energy (45 kcal/mol) is low compared to other carbon-halogen bonds. Therefore the C—I bond is easily stretched in the transition state. Thus this ion is a good leaving group. The iodide ion is larger in size and less solvated by the medium compare to other halide ions. Therefore attack by iodide ion is more favorable.

Problem 13.36:

Fluoride ion works as a good leaving group in aromatic nucleophilic substitution of 2, 4-dinitrofluorobenzene, even though it is a poor leaving group in aliphatic S_N1 and S_N2 mechanisms.

Solution: In aromatic nucleophilic substitution when the leaving group is CI, Br or I, the rate differs only by a factor of 5. This behavior is not expected in a reaction in which Ar—X bond is broken in the rate determining step. An increase in the electronegativity of the leaving group such as F causes a decrease in the electron density at the site of attack by the nucleophile, resulting in a fast reaction. When the leaving group is F, the rate is much faster compared to other halo groups. This indicates that the mechanism is different from S_N1 and S_N2 pathways.

Problem 13.37:

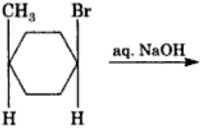
The rate of the following S_N2 reaction increases with increasing polarity of the solvent:

$$R_3\ddot{N} + R{-}X \xrightarrow{\text{Solvent}} R_4N^+X^-$$

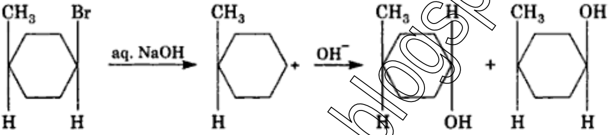
Solution: A polar solvent stabilizes the transition state it being ionic, more than the reactants which have no separation of charge due to ion-ion interactions. Therefore rate of the reaction increases with increase in the polarity of the solvent. An increase in solvent polarity decreases both ΔH and E_a .

Problem 13.38:

Write the structure of the products that would be obtained in an S_N1 reaction of *cis*-1-bromo-4-methylcyclohexane with dilute aqueous NaOH.

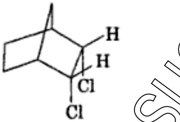


Solution:



Problem 13.39:

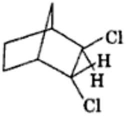
Which of the isomer in the following pair will eliminate faster in the presence of base? Write the structure of the product.



cis-2, 3-Dichloronorbornane

(I)

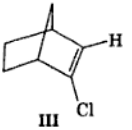
or



trans-2, 3-Dichloronorbornane

(II)

Solution: This is an example of *syn*- elimination in which leaving group cannot achieve *anti*-periplanar conformation. In compound (I) the *exo* hydrogen cannot achieve a dihedral angle of 180° with the *endo* CI group because of rigid structure of the molecule. The H—H and Cl—C pairs are in *cis*-conformation. Therefore they are not suitable for elimination of HCl. The compound (II) will eliminate by a concerted *syn* coplanar mechanism because H and CI pair is present in a *cis* conformation to give product (III).

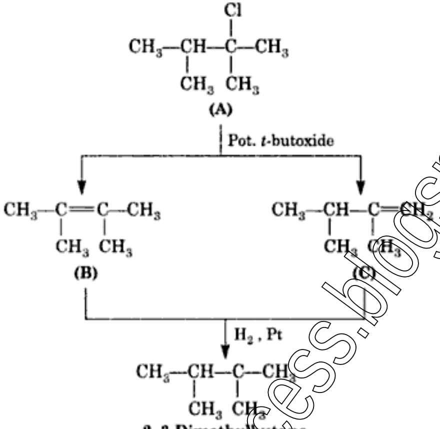


III

Problem 13.40:

An alkyl halide (A) of molecular formula $C_6H_{13}Cl$ on treatment with potassium *tert*-butoxide gives two isomeric alkenes (B) and (C) of molecular formula C_6H_{12}. Both alkenes on hydrogenation (H_2/Pt) give 2, 3-dimethylbutane. Identify (B) and (C).

Solution: Because the final product is 2, 3-dimethylbutane, the original alkyl halide A, can be only the following:

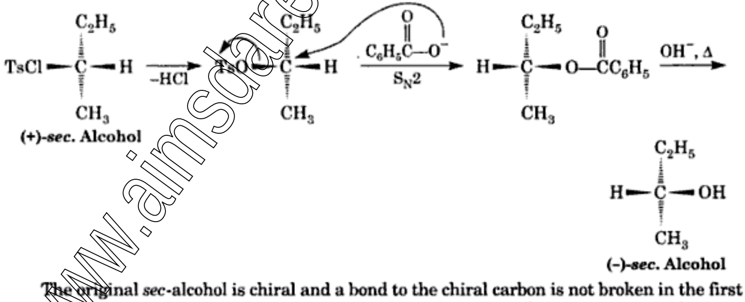


2, 3-Dimethylbutane

Problem 13.41:

When *sec*-butyl alcohol of rotation + 13.8° was treated with tosyl chloride and the resulting tosylate was allowed to react with sodium benzoate, there was obtained *sec*-butyl benzoate. Alkaline hydrolysis of this ester gave *sec*-butyl alcohol of rotation –13.4°. In which step must inversion have taken place? How do you account for this?

Solution: The sequence of reaction takes place in three steps.

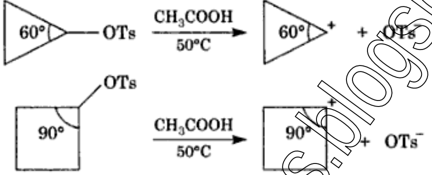


The original *sec*-alcohol is chiral and a bond to the chiral carbon is not broken in the first step because of the nature of reaction as is obvious inversion takes place in second step because it is an S_N2 displacement step.

Problem 13.42:

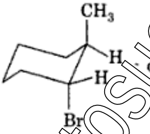
The first order acetolysis (50°C) rate of cyclobutyl *p*-toluenesulfonate is much higher than that of cyclopropyl *p*-toluenesulfonate. Explain.

Solution: This is due to bond angle strain (I-strain). This is higher for the smaller ring system. The normal bond angles in these rings are 60° and 90° respectively. On forming a carbocation this angle still remains the same though a carbocation has an angle of 120°. Thus there is a greater departure of bond angle in the smaller ring system inhibiting the ion formation. This results in slowing the acetolysis rate of cyclopropane derivative.

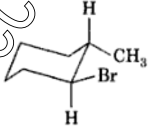


Problem 13.43:

Which of the following bromides (I or II) will solvolyze faster in S_N1 reaction and why?



or



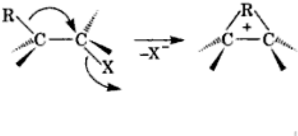
I II

Solution: Compound I will solvolyze faster. The rate of the S_N1 reaction depends on the difference in energy of the ground states rather than the transition states. The less stable diaxial compound (I) thus reacts faster.

Problem 13.44:

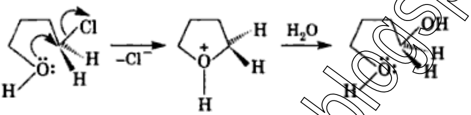
Describe neighbouring group participation with suitable examples.

Solution: A properly placed group in a molecule can assist in the departure of the leaving group. The involvement of a functional group with a reaction center in a molecule leading to reaction *via* a cyclic transition state is known as *neighbouring group participation.* If such a participating results in an increase in the rate, the pheinomenon is called *anchimeric assistance*. A participation group results in the formation of a bridged ion or a non-classical ion intermediate. In this type of intermediate the participating group R is bonded to both the carbons C_1—C_2 simultaneously. The positive charge is thus delocalized over all the carbon atoms. An attack of the solvent in a subsequent step at the carbon atom leads to products.

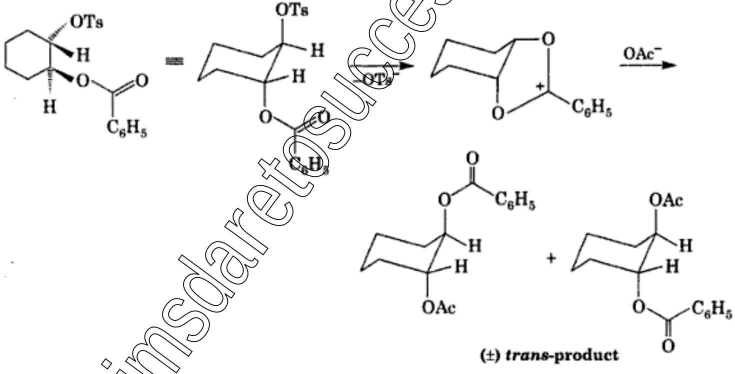


The participating group R may be any group containing O, N, S, C, halogens, a double bond or an aryl group. In a systematic study of chlorohydrins $Cl(CH_2)_nOH$, the rate of hydrolysis in water was found to be larger when $n = 4$, *i.e.* tetramethylene chlorohydrin. It was almost 100 times as high as in ethylene chlorohydrin $(n = 2)$ under identical experimental conditions. Neither resonance not inductive effects can account for this high reactivity. It seems that the hydroxy group in some way is involved in the reaction.

The hydroxy group participates as a neighbouring group and by pushing the leaving group form's *oxonium ion*. This cyclic ion in not observed since it undergoes immediate S_N2 attack by the solvent forming the normal acyclic product.



In 1, 2-disubstituted cyclohexane ring systems, the neighbouring group participation requires a diaxial (*trans*) geometry. This is demonstrated for the acetolysis of *cis*- and *trans*-1-benzoyloxycyclohexyl *p*-toluenesulfonate.

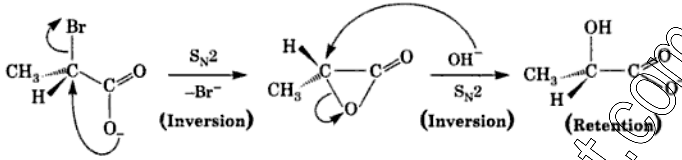


(±) ***trans*-product**

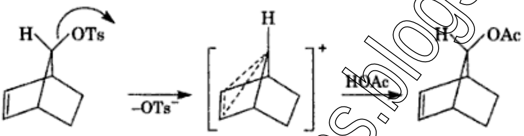
No such participation by the benzolyloxy group is observed in the *cis*-isomer.

Neighbouring group participation requires two sequential S_N2 displacements each of which must be accompanied by inversion of configuration at the reaction center. The net stereochemical result is 100% retention.

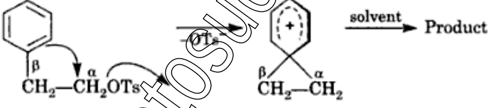
This is apparent from the basic hydrolysis of α-bromopropionic acid. The intermediate lactone undergoes a second S_N2 displacement to yield a product of overall retention of stereochemistry.



Another interesting case in which the participation by C═C bond takes place is the norbornenyl system. The acetolysis rate of *anti*-7-norbornenyl tosylate is faster than that of *anti*-7-norbornenyl tosylate. In the former a C═C bond participates to produce a non-classical ion intermediate. The product formed has 100% retention.



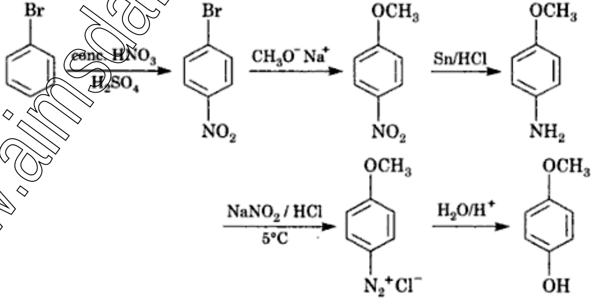
An aryl group also participates in certain solvolysis reactions. The β-aryl group assists in the departure of the leaving group leading to a bridged ion called the *phenonium ion*. The deriving force for this reaction is the formation of this ion. Its formation has been supported by enhanced rates of solvolysis and rearrangement of the aryl group.



Problem 13.45:

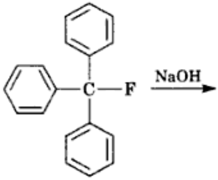
Synthesize 4-methoxyphenol from bromobenzene in NOT more than five steps.

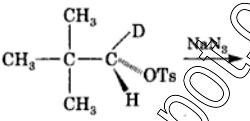
Solution:

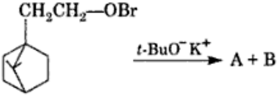


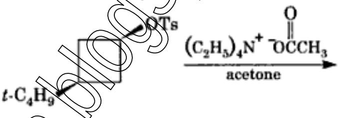
Problem 13.46:

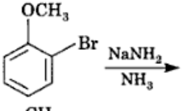
Predict the products of the following reactions:

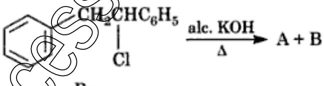
(a)


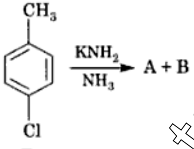
(b)


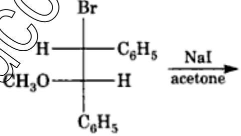
(c)


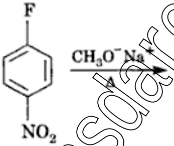
(d)


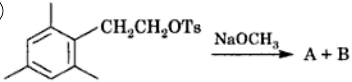
(e)


(f)


(g)


(h)


(i)


(j)


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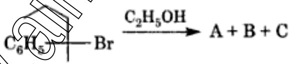
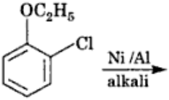
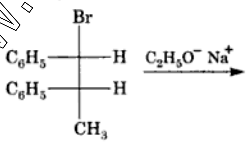
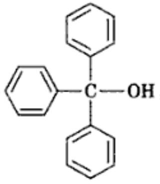
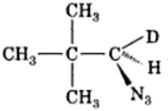
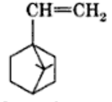
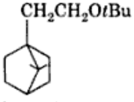


(l)


(m)


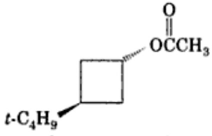
Solution: (*a*)  , the reaction proceeds *via* a triphenylmethyl carbocation.

(*b*)  , inversion of configuration takes place.

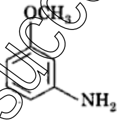
(*c*)  + 

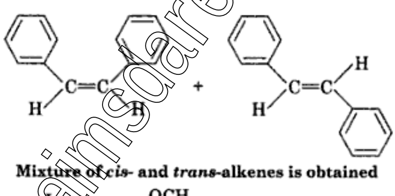
(Major) **(Minor)**

Since the base is bulky displacement occurs to a minor extent.

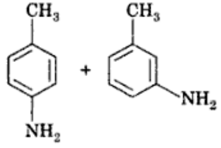
(*d*) 

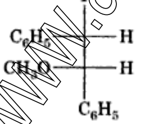
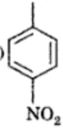
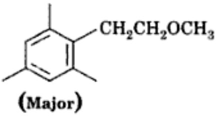
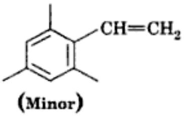
(*trans*-product)

(*e*)  , *via* benzyne intermediate

(*f*) 

Mixture of *cis*- and *trans*-alkenes is obtained

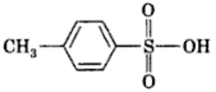
(*g*) 

(*h*)  (*i*)  (*j*)  + 

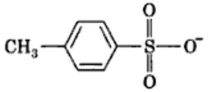
(Major) **(compare with C)** **(Minor)**

A strong base is present, therefore both substitution and elimination can occur. But the nucleophile is not bulky so substitution predominates.

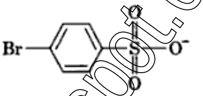
Sulfonate esters have approximately the same reactivities as alkyl bromides in substitution and elimination reactions. They are good leaving groups. In general good leaving groups are weak bases. Sulfonate anions are weak bases, they are the conjugate bases of sulfonic acids.



***p*-Toluenesulfonic acid**

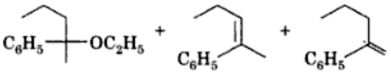


(-OTs) or
Tosylate anion

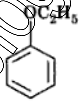


Brosylate (-OBr)

(*k*)



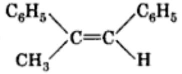
(*l*)



(Dehalogenation occurs)

, This reagent removes the halogen atom from the benzene ring.

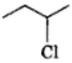
(*m*)



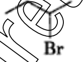
$$\begin{matrix} C_6H_5 & & C_6H_5 \\ & C{=}C & \\ CH_3 & & H \end{matrix}$$

Problem 13.47:

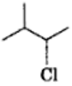
(*a*) Arrange in decreasing order of S_N2 reactivity



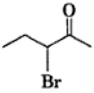
I



II

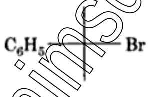


III

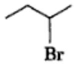


IV

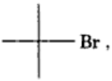
(*b*) Arrange in decreasing order of S_N1 reactivity



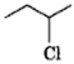
I



II

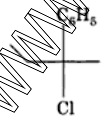


III



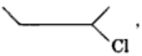
IV

(*c*) Arrange in increasing order of S_N1 reactivity

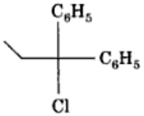


I

II



III



IV

Solution: (*a*) IV > II > I > III

An adjacent carbonyl group enhances the reactivity in S_N2 reaction.

(*b*) I > III > II > IV

I forms the most stable carbocation.

(*c*) III < II < I < IV

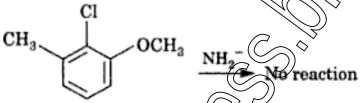
IV produces the most stable carbocation.

Problem 13.48:

Discuss briefly the chemistry of the benzyne intermediate.

Solution: An aryl halide like chlorobenzene does not undergo a direct displacement with a nucleophile. But when it is treated with a strong base like KNH_2, it is converted into aniline. This is not a simple displacement but an elimination-addition reaction proceeding through a benzyne intermediate.

If no *ortho* hydrogen is available then benzyne is not formed.

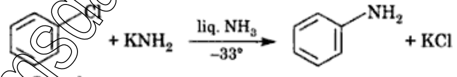


If sufficient strain is built into a molecule it can become so unstable that it attains the character of a reactive intermediate. A *benzene* is such an intermediate. It is benzene minus two *ortho* hydrogens and is thus also termed as *dehydrobenzene*. The triple bond does not have the same characterstics as in acetylene.

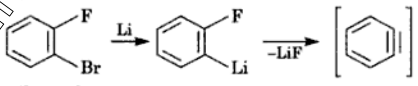
Benzyne
(Dehydrobenzene)

This intermediate may be generated by the following important methods:

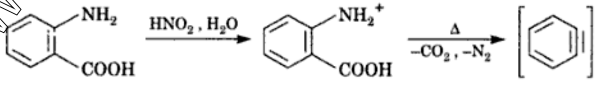
1. From Chlorobenzene



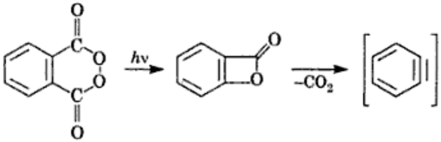
2. From Bromofluorobenzene



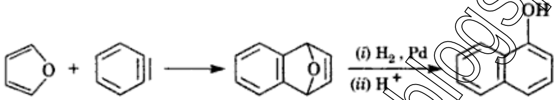
3. From anthranilic acid



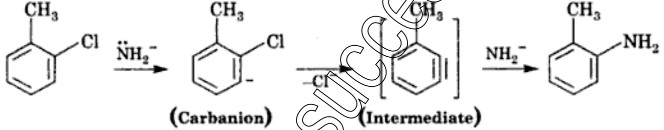
4. From phthaloyl peroxide



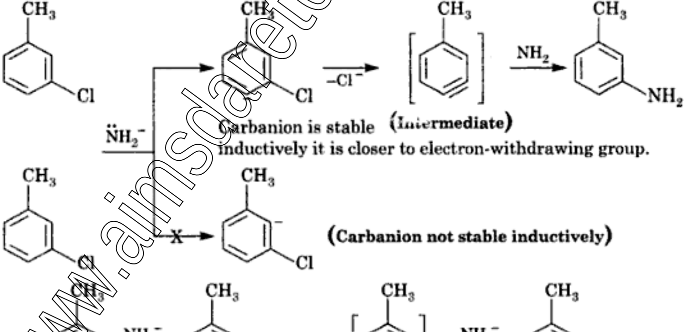
Benzynes undergo many interesting reactions. A benzyne functions as a reactive dienophile in the Diels-Alder reaction. The adducts so obtained are valuable synthetic intermediates, as illustrated by the formation of 1-napthol.



The substituted isomeric halobenzenes give different products through benzyne formation. The formation of the major product, however, can be predicted on the basis of inductive electronic effect of the stability of the intermediate carbanion. This is illustrated for isomeric chlorotoluenes and chloroanisoles. *o*-Chlorotoluene leads to *o*-toluidine.

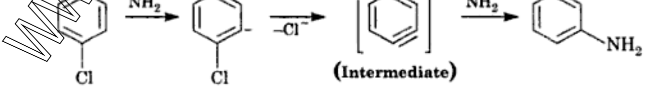


Note : The -CH_3 group is electron-donating inductively and this effect operates here.

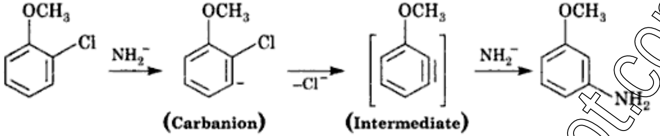


Carbanion is stable inductively it is closer to electron-withdrawing group.

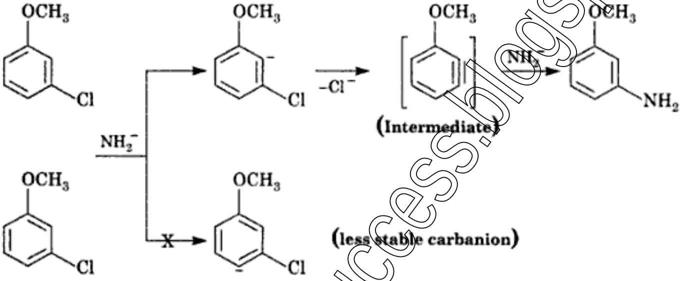
(Carbanion not stable inductively)

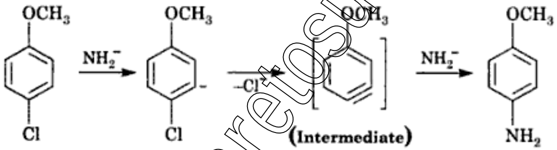


m- and *p*-Chlorotoluene yield the same product *m*-toluidines.

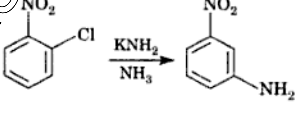


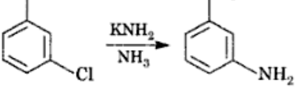
Note: Since the carbanion is not planar, only the inductive electron-withdrawing effect of -OCH_3 group operates here.





o-Chloroanisole and *m*-chloroanisole give the same product *m*-anisidine. *o*-Chloronitrobenzene and *m*-chloronitrobenzene under the conditions of benzyne formation also yield the *meta* derivatives.





Problem 13.49:

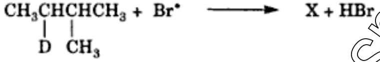
t-Butyl fluoride is solvolyzed only in strong acidic solutions.

Solution: F^- is a poor leaving group but formation of H-bond with a strong acid assists its departure.

Problem 13.50:

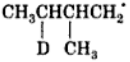
Select the correct answer.

(*a*) Consider the following reaction

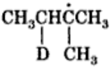


$$\mathrm{CH_3\underset{D}{CH}\underset{CH_3}{CH}CH_3 + Br^{\bullet} \longrightarrow X + HBr}$$

Identify the structure of the major intermediate product X.

A. 

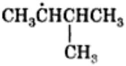
$\mathrm{CH_3\underset{D}{CH}\underset{CH_3}{CH}CH_2^{\bullet}}$

B. 

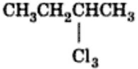
$\mathrm{CH_3\underset{D}{CH}\underset{CH_3}{\dot{C}}CH_3}$

C. 

$\mathrm{CH_3\underset{D}{\dot{C}}\underset{CH_3}{CH}CH_3}$

D. 

$\mathrm{CH_3\dot{C}H\underset{CH_3}{CH}CH_3}$

(*b*) 

$\mathrm{CH_3CH_2\underset{Cl_3}{CH}CH_3}$ obtained by chlorination of *n*-butane will be

A. Racemic mixture B. *meso* C. *d*-form D. *l*-form

(*c*) The order of reactivity of the following alkyl halides in S_N2 reaction is

A. RF > RCl > RBr > RI

B. RF > RBr > RCl > RI

C. RCl > RBr > RF > RI

D. RI > RBr > RCl > RF

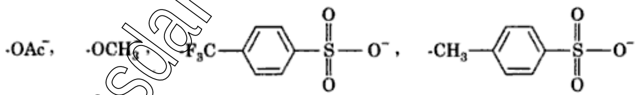
(*d*) Which of the following will react with water?

A. CCl_4 B. $CHCl_3$ C. CCl_3CHO D. $ClCH_2CH_2Cl$

(*e*) Chlorine (Cl_2) reacts with CS_2 in the presence of I_2 to give

A. CCl_4 B. $CHCl_3$ C. CH_3I D. C_2H_5Cl

(*f*) In the following groups



I II III IV

the increasing order of leaving group is

A. I > II > III > IV B. IV > III > I > II C. III > II > I > IV

D. II > III > III > I

(*g*) Which has the highest nucleophilicity ?

A. F^- B. OH^- C. CH_3^- D. NH_2^-

(*h*) Benzoyl chloride is prepared from benzoic acid by

A. Cl_2, *h*ν B. Cl_2, H_2O C. SO_2Cl_2 D. $SOCl_2$

(*i*) In the reaction of *p*-chlorotoluene with KNH_2 / NH_3 the major product is:

A. *o*-Toluidine B. *m*-Toluidine C. *p*-Toluidine D. *p*-Chloroaniline

(*j*) An unknown alkyl halide A reacts with alc. KOH to produce a hydrocarbon B, C_4H_8. Ozonolysis of B affords one mole of propionaldehyde and one mole of formaldehyde. Suggest which structure among the following is the correct structure of A.

A. $CH_3(CH_2)_3Br$ B. $Br(CH_2)_4Br$ C. $CH_3CH_2CHBrCH_3$ D. $CH_3CHBrCHBrCH_3$

(*k*) Among the compounds

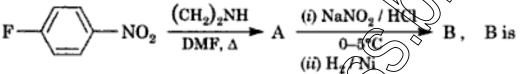
A. Toluene	B. *o*-Dichlorobenzene	C. *m*-Dichlorobenzene	D. *p*-Dichlorobenzene
I	II	III	IV

the order of increasing dipole moment is:

A. I < IV < II < III B. IV < II < I < III C. IV < I < III < II

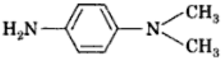
D. IV < I < II < III

(*l*)

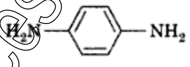


B is

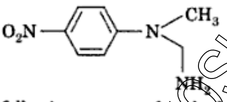
A.



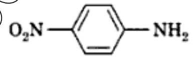
B.



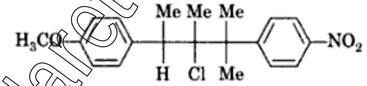
C.



D.

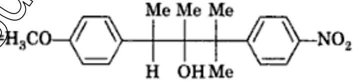


(*m*) The following compound on hydrolysis in aqueous acetone,

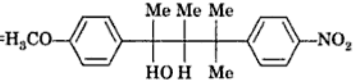


will give :

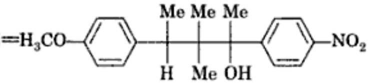
X=



Y=



Z=



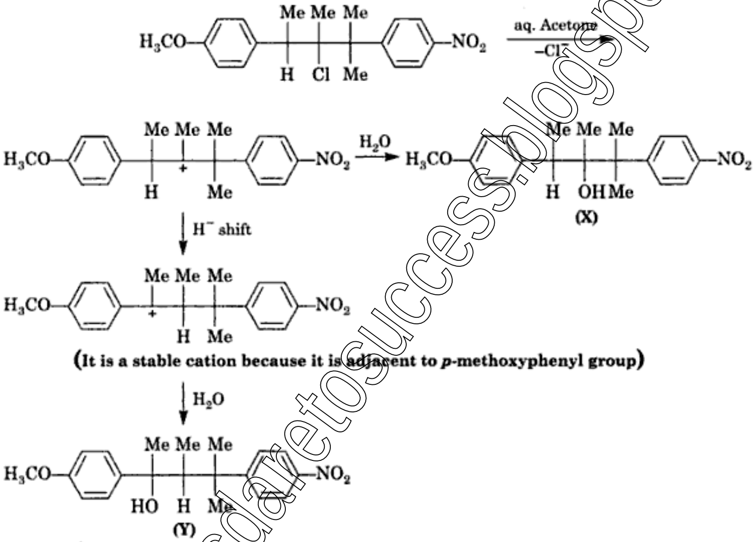
A. Mixture of X and Y B. Mixture of X and Z C. Only Z D. Only X

Solution: (*a*) B, it is a tertiary stable free radical intermediate. (*b*) A, mixture of *d*-and *l*. products would be formed. (*c*) D, I is a better leaving group than other halides. (*d*) C, the hydrated compound is stable. (*e*) A (*f*) B (*g*) C (*h*) D (*i*) B

(*j*) A, $CH_3CH_2CH_2CH_2Br \xrightarrow{\text{alc. KOH}} CH_3CH_2CH{=}CH_2 \xrightarrow{O_3} CH_3CH_2CHO + OCH_2$

(*k*) D (*l*) A

(*m*) A, Acetone is used to dissolve the halide. It is an S_N1 reaction and proceeds *via* the formation of a carbocation.



(X)

(It is a stable cation because it is adjacent to *p*-methoxyphenyl group)

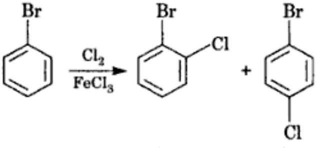
(Y)

(Compound Z will not be obtained because by a $-CH_3$ shift it will lead to an unstable carbocation)

Problem 13.51:

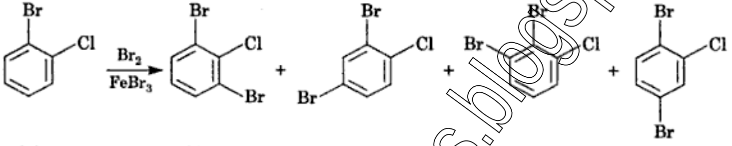
When bromobenzene is monochlorinated, two isomeric compounds A, and B, are obtained. Monobromination of A, gives several isomeric products of molecular formula $C_6H_{13}ClBr_2$. Bromination of B, yields only two isomeric products C and D. Compound C, is identical with one of the compounds obtained from the monobromination of A, however D, is totally different from any of the isomeric compounds obtained from the bromination of A. Give the structures A to D and also structures of four isomeric monobrominated products of A. Support your answer with reasoning.

Solution: Group Br is *ortho-* and *para-* directing.



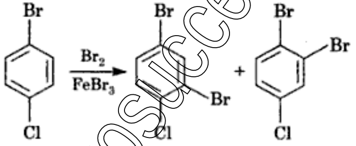
(A) (B)

From A, four products are obtained because both Br and Cl will control the orientation.



(A) (I) (II) (III) (IV)

Compound is symmetrical therefore, it gives only (I to IV) two products.



(B) (C) (D)

Compound (C) is identical with II.

Compound (D) is not identical with any of the four compounds.

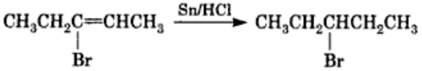
Problem 13.52:

An organic compound A, C_5H_9Br readily decolorizes bromine water and $KMnO_4$ solution, A gives B, $C_5H_{11}Br$ on treatment with Sn/HCl. The reaction of A with $NaNH_2$ produces C with the evolution of ammonia.

Compound C, neither reacts with sodium nor forms any metal acetylide but reacts with Lindlar catalyst and H_2 to give D, and on reaction with Na/liq. NH_3 produces E. Both compounds D and E are isomers. Propose structures for each A to E with reasoning.

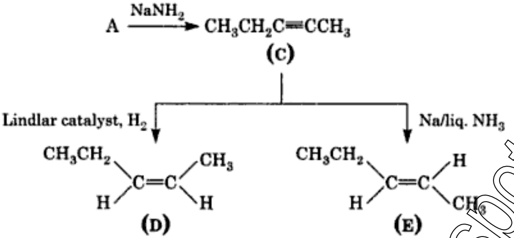
Solution: The last two reduction indicate that C is an internal alkyne and A is an alkene.

Therefore A, is



$$\underset{\substack{|\\ Br}}{CH_3CH_2C}{=}CHCH_3 \xrightarrow{Sn/HCl} CH_3CH_2\underset{\substack{|\\ Br}}{CH}CH_2CH_3$$

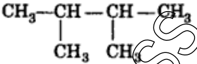
(B)



Problem 13.53:

An alkyl halide X, $C_6H_{13}Cl$ on treatment with pot *t*. butoxide gives two isomeric alkenes Y, and Z, C_6H_{12}. Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of X, Y and Z.

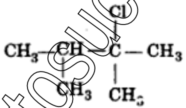
Solution: Both Y and Z alkenes give



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

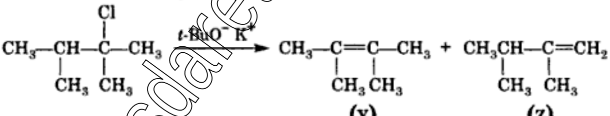
2, 3-Dimethylbutane

There the corresponding alkyl chloride X, is one in which the Cl is linked to the 2-position in 2, 3-dimethylbutane. Only this will yield isomeric alkenes.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

This on elimination will give two isomeric alkenes.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3 \xrightarrow{t\text{-}BuO^-K^+} \underset{(Y)}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3} + \underset{(Z)}{CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2}$$

Problem 13.54:

An organic compound A, of molecule mass 185 g mole^{-1} contains C = 51.9%. H = 4.8%, and Br = 40.32%. Compound A cannot be easily hydrolyzed with aq NaOH but on photochlorination B, is obtained which on hydrolysis yields C, C_8H_9OBr. Compound C, reacts with conc. H_2SO_4 to give D, C_6H_7Br. Compound D on oxidation with alk. $KMnO_4$ gives E, $C_7H_5O_2Br$. E, can also be obtained by direct oxidation of A. Deduce structures A to E and justify your answer.

Solution: Empirical Formula of A

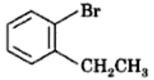
Element	*Percentage Composition*	*At. Weight*	*Rel. No. of atoms ratio*	*Simplest*
C	51.9	12	4.30	8
H	4.8	1	4.80	9
Br	40.32	80	5.04	1

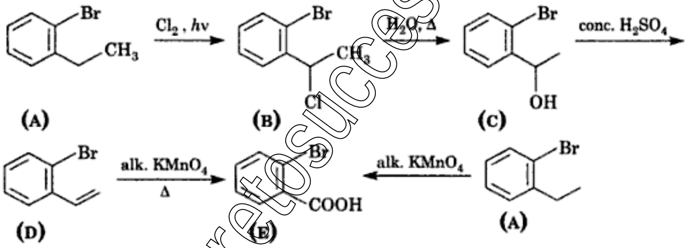
Empirical formula of A is C_8H_9Br

Mol. wt = 185

Mol. formula is C_8H_9Br

The compound A cannot be easily hydrolyzed it indicates that, Br atom is attached to the benzene ring.

∴ A is  or any of its *m*- or *p*-isomer.



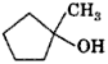
CHAPTER

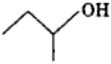
14

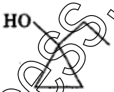
Alcohols and Phenols

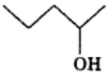
Problem 14.1:

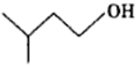
Classify the following alcohols into primary, secondary and tertiary.

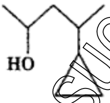
(a)


(b)


(c)


(d)


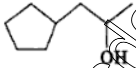
(e)


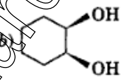
(f)


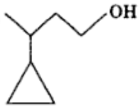
Solution: (a) Tertiary (b) Secondary (c) Tertiary (d) Secondary (e) Primary (d) Secondary.

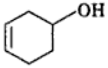
Problem 14.2:

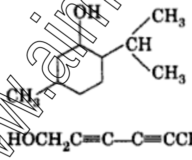
Suggest IUPAC name for each of the following alcohols :

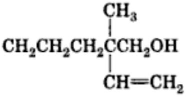
(a)


(b)


(c)


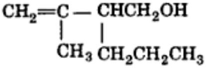
(d)


(e)


(f)


$$\begin{array}{c} CH_3 \\ | \\ CH_2CH_2CH_2CCH_2OH \\ | \\ CH{=}CH_2 \end{array}$$

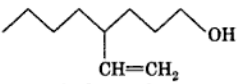
(g) $HOCH_2C{\equiv}C{-}C{\equiv}CCH_2OH$

(h)


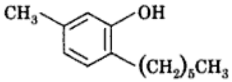
$$\begin{array}{l} CH_2{=}C - CHCH_2OH \\ \phantom{CH_2{=}}|| \\ \phantom{CH_2{=}}CH_3\ CH_2CH_2CH_3 \end{array}$$

(i) $CH{\equiv}CCH_2OH$

(j)



(k)

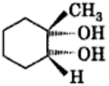


Solution: (*a*) 3-Cyclopentylpropan-2-ol (*b*) *cis*-1, 2-Cyclohexanediol (*c*) 3-Cyclopropylbutan-2-ol (*d*) Cyclohex-3-en-1-ol (*e*) 2-Isopropyl-5-methylcyclohexanol (*f*) 2-Methyl-2-propyl-3-buten-1-ol (*g*) Hexa-2, 4-diyn-1, 6-diol (*h*) 3-Methyl-2-propyl-3-butane-1-ol (*i*) 2-Propynol (Propargyl alcohol) (*j*) 4-Butyl-5-hexen-1-ol (*k*) 4-*n*-Hexylresorcinol.

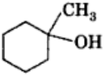
Problem14.3:

Starting from 1-methylcyclohexene, prapare the following alcohols:

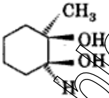
(*a*)



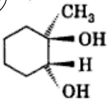
(*b*)



(*c*)

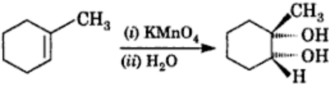


(*d*)

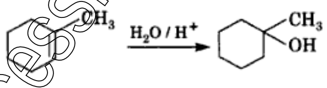


Solution:

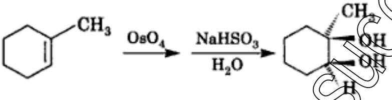
(*a*)



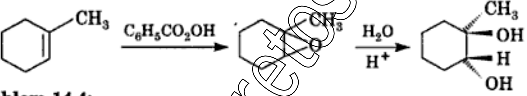
(*b*)



(*c*)



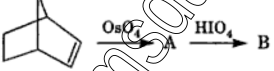
(*d*)



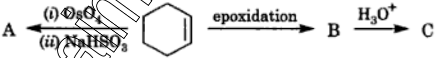
Problem 14.4:

Complete the following reactions:

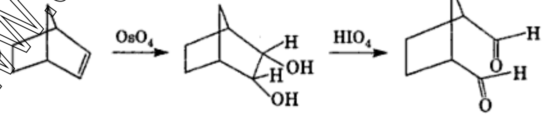
(*a*)



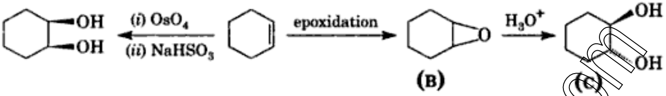
(*b*)



Solution: (*a*)

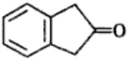


(b)



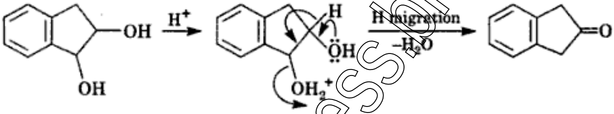
Problem 14.5:

From which glycol can the following compound (A) be synthesized by a pinacol-pinacolone rearrangement:



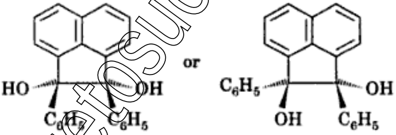
(A)

Solution: To obtain the precursor of (A), remove the keto group and put two -OH groups on adjacent C-atoms

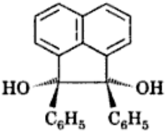


Problem 14.6:

Which of the following two diols would react faster in the pinacol-pinacolone rearrangement. Why ?

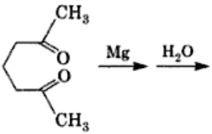


Solution: The following diol will react faster because the leaving and the migrating groups are *trans* to each other. In the second these are in *cis*- configuration.

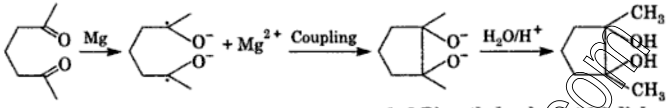


Problem 14.7:

Write the product and its IUPAC name in the following reaction:



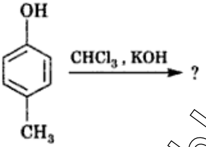
Solution:



1, 2-Di-methylcyclopent-1,2-diol

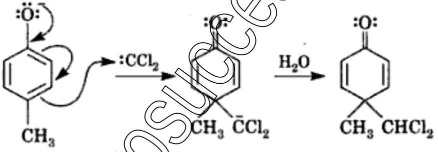
Problem 14.8:

What product would you expect in the following reaction ? Explain.



Solution: $CHCl_3$ + aq. KOH ⟶ $:CCl_2$ +
(**Dichlorocarbene**)

Dichlorocarbene and *p*-cresol react in the Reimer-Tiemann reaction.



It is an 'abnormal' product formed in the Reimer-Tiemann reaction when the dienone cannot tautomerize to regenerate a phenolic system.

Problem 14.9:

Write short notes on the following:

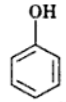
Absolute alcohol, destructive distillation of wood, power alcohol, acidity of phenols, fermentation, the Collins reagent, methyl alcohol and industrial alcohol.

Solution: Absolute alcohol. *Absolute alcohol* is 100% alcohol obtained by passing 95% alcohol through a dehydrating agent such as calcium oxide (anhydrous).

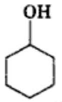
Destructive Distillation of Wood. This is a method of producing methyl alcohol from dried wood on heating it in large containers in the absence of air. Two fractions are obtained, gaseous and liquid. The liquid fraction on further treatment yields methanol.

Power Alcohol. The mixture obtained by mixing alcohol with benzene and petroleum used as motor fuel is called *power alcohol.*

Acidity of Phenols. The display of acidic character by most phenols is referred to as acidity of phenols. Phenol is much stronger acid than cyclohexanol. This is evident from the ionization constants of the two alcohols.

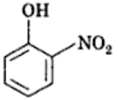


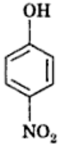
1×10^{-10}

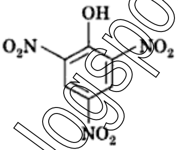


1×10^{-18}

Moreover, K_a this acidity can be further increased by electron-withdrawing substituents such as $-NO_2$ or -CN present on the aromatic nucleus at the *ortho* and *para* positions.

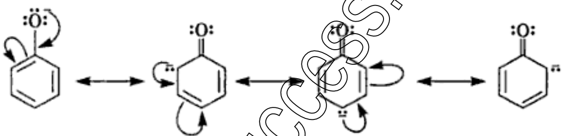






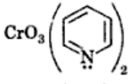
K_a 6.8×10^{-8} 6.5×10^{-8} 0.4

The resonance effect of the phenoxide ion is responsible for the acidity of phenols.



Fermentation. This is a process which involves the decomposition of molasses, sugars or starch by living organisms. It is purely a chemical process but is brought about almost by a specific enzyme—yeast, secreted by the cell of the organism. There are two types of yeast—Baker's yeast and alcohol yeast.

Collins reagent. A primary alcohol is oxidized to an aldehyde by $K_2Cr_2O_7$ in aqueous $K_2Cr_2O_7$. However, if water is present, it is difficult to stop the reaction at the aldehyde stage as it is further oxidized to a carboxylic acid. For this reason anhydrous preparations of Cr (VI) are used for the preparation of an aldehyde from a primary alcohol. A complex of pyridine, and two moles of pyridine in CH_2Cl_2 solvent is called the Collins reagent.



Methyl Alcohol. *Methyl alcohol* or methanol is also known as wood alcohol because at one time it was obtained by the destructive distillation of wood. Nowadays, methanol is obtained commercially from water gas $(CO + H_2O)$. Methanol is poisonous and causes permanent blindness if taken internally. It is used to denature ethyl alcohol. Methanol is used extensively as an anti freeze, as solvent and in the synthesis of formaldehyde. It is also used as a fuel.

Ethyl Alcohol. *Ethyl alcohol* is generally called industrial alcohol. It is prepared by two important processes—fermentation of molasses, sugar or starch and synthetically by the hydration of ethylene. Ethyl alcohol simply called alcohol is miscible with water in all proportions. About 70% of industrial alcohol is used by the chemical industry for the production of chemicals, the most important of which is acetaldehyde. It is also used as a solvent and a thinner. It is also employed in pharmaceuticals, toilet preparations and in the food industry.

Problem 14.10:

How would you distinguish between the following pairs?

(*a*) *o*-Cresol and benzyl alcohol (*b*) Phenol and cyclohexanol (*c*) Ethyl alcohol and methyl alcohol (*d*) 1-Pentanol and 3-pentanol (*e*) 1-Propanol and phenol.

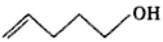
Solution: (*a*) *o*-Cresol gives coloration with $FeCl_3$ solution. (*b*) Phenol gives coloration with $FeCl_3$ solution. (*c*) Ethyl alcohol responds to the iodoform test. (*d*) 1-Pentanol responds to the iodoform test. (*e*) Phenol gives coloration with $FeCl_3$ solution.

Problem 14.11:

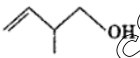
Write structural formulas for all the isomeric alcohols of formula C_5H_9OH and suggest their IUPAC names.

Solution:

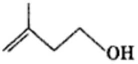
There are nine isomers of formula C_5H_9OH



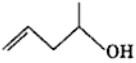
4-Penten-1-ol



2-Methyl-3-buten-1-ol

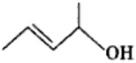


3-Methyl-3-buten-1-ol



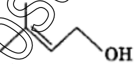
1-Methyl-3-buten-1-ol

3-Penten-1-ol

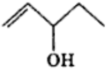


1-Methyl-2-buten-1-ol

2-Penten-1-ol



3-Methyl-2-buten-1-ol



4-Penten-3-ol

Problem 14.12:

Write the products of the reactions of *t*-butyl alcohol with PBr_3, conc. H_2SO_4, CH_3COCl, Na, CH_3MgBr, $Na_2Cr_2O_7/H_2SO_4$.

Solution: $(CH_3)_3CBr, (CH_3)_2C{=}CH_2; (CH_3)_3COCOCH_3, (CH_3)_3COO^-Na^+, CH_4$, no reaction.

Problem 14.13:

Arrange the following alcohols in the order of ease of dehydration.

$(C_6H_5)_3CCH_2OH,\ (C_6H_5)CHOHCH_3,\ (C_6H_5)_2COHCH_3.$

Solution: $(C_6H_5)_3COHCH_3 > (C_6H_5)_2CHOHCH_3 > (C_6H_5)_3CCH_2OH$

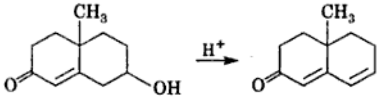
The order parallels the stability of the intermediate cation. The first alcohol forms the most stable tertiary cation.

Problem 14.14:

Offer explanation for the following observations:

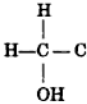
(*a*) Why is phenol unstable in the keto form?

(*b*) The following dehydration is extremely facile:



(*c*) Why does thinoyl chloride provide alkyl chlorides of high purity? (*d*) 2-Methyl-2-pentanol dehydrates faster than 2-methyl-1-pentanol. (*e*) Phenol is acidic but ethyl alcohol is neutral. (*f*) Ethanol responds to iodoform test but *tert* butanol does not. (*g*) A tertiary alcohol reacts faster than a primary alcohol in the Lucas test.

Solution: (*a*) Phenol loses the aromatic stabilization in the keto form. (*b*) The alkene formed is more stable due to resonance. (*c*) Because the other products formed during the reaction of thionyl chloride with alcohols are gaseous, and excape leaving pure alkyl chloride. (*d*) 2-Methyl-2-pentanol yields a stable alkene. (*e*) The phenoxide ion formed from phenol is stabilized by resonance.



(*f*) Ethanol contains the $\underset{\displaystyle OH}{\overset{\displaystyle H}{H—\overset{|}{\underset{|}{C}}—CH_3}}$ grouping but a tertiary alcohol does not.

(*g*) A tertiary alcohol forms a stable tertiary carbocation.

Problem 14.15:

Illustrate how ethyl alcohol and phenol differ or behave similarly towards the following reagents:

K, NaOH, PBr_3, HBr, PCl_5, $SOCl_2$ and $CH_3COOH/H^+/\Delta$

Solution:	*C_2H_5OH*	*C_6H_5OH*
K	H_2 evolved	No reaction
NaOH	No reaction	Forms salt
PBr_3	Forms bromide	No reaction
HBr	Forms bromide	No reaction
PCl_5	Forms chloride	No reaction
$SOCl_2$	Forms chloride	No reaction
CH_3COOH/H^+	Forms acetate	Forms acetate

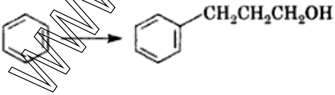
Problem 14.16:

How will you effect the following conversions?

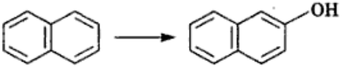
(*a*)

(*b*) $C_2H_5OH \longrightarrow CH_3CH_2CH_2OH$

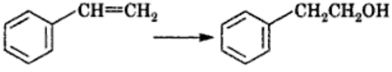
(*c*)



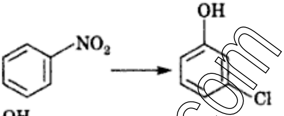
(*d*)



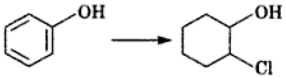
(*e*)



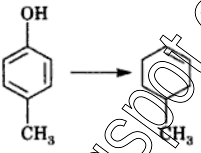
(*f*)



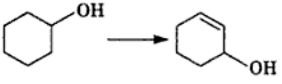
(*g*)



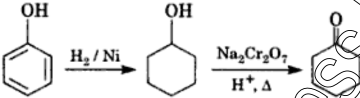
(*h*)



(*i*)

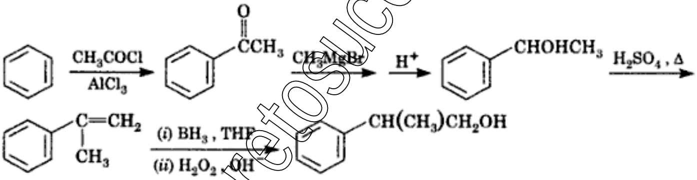


Solution: (*a*)

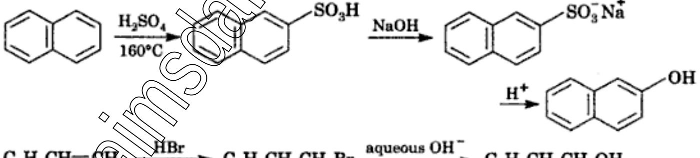


(*b*) $C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl \xrightarrow{KCN} C_2H_5CN \xrightarrow{Red} C_2H_5CH_2NH_2 \xrightarrow{HNO_2} C_2H_5CH_2OH$

(*c*)

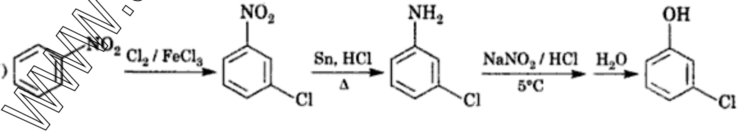


(*d*)

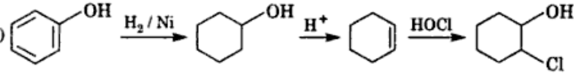


(*e*) $C_6H_5CH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr} C_6H_5CH_2CH_2Br \xrightarrow{\text{aqueous } OH^-} C_6H_5CH_2CH_2OH$

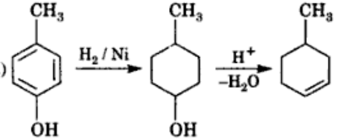
(*f*)



(g)



(h)



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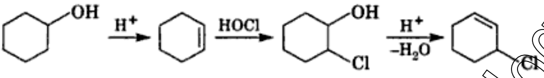
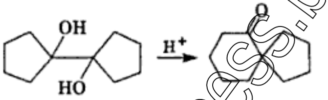
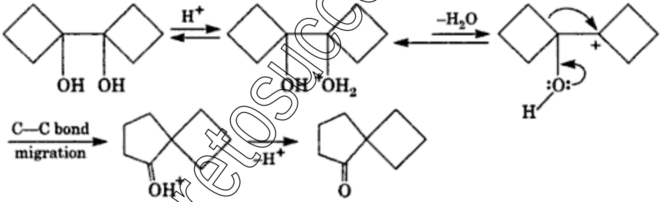


Problem 14.17:

Postulate a mechanism for the following reaction:



Solution:



Under acidic conditions, the diol in initially protonated at one of the -OH groups. This is followed by loss of water and formation of a carbocation. Then a C—C bond shifts resulting in the expansion of the ring and formation of an α-hydroxy carbocation. Such a cation is more stable than an ordinary cation. Finally loss of H⁺ yields the product.

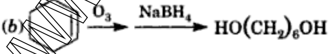
Problem 14.18:

(*a*) Why does ethylene glycol have a higher boiling point than dimethyl ether?

(*b*) How would you convert cyclohexene into 1, 6-hexanediol?

Solution: (*a*) Because of intramolecular hydrogen-bonding in ethylene glycol.

(*b*)



Problem 14.19:

Give chemical tests for phenolic and alcoholic groups in an organic compound.

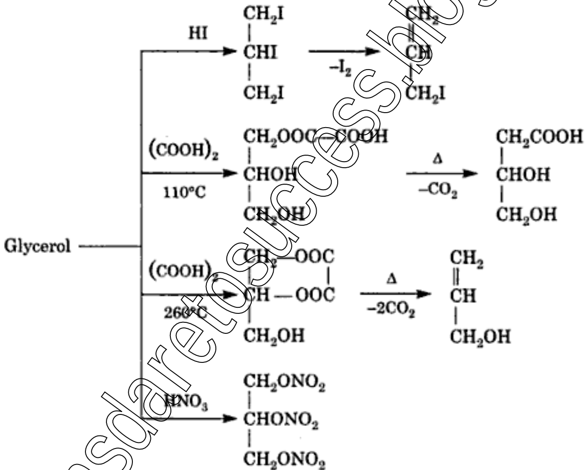
Solution: The following reagents may be used to test a phenolic and alcoholic groups.

Test	*C_6H_5OH*	*C_2H_5OH*
$FeCl_3$	Coloration	No colour
$K_2Cr_2O_7$ / H_2SO_4	No reaction	Oxidized to aldehyde
Na	No reaction	Evolves H_2 gas
Br_2	A solid derivative	No reaction
HBr	No reaction	A bromide

Problem 14.20:

How does glycerol react with (*a*) HI (*b*) $(COOH)_2$ and (*c*) Conc. HNO_3?

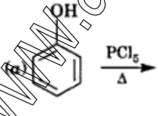
Solution:



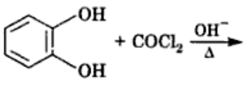
Problem 14.21:

Predict the product of the following reactions. If there is no reaction write N.R.

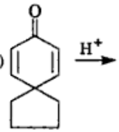
(*a*)

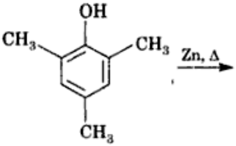


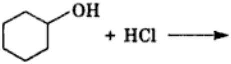
(*b*)

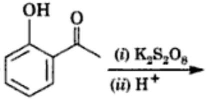


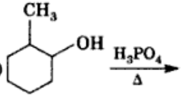
(*c*)



(*d*) 

(*e*) 

(*f*) 

(*g*) 

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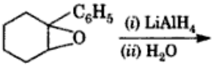
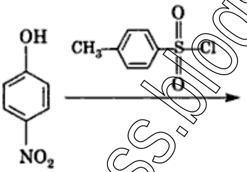
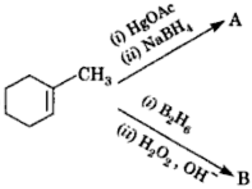
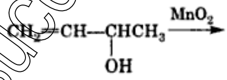
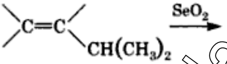
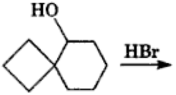
(*i*) 

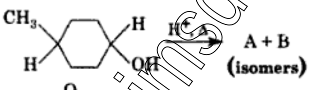
(*j*) 

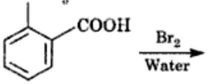
(*k*) 

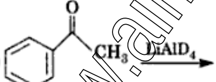
(*l*) 

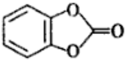
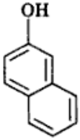
(*m*) 

(*n*) 

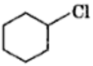
(*o*) 

(*p*) 

(*q*) 

Solution: (*a*) N.R. (*b*)  (*c*)  (*d*) 1, 3, 5-Trimethylbenzene

(e)



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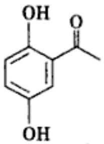

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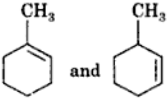

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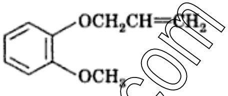

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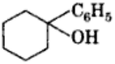

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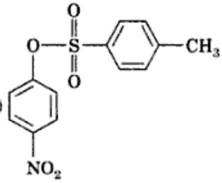

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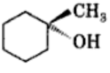
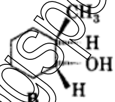
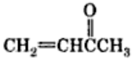


A



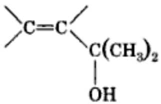
B

(l)



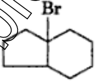
$$CH_2=CH\overset{\overset{O}{\|}}{C}CH_3$$

(m)



(Allylic oxidation)

(n)



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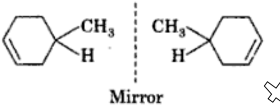

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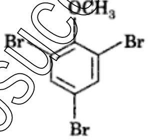

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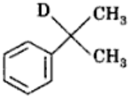


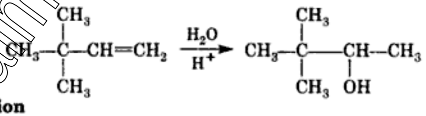
Problem 14.22:

List three methods with pertinent chemical equations for the preparation of alcohols from alkenes.

Solution: Three methods that can be considered are :

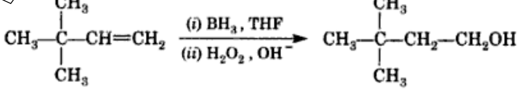
hydration, hydroboration and oxymercuration-demercuration of alkenes.

Hydration



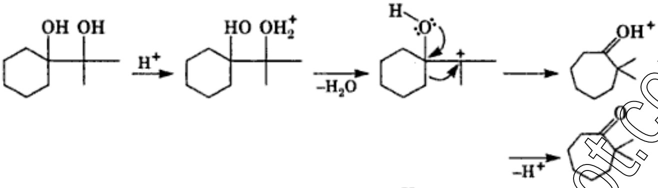
$$CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-CH=CH_2 \xrightarrow[H^+]{H_2O} CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-\underset{OH}{\underset{|}{C}H}-CH_3$$

Hydroboration

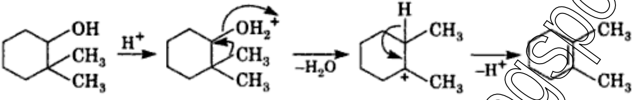


$$CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-CH=CH_2 \xrightarrow[(ii)\ H_2O_2\ ,\ OH^-]{(i)\ BH_3\ ,\ THF} CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-CH_2-CH_2OH$$

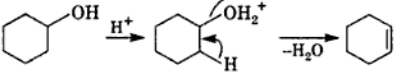
(*c*)



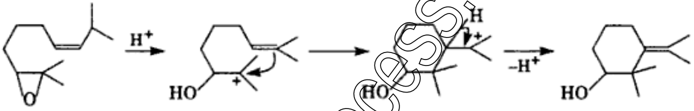
(*d*)



(*e*)



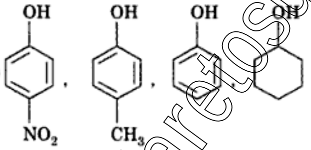
(*f*)



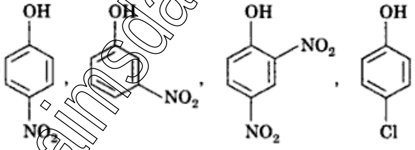
Problem 14.25:

Arrange each group of compounds in order of decreasing acidity:

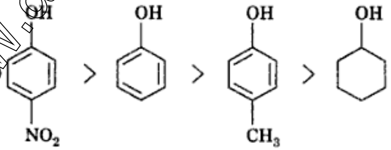
(*a*)

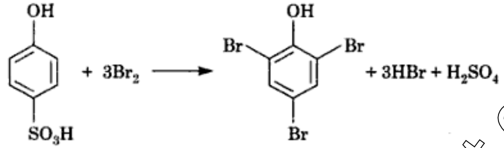


(*b*)



Solution: (*a*)

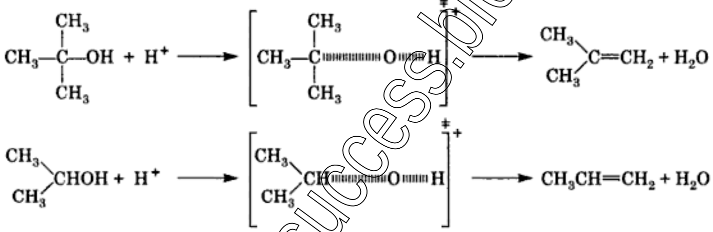


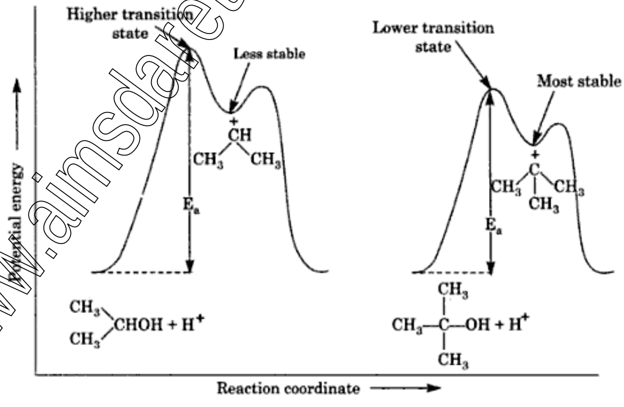


Problem 14.32:

Consider the dehydration of a secondary and a tertiary alcohol in the presence of an acid, the reaction is highly endothermic. On the basis of Hammond postulate discuss why a tertiary alcohol dehydrates faster than a secondary alcohol?

Solution: Dehydration of an alcohol catalyzed by an acid takes place *via* the protonation of the alcohol as the first step. This is followed by the formation of the carbocation by loss of water and a H^+ to yield an alkene. Since the reaction is endothermic there is strong resemblance between the transition state and the products in each case. Of the two transition states, the one which leads to the most stable carbocation is the lowest in potential energy. In both cases the transition state is stabilized by inductive electron donation.





The dehydration of a tertiary alcohol is faster because the carbocation formed in this case is more stable. Therefore, the transition state leading to this ion should be lower in energy and more stable (see figure). Protonation of the alcohol and subsequent loss of water to give a tertiary carbocation has the more stable transition state.

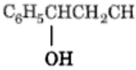
Problem 14.33:

Select the correct answer.

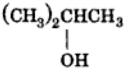
(*a*) Phenol reacts with Br_2 in CS_2 at low temperature to give.

A. *m*-Bromophenol B. *o*- and *p*-Bromophenol C. *p*-Bromophenol
D. 2, 4, 6-Tribromophenol

(*b*) Which of the alcohol does not give iodoform test?

A. 

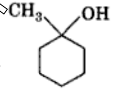
$C_6H_5\underset{OH}{CH}CH_2CH_3$

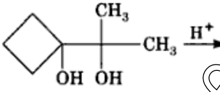
B. 

$(CH_3)_2\underset{OH}{C}HCH_3$

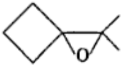
C. 

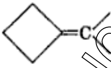
$CH_3CH_2\underset{OH}{CH}CH_3$

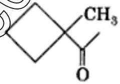
D. 

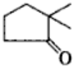
(*c*) For the reaction 

A, A is

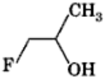
A. 

B. 

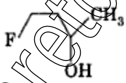
C. 

D. 

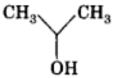
(*d*) The order of reactivity of the following alcohols towards conc. HCl is



I



II



III

IV

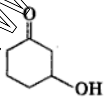
A. I > II > III > IV B. I > III > II > IV C. IV > III > II > I
D. IV > III > I > II

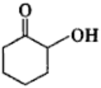
(*e*) The most appropriate reagent to convert

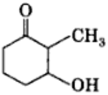
$$RCOOC_2H_5 \longrightarrow RCH_2OH \text{ is}$$

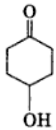
A. $LiAlH_4$ B. $NaBH_4$ C. H_2/Pd-C D. Li, NH_3

(*f*) Which of the following alcohol will have the fastest rate of dehydration?

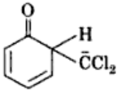
A. 

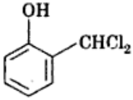
B. 

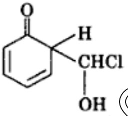
C. 

D. 

(*g*) 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. 

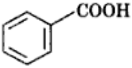
(*h*) Which of the following compounds is oxidized to prepare ethyl methyl ketone?

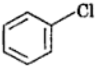
A. 2-Propanol B. 1-Butanol C. 2-Butanol D. *t*-Butylalcohol

(*i*) Benzenediazonium chloride on reaction with phenol in weakly basic medium gives :

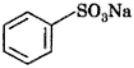
A. Diphenyl ether B. *p*-Hydroxyazobenzene C. Chlorobenzene D. Benzene

(*j*) Which of the following will not form phenol or phenoxide ion?

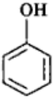
A. 

B. 

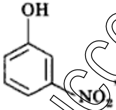
C. 

D. 

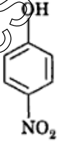
(*k*) The order of decreasing acidity in



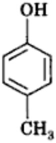
I



II



III



IV

is

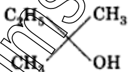
A. II > III > I > IV B. III > II > I > IV C. I > III > II > IV

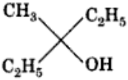
D. III > I > II > IV

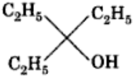
(*l*) Which of the following is basic?

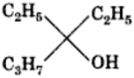
A. H_2O_2 B. CH_3COOH C. $HOCH_2CH_2OH$ D. C_2H_5OH

(*m*) Ethyl ester $\xrightarrow[\text{excess}]{CH_3MgBr}$ P, P wil be

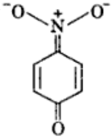
A. 

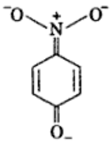
B. 

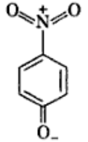
C. 

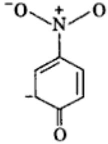
D. 

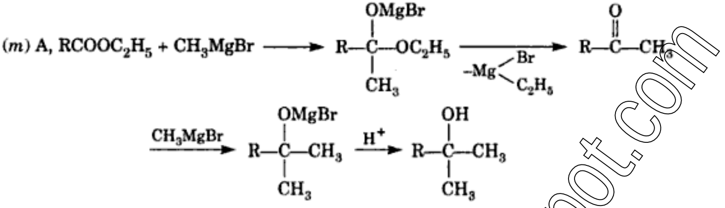
(*n*) The most unlikely representation of resonance structure of *p*-phenoxide ion is:

A. 

B. 

C. 

D. 



(m) A, $RCOOC_2H_5 + CH_3MgBr \longrightarrow R\text{—}\overset{OMgBr}{\underset{CH_3}{C}}\text{—}OC_2H_5 \xrightarrow[-Mg(Br)C_2H_5]{} R\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3$

$\xrightarrow{CH_3MgBr} R\text{—}\overset{OMgBr}{\underset{CH_3}{C}}\text{—}CH_3 \xrightarrow{H^+} R\text{—}\overset{OH}{\underset{CH_3}{C}}\text{—}CH_3$

$R = -C_2H_5$

(n) C, too many electrons around N atom. (o) B, *cis*-2-Butene, *trans*-2-Butene, 1-Butene

(p) B (q) C

Problem 14.34:

When 0.0088 g of compound A, was dissolved in 0.50 g of comphor, the melting point of comphor is lowered by 8°C. Analysis of A, gave C = 68.18%, H = 13.58%. Compound A, exhibited the following reactions.

(i) A reacted with acetyl chloride and evolved hydrogen with sodium.

(ii) When reacted with Lucas reagent a dense oily layer separated immediately.

Compound A on passing over heated Al_2O_3 at 350°C gave B. Compound B, on reductive ozonolysis gave two neutral compounds C and D.

(Kf for comphor is 40.0 K kg mol^{-1})

Assign structures to A, B, C and D.

Empirical Formula of A.

Element	*Percentage composition*	*Atomic weight*	*Rel. number of atoms*	*Simplest ratio*
C	68.18	12	5.68	5
H	13.58	1	13.58	12
O (By difference)	18.24	16	1.14	1

Empirical Formula is $C_6H_{12}O$

$$m = \frac{1000 \times K_f \times \omega}{W \times \Delta T} = \frac{1000 \times 40 \times .0088}{8 \times 0.5} = 88$$

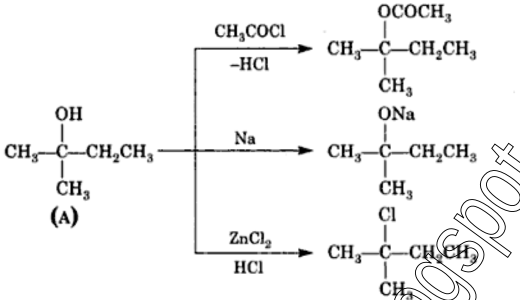
Mol. weight 88

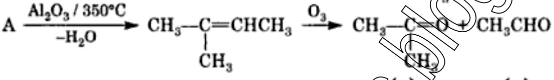
E.F. Weight 88

∴ Mol. Formula is $C_6H_{12}O$

The reaction of A indicate that it contains an -OH group and is an alcohol.

Further more, A reacts with the Lucas reagent $(ZnCl_2 + \text{Conc. } HCl)$ immediately, it is a tertiary alcohol.





$$A \xrightarrow[-H_2O]{Al_2O_3\,/\,350°C} CH_3-\underset{CH_3}{\underset{|}{C}}=CHCH_3 \xrightarrow{O_3} CH_3-\underset{CH_3}{\underset{|}{C}}=O + CH_3CHO$$

(C) (D)

Problem 14.35:

A biologically active compound, Bombykol $C_{16}H_{30}O$ is obtained from a neutral source. The structure of the compound is determined by the following reactions.

(*i*) On hydrogenation, Bombykol gives a compound A, $C_{16}H_{34}O$ which reacts with acetic anhydride to give an ester.

(*ii*) Bombykol also reacts with acetic anhydride to give another ester which on oxidative ozonolysis gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.

Determine the number of double bonds in Bombykol. Write the structures of compound A and Bombykal. How many geometric isomers are possible for Bombykol?

Solution: Since Bombykol adds two moles of H_2 on hydrogenation, it contains two double bonds.

$$C_{16}H_{30}O \xrightarrow{H_2} C_{16}H_{34}O$$

(A)

Further, A reacts with acetic anhydride it is a monohydroxy alcohol. Oxidative ozonolysis of Bombykol gives the following acids :

Butanoic acid	$CH_3CH_2CH_2COOH$
Oxalic acid	$\begin{array}{c}COOH\\ \vert\\ COOH\end{array}$
10-Acetoxydecanoic acid	$CH_3\overset{O}{\overset{\Vert}{C}}OCH_2(CH_2)_8COOH$ acid

Combining these structures, the Bombykol structure can be constructed as follows:

$$HOCH_2CH_2(CH_2)_7CH{=}CH{-}CH{=}CHCH_2CH_2CH_2C_{16}H_{30}O$$

$$\big\downarrow H_2$$

$$HOCH_2CH_2(CH_2)_7CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

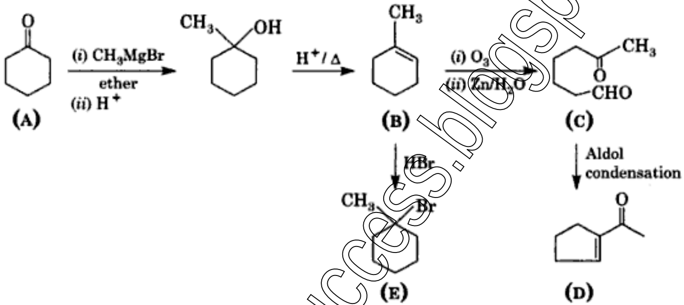
Four geometric isomers are possible since there are two double bonds.

Problem 14.36:

An organic compound A, $C_{16}H_{10}O$, on reaction with CH_3MgBr followed by acid treatment and heating gives compound B. Compound B, on ozonolysis gives C, which in the presence of a base gives 1-acetoxy cyclopentene D. The compound B, on reaction with HBr gives E. Deduce structures A to E and explain.

Solution: Formation of D, a cyclic compound from C to formed by an intramolecular aldol condensation. The two carbonyl groups are contained in the same molecular.

Therefore, it may be concluded that A is a cyclic ketone.



Problem 14.37:

An organic compound A, has 76.6% C and 6.38% H. Its vapor density is 47. It gives characteristic color with aqueous $FeCl_3$ solution. A when treated with CO_2 and NaOH at 140°C under pressure gives B, which on acidification gives C, Compound C, reacts with acetyl chloride to give a well known pain killer. Identify A to D and explain the reactions involved.

Solution: Empirical Formula of A

Element	*Percentage composition*	*Atomic weight*	*Rel. number of atoms*	*Simplest ratio*
C	76.6	12	6.38	6
H	6.38	1	6.38	6
O	17.02	16	1.06	1

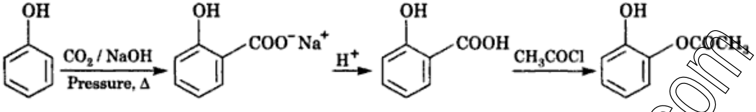
Empirical Formula is C_6H_6O

Mol. weight = $47 \times 2 = 94$

Empirical Formula weight = 94

Therefore, Molecular Formula = C_6H_6O

Since A gives a characteristic color with $FeCl_3$, a typical reaction of phenol, therefore it is indeed a phenol

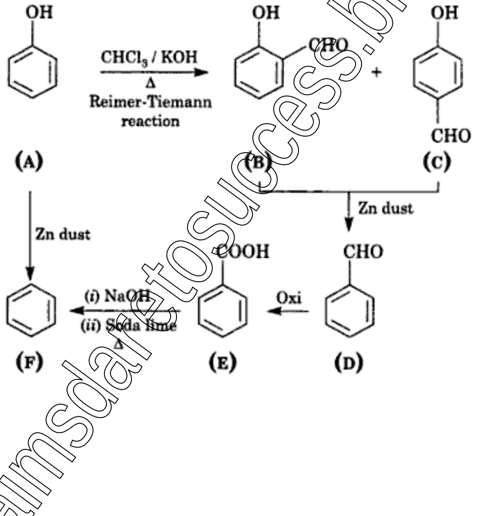


(A) (B) (C) (D)

Problem 14.38:

An organic compound A, on treatment with $CHCl_3$/KOH gives B, and C, both of which in turn give the same compound D, when distilled with Zn dust. Oxidation of D, yields E, $C_7H_6O_2$. The sodium salt of E, on heating with soda lime gives F, which can also be obtained by distilling with Zn dust. Deduce structures A to F.

Solution: Sodium salt of compound E, $C_7H_6O_2$ on heating with soda lime decarboxylates to F. This implies that E is benzoic acid and F is benzene. The reaction of A with Zn dust also gives, F, therefore, A is phenol.



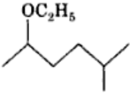
CHAPTER 15

Ethers and Epoxides

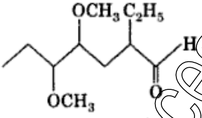
Problem 15.1:

Give systematic name for each of the following ethers:

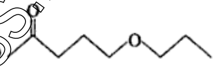
(a)



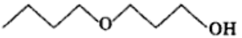
(b)



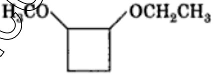
(c)



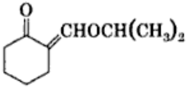
(d)



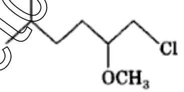
(e)



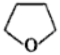
(f)



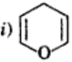
(g)



(h)



(i)



Solution: Ethers are never cited as principal groups.

(a) 2-Ethoxy-5-methylhexane (Alkoxy groups are always cited as substituents)

(b) 2-Ethyl-4, 5-dimethoxyheptanal (c) 5-Propoxy-2-pentanone (d) 3-Butoxy-1-propanol

(e) 1-Ethoxy-2-methoxycyclobutane (f) 2-Isopropoxymethylenecyclohexanone

(g) 1-Chloro-2-methoxy-5-methylhexane (h) Oxolane (tetrahedrofuran)

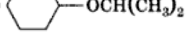
(i) 1-Oxa-2, 5-cyclohexadiene

Problem 15.2:

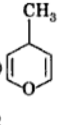
Suggest a suitable name for each of the following ethers:

(a)

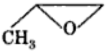
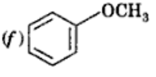
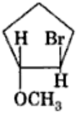
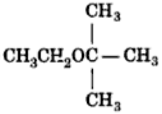
(b)



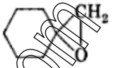
(c)



(d) $CH_3OCH_2CH_2OCH_2CH_2OCH_3$

(*e*)  (*f*)  (*g*)  (*h*) 

$$\mathrm{CH_3CH_2O\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_3}$$

(*i*) 

Solution: (*a*) Cyclohexene oxide (*b*) Cyclohexyl isopropoxy ether (*c*) 4-Methylpyran (*d*) *bis*-β-Methoxyethyl ether (Diglyme) (*e*) Propylene oxide (2-Methyloxirane) (*f*) Methyl phenyl ether (Anisole) (*g*) *trans*-2-Bromomethoxycyclopentane (*h*) *tert*-Butyl ethyl ether (*i*) Methylene cyclohexane oxide.

Problem 15.3:

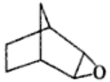
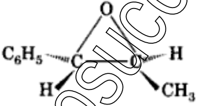
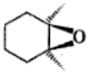
The basicity of the following ethers towards BF_3 has the following order, explain.

 $> (CH_3)_2\ddot{\underset{..}{O}} > (C_2H_5)_2\ddot{O} > [(CH_3)_2CH]_2\ddot{\underset{..}{O}}$

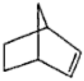
Solution: There are steric effects in the Lewis acid-Lewis base complex formation between BF_3 and the respective ethers accounting for the difference.

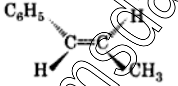
Problem 15.4:

Write the starting alkene and the experimental conditions that would give the following products:

(*a*)  (*b*)  (*c*) 

Solution: Alkene **Conditions**

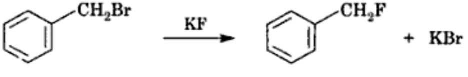
(*a*)  $\mathrm{C_6H_5\overset{\overset{O}{\|}}{C}OOH,\ CH_2Cl_2\ ,\ \Delta}$

(*b*)  $\mathrm{C_6H_5\overset{\overset{O}{\|}}{C}OOH,\ CH_2Cl_2\ ,\ \Delta}$

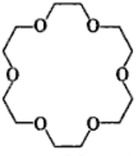
(*c*)  $\mathrm{C_6H_5\overset{\overset{O}{\|}}{C}OOH,\ CH_2Cl_2\ ,\ \Delta}$

Problem 15.5:

What are crown ethers ? How can the following reaction be made to proceed?



Solution: Crown ethers are large ring polyethers and are basically cyclic oligomers of oxirane which may have annulated rings. They are designated according to ring size and the number of complexing oxygen atoms. Thus [18]-crown-6 denotes an 18-membered ring with 6-oxygens. The molecule is shaped like a "*doughnut*", and has a hole in the middle. These act as phase transfer catalysts. This is a unique example of "host-guest relationship". The crown ether is the host, the cation is the guest. The cavity is well suited to fit a K^+ or Rb^+ ion which is held as a complex. Interaction between host and guest in all these complexes are mainly through electrostatic forces and hydrogen bonds.



This reaction can be made to proceed by using catalytic amount of crown ether, [18]-crown-6.

Problem 15.6:

Predict the major product of the following reactions:

(*a*) $CH_3O^- Na^+ + (CH_3)CCl \longrightarrow$

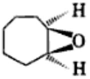
(*b*)


$+ CH_3I \xrightarrow{Na}$

(*c*) $CH_3(CH_2)_4CH_2—O—C(CH_3)_3 \xrightarrow{HBr}$

(*d*)

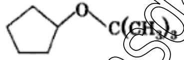

$+ CH_3OH \xrightarrow[\Delta]{H^+}$

(*e*)


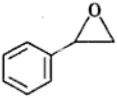
$\xrightarrow{CH_3COOH}$

(*f*)

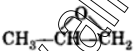

$+ CH_3OH \xrightarrow[\Delta]{OH^-}$

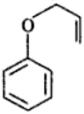
(*g*)


$\xrightarrow{H^+, \Delta}$

(*h*)


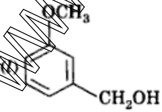
$\xrightarrow{HCl}$

(*i*)

$CH_3—\overset{O}{CH—CH_2} \xrightarrow{NaBr,\ H_2O}$

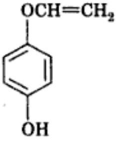
(*j*)


$\xrightarrow{Heat}$

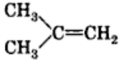
(*k*) $CH_3CH_2O^- + ClCH = CH_2 \longrightarrow$

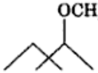
(*l*)


$\xrightarrow[Pyridine]{SOCl_2,\ \Delta}$

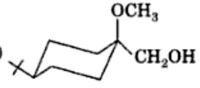
(*m*)


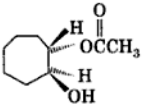
$\xrightarrow[\Delta]{H^+/H_2O}$

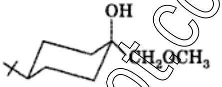
Solution: (*a*) 
$(CH_3)_2C{=}CH_2$

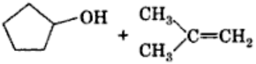
(*b*) 

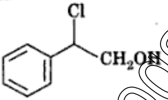
(*c*) $CH_3(CH_2)_4CH_2OH + (CH_3)_3CBr$

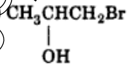
(*d*) 

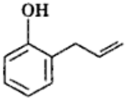
(*e*) 

(*f*) 

(*g*) 

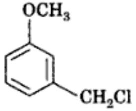
(*h*) 

(*i*) 
$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2Br$

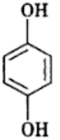
(*j*) 

(**Claisen rearrangement**)

(*k*) N.R., A vinyl halide does not react in S_N2 reaction.

(*l*) 

(**Pyridine traps the HCl formed and thus cleavage of ether is prevented**)

(*m*) 

Problem 15.7:

Explain why  is much more soluble than furan in water.

Solution: THF is more soluble than furan. In THF, in contrast to furan the electron pairs are available for H-bonding with water which makes it more soluble.

Problem 15.8:

What chemical methods can be used to distinguish between the following pairs of compounds.

(*a*) Methyl ether and ethanol (*b*) Ethoxy ethanol and methyl isopropyl ether (*c*) Butyl iodide and butyl ethyl ether (*d*) Ethyl propyl ether and ethyl allyl ether (*e*) *p*-Methoxyphenol and *p*-methoxybenzyl alcohol.

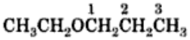
Solution: (*a*) Ethanol gives iodoform test (*b*) Ethoxyethanol gives iodoform test (*c*) Butyl iodide with $AgNO_3$ yields AgI precipitate (*d*) Ethyl allyl ether decolorizes bromine water (*e*) *p*-Methoxyphenol gives coloration with $FeCl_3$

Problem 15.9:

Write the structural formulas and names for all the isomeric ethers of the formula $C_{15}H_{12}O$.

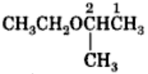
Solution:

The structural formulas for all the isomeric ethers of the formula $C_{15}H_{12}O$.



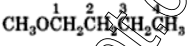
$CH_3CH_2O\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_3$

1-Ethoxypropane



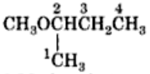
$CH_3CH_2O\underset{\underset{CH_3}{|}}{\overset{2}{C}}H\overset{1}{C}H_3$

Ethoxypropane



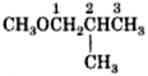
$CH_3O\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3$

1-Methoxybutane



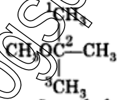
$CH_3O\underset{\underset{^{1}CH_3}{|}}{\overset{2}{C}}H\overset{3}{C}H_2\overset{4}{C}H_3$

2-Methoxybutane



$CH_3O\overset{1}{C}H_2\underset{\underset{CH_3}{|}}{\overset{2}{C}}H\overset{3}{C}H_3$

1-Methoxy-2-methylpropane



$CH_3O\underset{\underset{^{3}CH_3}{|}}{\overset{\overset{^{1}CH_3}{|}}{C}}\overset{2}{-}CH_3$

2-Methoxy-2-methylpropane

Problem 15.10:

An organic compound with the molecular formula $C_4H_{10}O_3$ shows the properties of both an alcohol and ether. When treated with excess HBr, it yields only ethylene dibromide. Suggest a structure.

Solution: The compound containing both the ether and alcohol functionalities is

$$HOCH_2CH_2OCH_2CH_2OH \xrightarrow[-H_2O]{HBr} \underset{+\ HOCH_2CH_2OH}{HOCH_2CH_2Br} \xrightarrow[-H_2O]{HBr\ (excess)} BrCH_2CH_2Br$$

Problem 15.11:

An unknown ether is cleaved by HI to give two different alkyl iodides A and B. A contains 89.4% iodine and B contains 81.41% iodine. On hydrolysis with conc. potassium hydroxide solution. B, gives a gaseous hydrocarbon. Suggest a structure for the original ether.

Solution: The alkyl halides have the general molecular formula

$$C_nH_{2n+1}X$$

$$\text{The molecular weight of A} = \frac{127}{89.4} \times 100 = 142.06$$

$$\text{The molecular weight of B} = \frac{127}{81.41} \times 100 = 156$$

If n is the number of carbon atoms of A, then for A :

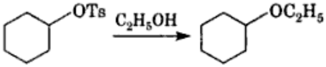
$$12n + 2n + 1 + 127 = 142$$
$$n = 1$$
$$\text{for B, } 12n + 2n + 1 + 127 = 156$$
$$n = 2$$

So the molecular formula of A is CH_3I and that of B is C_2H_5I. The original ether is $CH_3OCH_2CH_3$.

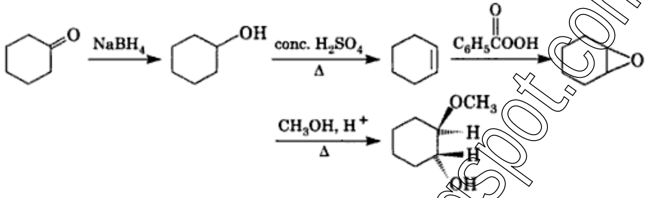
The sequence of reactions is:

$$CH_3OCH_2CH_3 \xrightarrow{HI} \underset{(A)}{CH_3I} + \underset{(B)}{CH_3CH_2I} \xrightarrow{\text{pot. hydroxide}} CH_2{=}CH_2$$

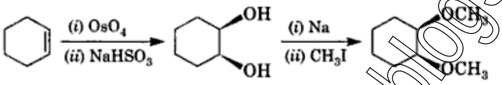
(c)



(d)

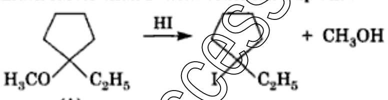


(e)

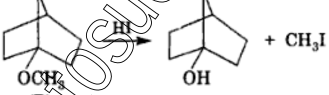


Problem 15.14:

Ether A cleaves much faster than B with conc. HI. Explain :

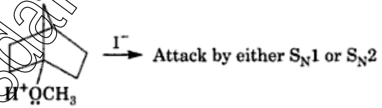


(A)



(B)

Solution: The cleavage reaction of an ether by HI is initiated by protonation of the ether oxygen followed by attack by I⁻.

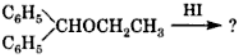


(B)

Since compound (B) is rigid, either type of attack is very slow. The ether (A) in contrast, does not pose such a problem and reacts faster.

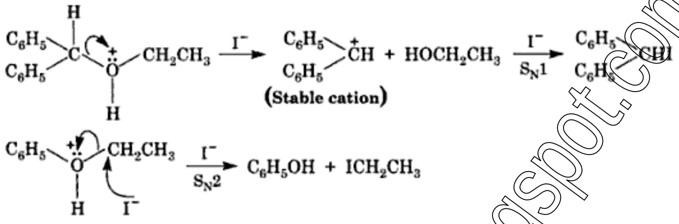
Problem 15.15:

Write the products of the following reactions and comment on their formation.



$$(C_6H_5)_2CHOCH_2CH_3 \xrightarrow{HI} ? \qquad C_6H_5OCH_2CH_3 \xrightarrow{HI} ?$$

Solution: The formation of a particular product depends on the stablity of the intermediate carbocation formed by the cleavage of oxonium ion in the first step of the reaction.



Problem 15.16:

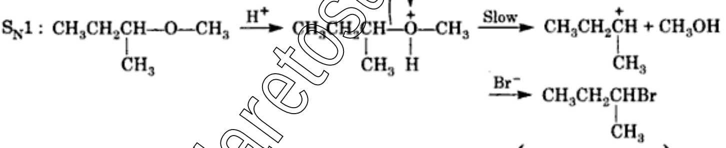
Why would sulfuric acid not be used to cleave phenyl methyl ether?

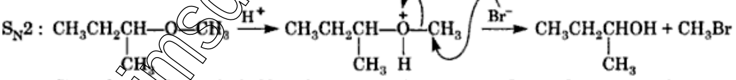
Solution: An acid would cleave the ether to give phenol and methanol. It is likely that sulfonation of the reactive phenol will takes place in the presence of sulfuric acid.

Problem 15.17:

It is found that cleavage of optically active *sec*-butyl methyl ether by anhydrous HBr produces mainly methyl bromide and *sec*-butyl alcohol. The alcohol has the same configuration and optical purity as the starting material. Account for these results.

Solution: The reaction of *sec*-butyl methylether in acidic condition takes place either by S_N1 or S_N2 mechanism.





Since the resultant alcohol has the same configuration and optical activity as the starting ether, the bond *sec*-Bu—O is not broken. Therefore, on the basis of results the reaction proceeds by the S_N2 pathway, in the manner shown.

Problem 15.18:

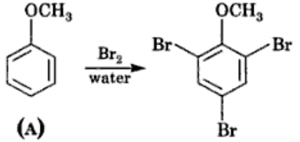
Give reasons for the following observations :

(*a*) *p*-Cresol has higher boiling point than anisole.

(*b*) Sodium can be used for drying diethyl ether and not ethanol.

(*c*) In the reaction between BF_3 and $C_2H_5OC_2H_5$ which one will act as an acid and why?

If A does not dissolve in NaOH, it is not a free phenol rather an anisole.



(A)

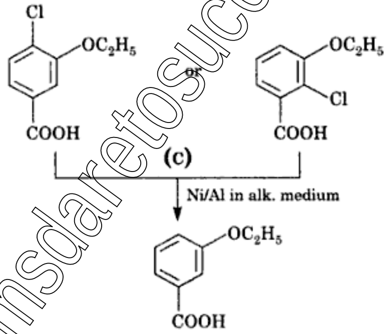
Both -OH and -OCH_3 are powerful activating groups.

Problem 15.22:

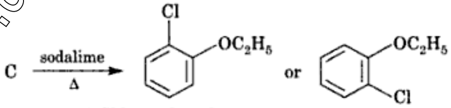
Two isomeric forms of an organic compound A, $C_{11}H_{13}OCl$ readily decolorize bromine water, and give same compound B, on catalytic hydrogenation. Both the isomeric forms of A, on vigorous oxidation give C, which on treatment with soda lime and heating gives 2-chloroethoxybenzene. However, C, on treatment with Ni/Al in alkaline medium gives 3-ethoxy benzoic acid. Only one of the isomers of A, gives geometric isomers D, and E. Assign structures to A and E.

Solution: Compound C on heating with soda lime gives 2-chloroethoxybenzene, C is a carboxylic acid derivative. Further C on reaction with Ni/Al in alkali gives 3-ethoxybenzoic acid, the -COOH group is present at 3-position to ethoxy group in C.

The following two structures can be considered for C.

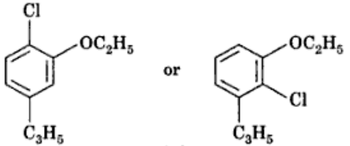


Compound C, on heating with soda lime decarboxylates.



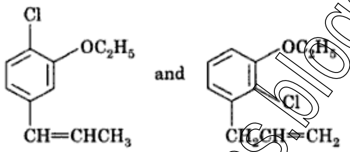
2-Chloroethoxybenzene

The structure of A, based on C is

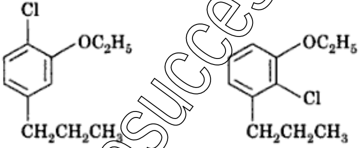


(A)

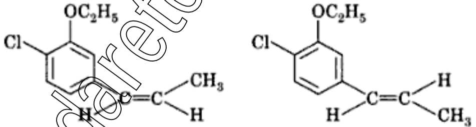
Compound A decolorizes bromine water and can be hydrogenated catalytically, Therefore, it contains a double bond in the side chain. Therefore two isomers of A can be written as



On catalytic hydrogenation, both forms of A give the same compound.



Besides the first form of A shows geometric isomerism.



(*cis*) (*trans*)

Problem 15.23:

A sample of 0.369 g of a bromo derivative A, of a hydrocarbon when vaporized occupied 67.2 ml at NTP. Compound A, on reaction with aq. NaOH gives B. B, when passed over alumina at 250°C gives a neutral compound C, while at 350°C it gives a hydrocarbon D. D, when heated with HBr gives an isomer of A. When D, is treated with conc. H_2SO_4 and the product is diluted with water and distilled E, is obtained. Deduce structures of all the lettered compounds and write the reactions.

Solution: Mol. weight of A = $\frac{\omega}{V} \times 22400$

(Victor Meyers method) = $\frac{0.369}{07.2} \times 22400 = 123$

It being a bromo derivative, it can be written as RBr.

Mol. wt of RBr = R + 80 where R is an alkyl group.

or $R + 80 = 123$

$\therefore$ $R = 43$

R can be written as C_nH_{2n+1}

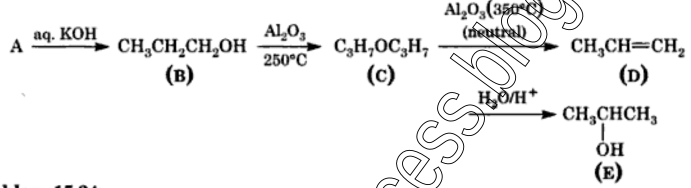
Weight of $C_nH_{2n+1} = (n \times 12) + (2n + 1) \times 1 = 43$

$\therefore$ $n = 3$

So R is C_3H_4 and A is C_3H_7Br. The given reactions indicate that R is an *n*-propyl group, therefore A is

$$\underset{\textbf{(A)}}{CH_3CH_2CH_2Br}$$

The sequence of reactions is as follows :



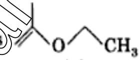
$$A \xrightarrow{\text{aq. KOH}} \underset{\textbf{(B)}}{CH_3CH_2CH_2OH} \xrightarrow[250°C]{Al_2O_3} \underset{\textbf{(C)}}{C_3H_7OC_3H_7} \xrightarrow[\text{(neutral)}]{Al_2O_3(350°C)} \underset{\textbf{(D)}}{CH_3CH{=}CH_2} \xrightarrow{H_3O/H^+} \underset{\textbf{(E)}}{\underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_3}}$$

Problem 15.24:

An organic compound A, molecular formula $C_5H_{10}O$ when treated with dil H_2SO_4 gives two compounds B, and C. Both give positive iodoform test. The reaction of $C_5H_{10}O$ with dil H_2SO_4 gives reaction 10^5 times faster than ethylene. Identify the organic compounds B and C. Give reason for the extra stability of A.

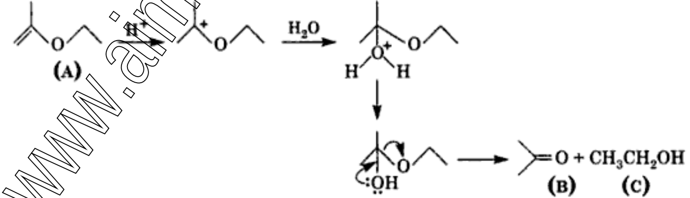
Solution: Both B and C give positive iodoform *test*, therefore, these are a kectone and an alcohol. A is probably an ether 

Since A reacts 10^5 times faster than ethylene, therefore, A contains an unsaturation.

A thus can be postulated as 

(A)

Compound A gives B and C in the following manner :



A reacts faster than ethylene because A leads to a stable tertiary cation on protonation. A is also stable because of resonance with the adjacent oxygen atom.

CHAPTER

16

Thiols and Thioethers

Problem 16.1:

Write the functional group of thiols and thioethers.

Solution:

Compound	Functional group
Thiols	-SH
Thioethers	-SR
	(R is an alkyl group)

The oxygen of alcohols and ethers has been replaced by the sulfur atom.

Thiols are named in the common system as mercaptans, and -SH is the mercapto group.

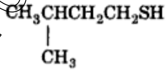
Thioethers are named as sulfides. The functional group is R—S—R.

In 1UPAC nomenclature, the -OH group gets preferences over the -SH group.

Problem 16.2:

Write systematic name for each of the following thiols.

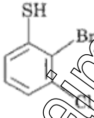
(*a*) $CH_3CH_2CH_2SH$ (*b*)



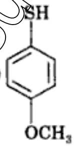
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2SH$

(*c*) $CH_2{=}CHCH_2SH$

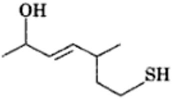
(*d*)



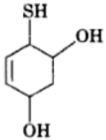
(*e*)



(*f*)



(*g*)

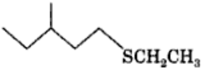


Solution: (*a*) Propanethiol (*b*) 3-Methyl-1-butanethiol (*c*) 2-Propenethiol (*d*) 2-Bromo-3-chlorobenzenethiol (*e*) 4-Methoxybenzenethiol (*f*) 7-Mercapto-5-methyl-3-hapten-2-ol (*g*) 6-Mercapto-4-cyclohexen-1,3-diol.

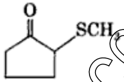
Problem 16.3:

Suggest 1UPAC name for each of the following thioethers.

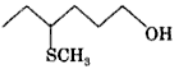
(*a*) $CH_3CH_2CH_2—S—CH_3$ (*b*)



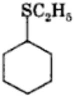
(*c*)



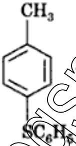
(*d*)



(*e*)



(*f*)



Solution: Similar to ethers, the sulfides are never cited as principal groups. Alkylthio groups (-SR) are always cited as substituents.

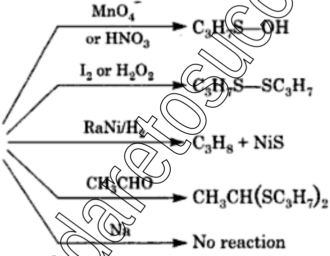
(*a*) 1-(Methylthio) propane (*b*) 3-Methyl-1-ethylthiopentane (*c*) 2-(Methylthio) cyclopentanone (*d*) 4-(Methylthio) hexan-1-ol (*e*) Ethylthiocyclohexane (*f*) Phenyl *p*-tolyl sulfide.

Problem 16.4:

Write the major organic product of the reaction of propanethiol with :

(*a*) MnO_4^- (one equivalents) (*b*) I_2 or H_2O_2 (*c*) Raney Ni, H_2 (*d*) CH_3CHO (*e*) Na metal

Solution: C_3H_7SH



$$C_3H_7SH \xrightarrow[\text{or } HNO_3]{MnO_4^-} C_3H_7S—OH$$

$$C_3H_7SH \xrightarrow{I_2 \text{ or } H_2O_2} C_3H_7S—SC_3H_7$$

$$C_3H_7SH \xrightarrow{RaNi/H_2} C_3H_8 + NiS$$

$$C_3H_7SH \xrightarrow{CH_3CHO} CH_3CH(SC_3H_7)_2$$

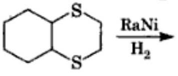
$$C_3H_7SH \xrightarrow{Na} \text{No reaction}$$

Problem 16.5:

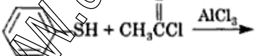
Write the structure of the major organic product in the following reactions :

(*a*)

(*b*)

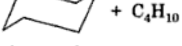


(*c*)

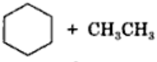


(*d*) $CH_3SCH_3 + CH_3I$

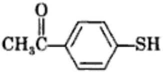
Solution: (*a*)



$+ C_4H_{10}$ (*b*)



$+ CH_3CH_3$ (*c*)

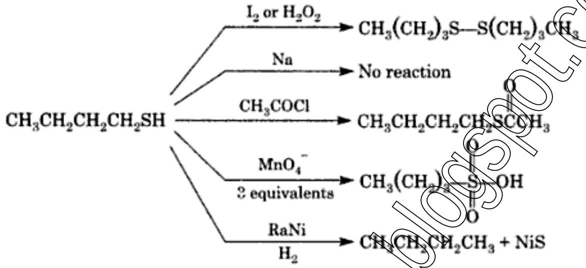


(*d*) $(CH_3)_3S^+ I^-$ (Trimethylsulfonium iodide)

Problem 16.6:

Show the products of the reaction (if any) of 1-butanethiol with I_2, or H_2O_2 or Na, CH_3COCl, MnO_4^- (3 equivalents) and $RaNi/H_2$.

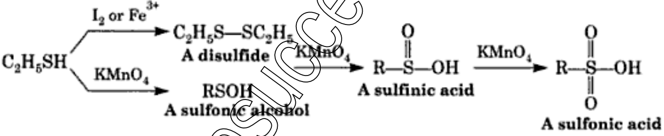
Solution:



Problem 16.7:

What classes of products may be obtained by the oxidation of a thiol by different oxidizing agents ?

Solution:



Problem 16.8:

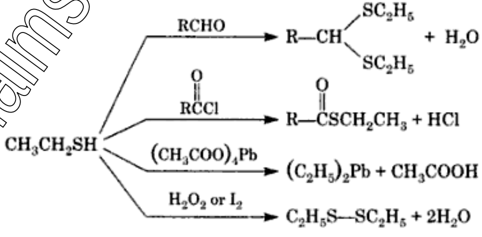
What are mercaptans ? How does ethyl mercaptan react with:

(*i*) an aldehyde, (*ii*) an acid chloride, (*iii*) lead acetate and (*iv*) I_2 or O_2 ?

Solution: Thiols are named in the common system as mercaptans, for instance:

$CH_3CH_2CH_2SH$

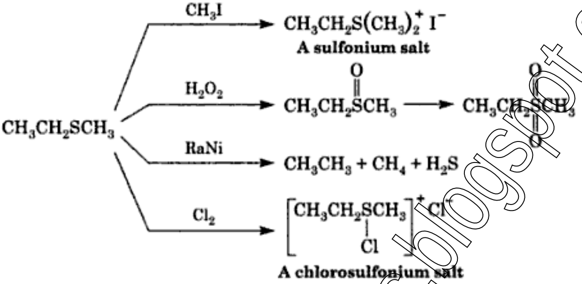
Propyl mercaptan



Problem 16.9:

How does 1-(methylthio) ethane react with

(*i*) CH_3I (*ii*) H_2O_2 (*iii*) RaNi (*iv*) Cl_2



Problem 16.10:

The products of combustion of an aliphatic thiol (RSH) at 298 K are

A. $CO_2(g)$, $H_2(g)$ and $SO_2(g)$

B. $CO_2(l)$, $CH_4(l)$ and $SO_2(g)$

C. $CO_2(g)$, $H_2O(l)$ and $SO_2(g)$

D. $CO_2(g)$, $H_2O(l)$ and $SO_2(l)$

Solution: C

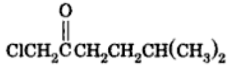
CHAPTER

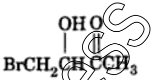
17

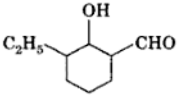
Aldehydes and Ketones

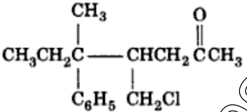
Problem 17.1:

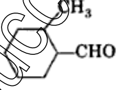
Write 1UPAC name for each of the following compounds:

(a) 
$ClCH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH(CH_3)_2$

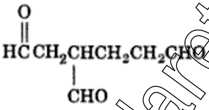
(b) 
$BrCH_2\overset{OH}{\overset{|}{C}H}\overset{O}{\overset{\|}{C}}CH_3$

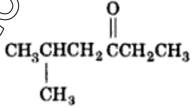
(c) 

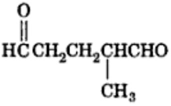
(d) 
$CH_3CH_2\underset{C_6H_5}{\overset{CH_3}{C}}-\underset{CH_2Cl}{CH}CH_2\overset{O}{\overset{\|}{C}}CH_3$

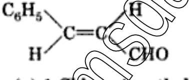
(e) 

(f) 
$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CHO$

(g) 
$H\overset{O}{\overset{\|}{C}}CH_2\underset{CHO}{CH}CH_2CH_2CHO$

(h) 
$CH_3\underset{CH_3}{CH}CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$

(i) 
$H\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{CH_3}{CH}CHO$

(j) 

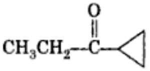
Solution: (a) 1-Chloro-4-methylpentan-2-one (b) 4-Bromo-3-hydroxybutan-2-one (c) 3-Ethyl-2-hydroxycyclohexancarbaldehyde (d) 4-Chloromethyl-5-methyl-5-phenylheptan-2-one (e) 2-Methyl-cyclohexanecarbaldehyde (f) 4-Oxopentanal (g) 3-Formyl-1,6-hexanedial (h) 5-Methyl-3-hexanone (i) 2-Methylpentanedial (j) *trans*-cinnamaldehyde

Problem 17.2:

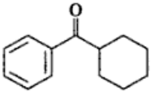
Draw structures for the following compounds.

(a) Cyclopropyl ethyl ketone (b) Cyclohexyl phenyl ketone (c) 1-Hydroxy-4-methyl-3-heptanone (d) 6-Bromooct-3-yn-2-one (e) 2-Propylcyclohexan-1,3-dione (f) 3-Methyl-4-phenylbutanal (g) 3-Cyclohexen-1-one.

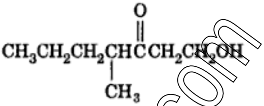
Solution: (*a*)



(*b*)

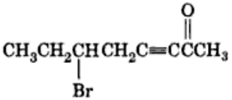


(*c*)



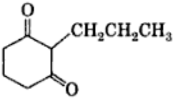
$\mathrm{CH_3CH_2CH_2\underset{CH_3}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}CH_2CH_2OH}$

(*d*)



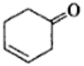
$\mathrm{CH_3CH_2\underset{Br}{\underset{|}{CH}}CH_2C{\equiv}C\overset{O}{\overset{\|}{C}}CH_3}$

(*e*)



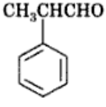
(*f*)

(*g*)

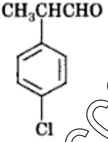


Problem 17.3:

Rank in the order of decreasing acidity:

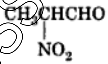


(*a*)



(*b*)

and



$\mathrm{CH_3\underset{NO_2}{\underset{|}{C}}HCHO}$

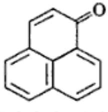
(*c*)

Solution: $b < c < a$

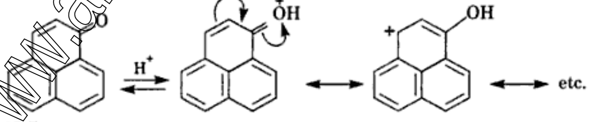
Anion of (*a*) will be stabilized both by inductive and resonance effect. Therefore, (*a*) is more acidic than the other two.

Problem 17.4:

The following ketone is usually basic. Explain.



Solution: Aldehydes and ketones are slightly basic because they can accept a proton. In this case the protonated ketone is extensively stabilized by resonance.



Problem 17.5:

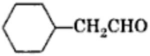
Suggest suitable reagents for the following conversions:

(*a*) $\mathrm{CH_3CH_2CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH_2CH_2CHO}$

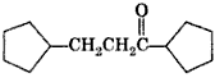
Problem 17.8:

Write the structure of the alkyne that would yield the following compounds on hydroboration-oxidation.

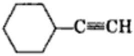
(*a*)



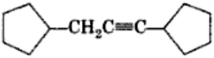
(*b*)



Solution: (*a*)

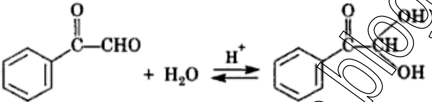


(*b*)



Problem 17.9:

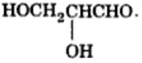
Would you expect phenylglyoxal to form a stable hydrate?



Solution: Yes, because the two -OH groups are linked to a strongly electron-withdrawing carbonyl group.

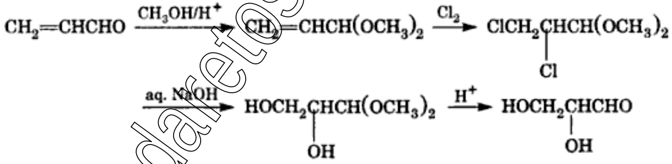
Problem 17.10:

Taking advantage of the fact that acetals are hydrolyzed in an acid medium, show how by protecting the aldehyde group as an acetal, acrolein $CH_2{=}CHCHO$, can be converted to



$$HOCH_2\underset{|\atop OH}{C}HCHO.$$

Solution:



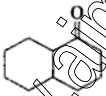
$$CH_2{=}CHCHO \xrightarrow{CH_3OH/H^+} CH_2{=}CHCH(OCH_3)_2 \xrightarrow{Cl_2} ClCH_2\underset{|\atop Cl}{C}HCH(OCH_3)_2$$

$$\xrightarrow{aq.\ NaOH} HOCH_2\underset{|\atop OH}{C}HCH(OCH_3)_2 \xrightarrow{H^+} HOCH_2\underset{|\atop OH}{C}HCHO$$

Problem 17.11:

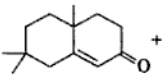
Complete the following reactions :

(*a*)

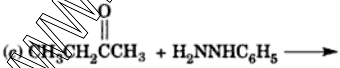


+ HCN ⟶

(*b*)

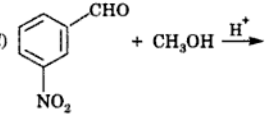


+ $HSCH_2CH_2SH$ ⟶

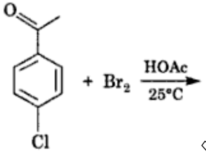


(*c*) $CH_3CH_2\overset{O \atop \|}{C}CH_3 + H_2NNHC_6H_5 \longrightarrow$

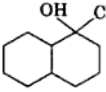
(*d*)



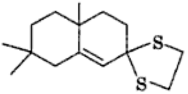
(*e*)



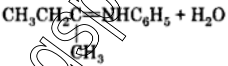
Solution: (*a*)



(*b*)

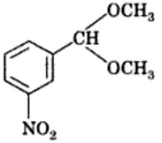


(*c*)

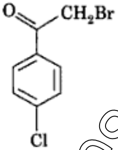


$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NHC_6H_5 + H_2O$$

(*d*)



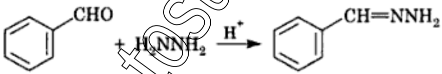
(*e*)



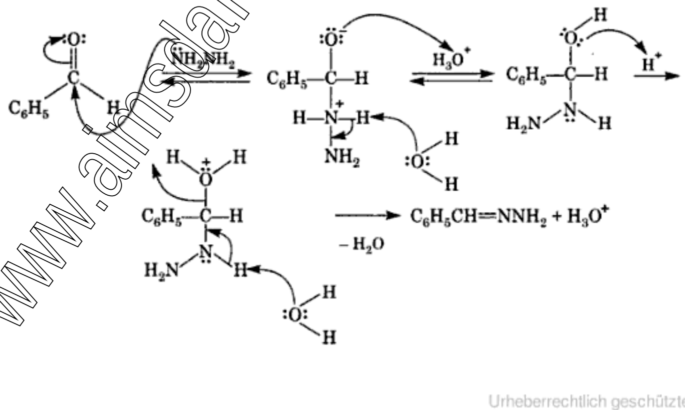
(Halogenation of aldehydes or ketones in acidic solution results in replacement of one α-H by halogen).

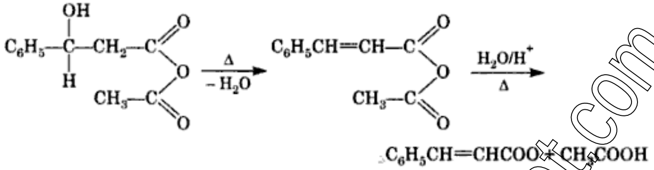
Problem 17.12:

Suggest a mechanism for the following reaction.



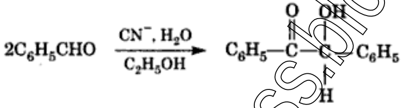
Solution: The reaction starts by an initial attack of hydrazine on the carbonyl group. After protonation and loss of water, the product is obtained.





Cinnamic acid

(*c*) **Benzoin Condensation.** Aromatic aldehydes, in the presence of cyanide ion as catalyst, are converted to acyloins. The reaction is known as the *benzoin condensation.* This condensation is not catalyzed by any other base. It is specifically catalyzed by the cyanide ion. This is so because the cyanide ion can stabilize the carbanion and can also easily depart in the last step.

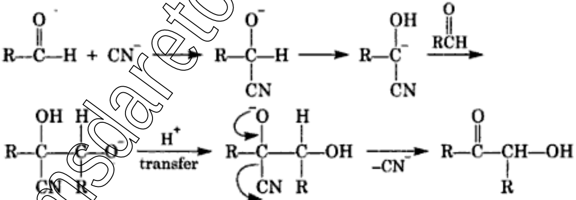


$$2C_6H_5CHO \xrightarrow[C_2H_5OH]{CN^-,\ H_2O} C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{OH}{C}}-C_6H_5$$

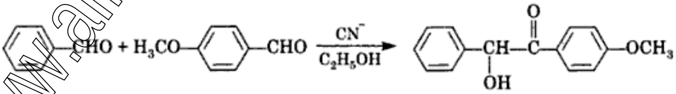
Benzaldehyde **Benzoin**

An α-hydroxyketone is called a benzoin.

Mechanism. The CN^- ion adds first to the carbonyl group to form a cyanohydrin. The hydrogen atom of the aldehyde being α to the cyano group now becomes adequately acidic and can be removed by a base. The resulting carbanion then adds to another molecule of the aldehyde and benzoin is obtained as shown. The benzoin condensation is largely influenced by the presence of electron-donating groups on the aromatic nucleus. Electron-donating effect of the substituents makes the carbonyl carbon atom less electrophilic and thus susceptible to attack by the cyanide ion.

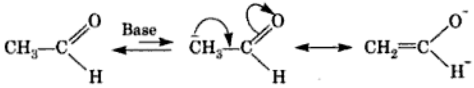


Benzoin from mixed ketones can also be obtained in a similar manner.



4-Methoxybenzoin

(*d*) **The aldol Condensations.** A carbon atom located next to a carbonyl carbon is referred to as the *α-carbon* and a hydrogen attached to an α-carbon is called an *α-hydrogen*. This hydrogen is acidic due to the fact that the anion, also known as the *enolate anion*, is stabilized by resonance.

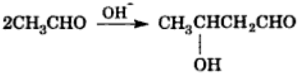


Enolate anion

In aqueous base, two acetaldehyde molecules react to form a β-hydroxyaldehyde called *aldol*. The reaction is called the *aldol condensation*.

Only α-hydrogen is involved in aldol condensation.

The enolate ion is the intermediate in the aldol condensation of aldehydes and ketones. Acetaldehyde, for instance, forms a dimeric product aldol in the presence of a dilute base (10% NaOH).

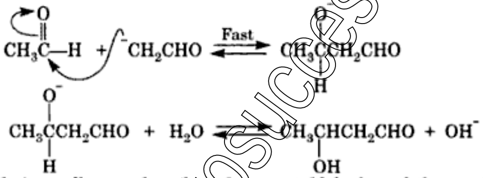


$$2CH_3CHO \xrightarrow{OH^-} \underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_2CHO}$$

β-Hydroxybutyraldehyde (aldol)

Mechanism. The formation of the aldol proceeds through a series of equilibrium steps.

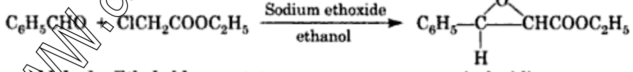
$$CH_3CHO + OH^- \underset{}{\overset{\text{Slow}}{\rightleftharpoons}} {}^-CH_2CHO + H_2O$$



A hydroxide ion pulls an α-hyrodgen from acetaldehyde and the resultant enolate ion makes a nucleophilic attack on a second molecule of acetaldeyde in a fast step. This ion then picks up a proton from water to form an aldol and the catalyst (OH⁻) is regenerated. Ketones condense similarly.

Aldols (aldehyde-alcohols) are stable and may be isolated. They, however, can be dehydrated easily by heating the basic reaction mixture or by a separate acid-catalyzed reaction. Thus if the above reaction mixture is heated, the product is dehydrated to crotonaldehyde (2-butenal).

(*e*) **The Darzens Condensation.** The reaction of a halogenomethylene compound, in the presence of a strong base with an aldehyde or a ketone to yield an α, β-epoxy ester or a glycidic ester is called the *Darzens condensation*. Benzaldehyde, on condensation with α-choloracetate, in the presence of sodium ethoxide yields ethyl β-phenylglycidate.

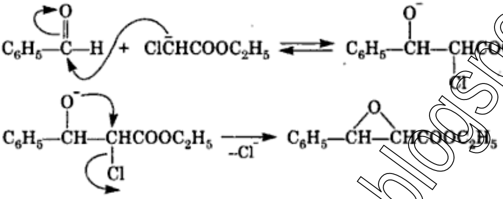


Benzaldehyde Ethyl chloroacetate A glycidic ester

Both aromatic aldehydes and ketones give good yields in this reaction but aliphatic aldehydes give poor yields, presumably they form aldol products. Aldehydes also react faster than ketones.

A number of base-solvent systems have been employed but pot-*t*-butoxide/*t*-butanol has proved to be the most suitable combination. The Darzens condensation is carried out under nitrogen atmosphere and with the exclusion of moisture. An essential requirement for this reaction is that the halogenomethylene compound should contain an α-hydrogen. The mechanism of the reaction proceeds through an enolate ion and is formulated below :

$$ClCH_2COOC_2H_5 + :B \rightleftharpoons Cl\bar{C}HCOOC_2H_5 + BH^+$$



The first two steps are similar to the aldol condensation. In the last step an intermolecular S_N2 attack takes place with the closure of the epoxide ring.

(f) **The Wittig Reaction.** Trialkyl- or triphenyl-phosphorus compounds (phosphines) can be alkylated by nucleophilic displacement of an alkyl halide.

$$(C_6H_5)_3P: + CH_3I \xrightarrow{S_N2} (CH_6H_5)_3P^+—CH_3I^-$$

Triphenyl phosphine **Methyltriphenyl phosphonium iodide**

These quaternary phosphonium salts react with strong bases to form *vicinal* ionic intermediates called *ylids*. Phosphorus ylids are generally stable though highly reactive.

$$(C_6H_5)_3\overset{+}{P}—CH_3I^- \xrightarrow[-H^+]{C_4H_9Li} [(C_6H_5)_3\overset{+}{P}—CH_2^- \longleftrightarrow (C_6H_5)_3P=CH_2]$$

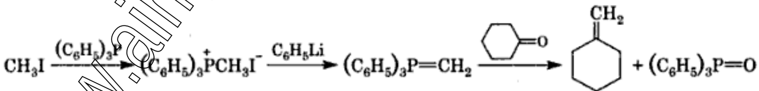
A ylide

Ylids are strong nucleophiles and can condense with an aldehyde or ketone with the resultant formation of an alkene and the reaction is called the *Wittig reaction*.

$$(C_6H_5)_3P=CH_2 + {>}C=O \longrightarrow {>}C=CH_2 + (C_6H_5)_3P=O$$

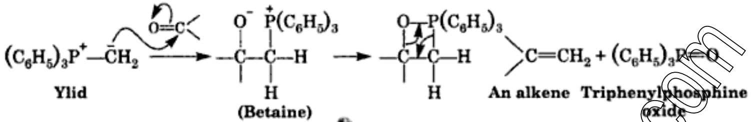
Triphenylphosphine oxide

This reaction thus provides a versatile means for the synthesis of alkenes, as illustrated for the formation of methylenecyclohexane.



The reaction is simple and proceeds under mild conditions.

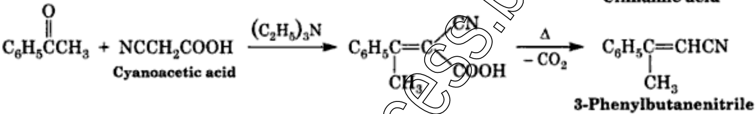
Mechanism. The reaction proceeds in two steps. Initial addition of the ylid to the carbonyl group takes place to give a dipolar intermediate called a *betaine*. This reacts further to give the oxaphosphetane which is stable at low temperature, but decomposes on warming to yield an alkene and triphenylphosphine oxide. The sequence of reactions is shown below:



(*g*) **The Knoevenagel Condensation (Amine catalyzed condensation).** When malonic ester of acetoacetic ester in the presence of an amine or base as catalyst, reacts with aldehydes or ketones, α, β-unsaturated esters are formed. This type of reaction is called the *Knoevenagal condensation*. Piperidine, pyridine or triethylamine are normally used as base catalyst. The following two examples illustrate this reaction:

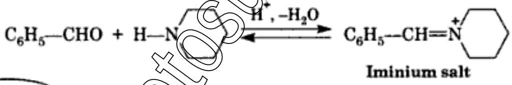
$$\underset{\textbf{Malonic ester}}{C_6H_5CHO + CH_2(COOC_2H_5)_2} \xrightarrow{\text{Pyridine}} \underset{\textbf{Ethyl benzalmalonate}}{C_6H_5CH{=}C(COOC_2H_5)_2} \xrightarrow[(ii)\ \text{HCl}]{(i)\ \text{KOH}}$$

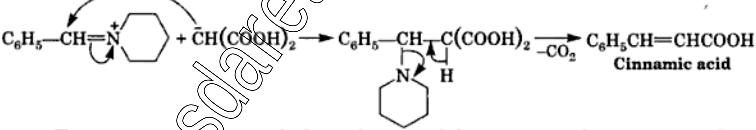
$$C_6H_5CH{=}C(COOH)_2 \xrightarrow[-CO_2]{\Delta} \underset{\textbf{Cinnamic acid}}{C_6H_5CH{=}CHCOOH}$$



$$C_6H_5\overset{O}{\overset{\|}{C}}CH_3 + \underset{\textbf{Cyanoacetic acid}}{NCCH_2COOH} \xrightarrow{(C_2H_5)_3N} C_6H_5\underset{CH_3}{\underset{|}{C}}{=}C\begin{matrix}CN\\COOH\end{matrix} \xrightarrow[-CO_2]{\Delta} \underset{\textbf{3-Phenylbutanenitrile}}{C_6H_5\underset{CH_3}{\underset{|}{C}}{=}CHCN}$$

Mechanism. The Knoevenagel condensation requires the presence of a catalytic amount of an acid in addition to the base. Therefore, intermediate formation of an imine or iminium salt is involved and the mechanism may be formulated in the following steps.



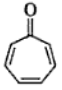


The iminum salt reacts with the enolate ion of the ester to produce an intermediate amino compound. This eliminates the amine to form the unsaturated product which on decarboxylation yields cinnamic acid.

Problem 17.16:

Offer explanation for the following observations:

(*a*) Benzaldehyde does not undergo aldol condensation. (*b*) Chloral hydrate is stable. (*c*) Boiling points of butanal (76°) and I-butanol (118°) are very different but their solubility in water is quite similar. (*d*) 2, 4-Pentanedione is highly acidic.

(*e*) The ketone  is very basic in character and forms stable salts with HCl.

(*f*) Wolff-Kishner reduction of ketones is preferred over the Clemmensen reduction. (*g*) Hydroxylamine is employed in the form of its hydrochloride salt. (*h*) Benzaldehyde reacts faster than *p*-methoxybenzaldehyde with HCN. (*i*) Acetophenone but not benzophenone forms an adduct with $NaHSO_3$. (*j*) Hydrazones of aldehydes and ketones are not prepared in highly acidic medium.

Solution: (*a*) Benzaldehyde does not possess an α-carbon atom (*b*) It forms intramolecular H-bonding (*c*) 1-Butanol is more polar, therefore, it can form intermolecular H-bond more efficiently than butanal. However, both form H-bond with water to the same extent (*d*) It contains an active methylene group (*e*) Because the protonated ketone is highly stabilized by resonance (*f*) Clemmensen reduction is subject to steric hindrance (*g*) Because hydroxylamine is stable as its hydrochloride (*h*) Electron-donating effect of $-OCH_3$ group reduces the electrophilicity of the carbonyl carbon atom. (*i*) Because of steric hindrance of the two phenyl groups. (*j*) They undergo hydrolysis.

Problem 17.17:

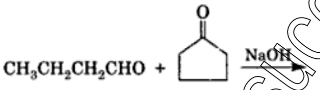
Explain why only the α-hydrogen atom in aldehydes and ketones is involved in the aldol condensation.

Solution: Because an α-hydrogen atom is acidic and the resulting enolate anion is stabilized by resonance.

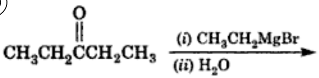
Problem 17.18:

Predict products of the following reactions :

(*a*)



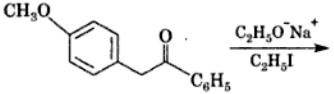
(*b*)



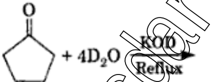
$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CH_3CH_2MgBr}$

(*c*) $C_6H_5CHO + CH_3CHO \xrightarrow{OH^-}$

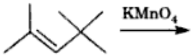
(*d*)



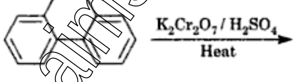
(*e*)



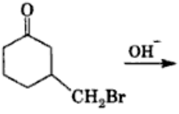
(*f*)



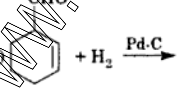
(*g*)



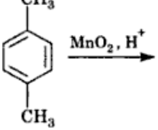
(*h*)



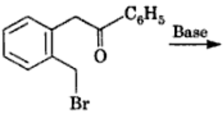
(*i*)

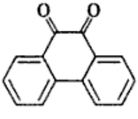
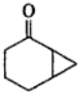
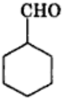
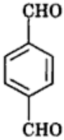
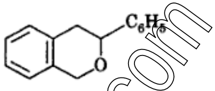


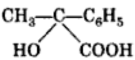
(*j*)



(*k*)

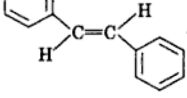


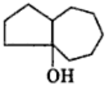
(g)  (h)  (i)  (j)  (k) 

(l) 

$CH_3-\underset{HO\ \ COOH}{C}-C_6H_5$

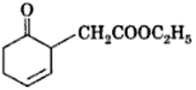
(Benzilic acid rearrangement)

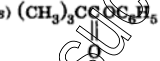
(m)  + *cis* isomer (n) $C_6H_5CH{=}CHNO_2$

(o) $HCOOH + CH_3OH$ (p) 

(Intramolecular aldol condensation)

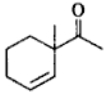
(q) p-ClC_6H_4CHO

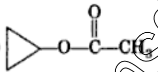
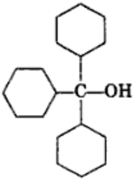
(r) 

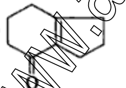
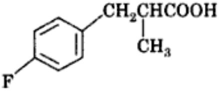
(s) 

$(CH_3)_3C\underset{\|\atop O}{C}OC_6H_5$

(t) $(CH_3)_3CCOOH + (CH_3)_3CCH_2OH$

(u)  (Note a proton is abstracted from the γ-position) (v) $CH_3CH{=}CHCOOH$

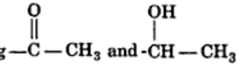
(w)  (Baeyer-villiger oxidation) (x) 

(y)  (z) 

Problem 17.19:

Which of the following compounds would give a positive idoform test?

(*a*) 2-butanol (*b*) 1-pentanol (*c*) acetone (*d*) 3-pentanone (*e*) 2-pentanone (*f*) 3-pentanol (*g*) I-phenylethanol (*h*) acetophenone



Solution: Compounds containing the grouping $-\overset{\overset{\large O}{\|}}{C}-CH_3$ and $-\overset{\overset{\large OH}{|}}{C}H-CH_3$ will give a positive iodoform test. Compounds containing these groups are 2-butanol, acetone, 2-pentanone 1-phenylethanol.

Problem 17.20:

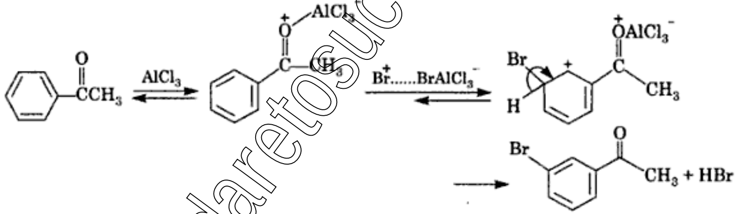
A liquid of the molecular formula, C_7H_6O, forms an oxime, reduces Fehling's solution and undergoes the Cannizzarro reaction. What structural formula would you assign to the liquid?

Solution: All the reactions suggest that the unknown compound contains an aldehydic group (-CHO). Therefore, the compound is benzaldehyde (C_6H_5CHO).

Problem 17.21:

An ether solution of acetophenone reacts with bromine in the presence of traces of $AlCl_3$ to give $C_6H_5COCH_2Br$ in good yield. If 2.5 molar equivalents of $AlCl_3$ are mixed with acetphenone immediately before addition of bromine, the mixture reacts slowly to give *m*-bromoacetophenone. Suggest a reason for the change in product formation.

Solution: In large quantities, $AlCl_3$ complexes with C=O group to give *m*-bromoacetophenone. In small amounts, however, it acts as a catalyst to form phenacyl bromide.

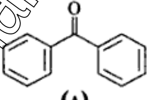


Problem 17.22:

(*a*) Arrange the following compounds in order of increasing reactivity towards addition of HCN.

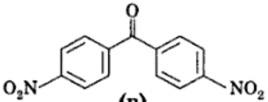
Acetone, acetaldehyde, methyl *t*-butyl ketone and di *t*-butyl ketone.

(*b*) Which ketone has the largest equilibrium constant for the addition of H_2O ?



(A)

or



(B)

Solution: (*a*) di-*t*-butyl ketone < methyl *t*-butyl ketone < acetone < acetaldehyde.

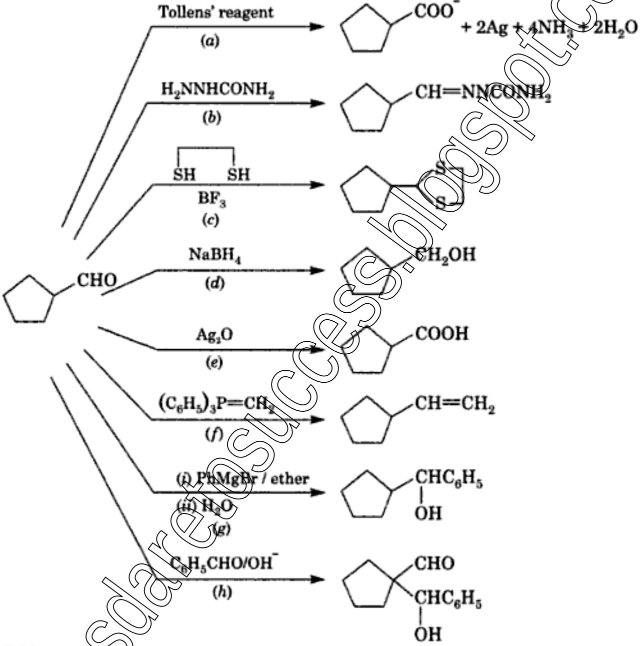
(*b*) Ketone B will have a larger value because the electron-withdrawing -NO_2 groups make the carbonyl carbon more electrophilic. Thus facilitating the attack of H_2O molecule.

Problem 17.28:

Predict the product when cyclopentanecarbaldehyde reacts with :

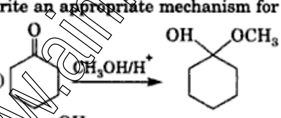
(*a*) Tollens' reagent (*b*) Semicarbazide/H^+ (*c*) $HSCH_2CH_2SH/BF_3$ (*d*) $NaBH_4$ (*e*) Ag_2O (*f*) $(C_6H_5)_3P{=}CH_2$ (*g*) C_6H_5MgBr followed by hydrolysis (*h*) C_6H_5CHO/OH^-

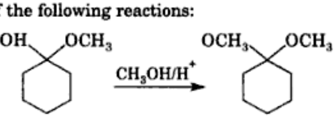
Solution:

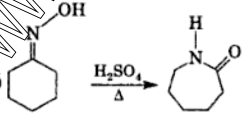


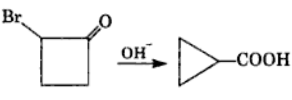
Problem 17.29:

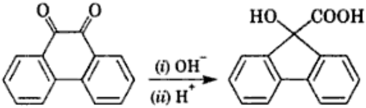
Write an appropriate mechanism for each of the following reactions:

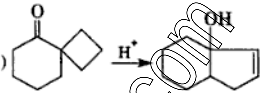
(*a*)


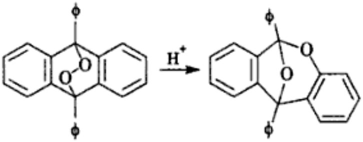
(*b*)


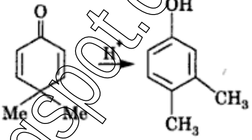
(*c*)


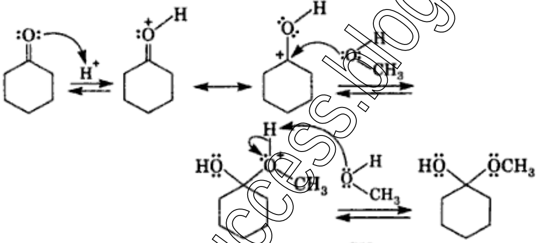
(*d*)


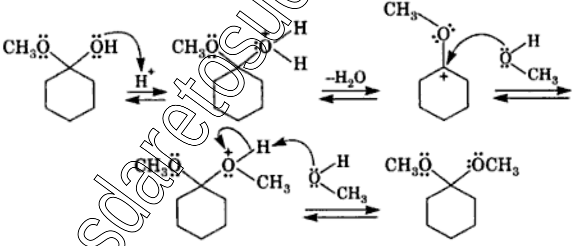
(e) 

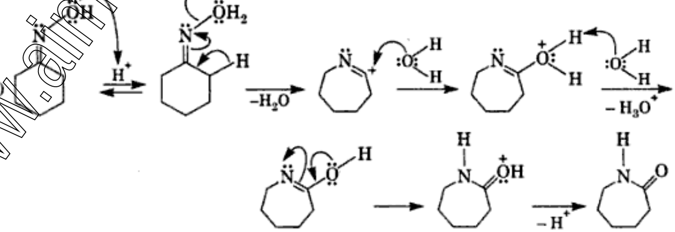
(f) 

(g) 

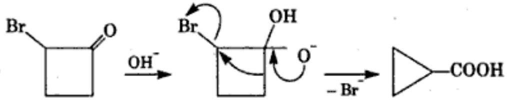
(h) 

Solution: (a) 

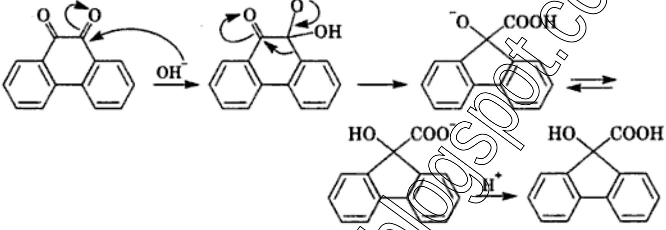
(b) 

(c) 

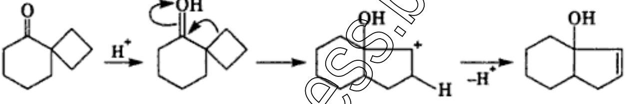
(*d*)



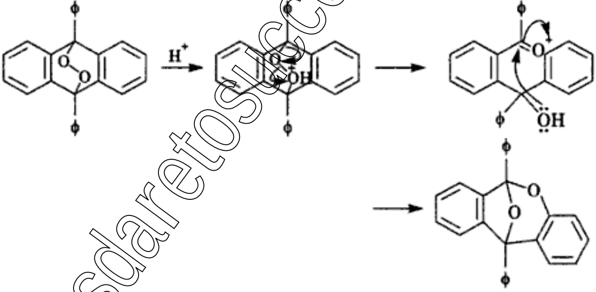
(*e*)



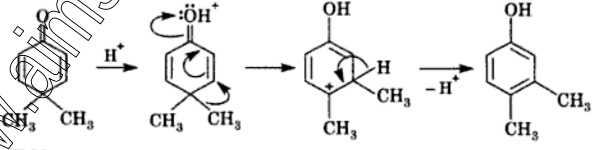
(*f*)



(*g*)



(*h*)



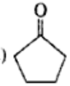
Problem 17.30:

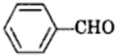
Acetophenone yields chloroform when heated with chlorine in aq. base but 2, 6-dimethylacetophenone produces only 2, 6-dimethyl-α, α, α-trichloroacetophenone. Explain.

Solution: Acetophenone undergoes the haloform reaction. But in the case of 2, 6-dimethylacetophenone, the two *ortho* methyl groups sterically hinder the approach of the OH^- to attack the $>C{=}O$ group and prevent hydrolysis.

Problem 17.31:

Within each pair which compound will react faster in carbonyl addition reaction of HCN ?

(*a*)

or


(*b*)

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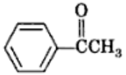
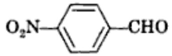


(*c*)

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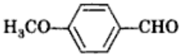
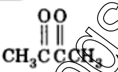
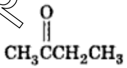


(*d*)


$CH_3\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}CH_3$

or


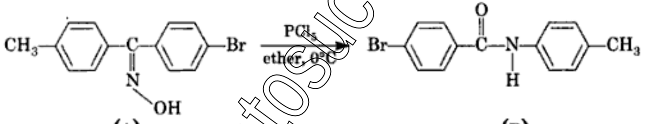
$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$

Solution: (*a*) Cyclopropanone (*b*) Benzaldehyde (*c*) *p*-Nitrobenzaldehyde (*d*) 2, 3-Butanedione

Problem 17.32:

A white solid (A) of formula $C_{14}H_{12}ONBr$ when dissolved in dry ether, treated with PCl_5 at 0°C and poured into cold water, yields compound B. Product B may be hydrolyzed to *p*-toluidine and *p*-bromobenzoic acid. Write structure for A and B.

Solution: Compound (A) undergoes the Beckmann rearrangement, therefore, it is an oxime with the following structure:



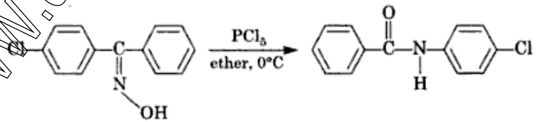
(A) (B)

Since product (B) yields *p*-bromobenzoic acid and *p*-toluidine on hydrolysis, therefore the tolyl group undergoes migration.

Problem 17.33:

A white solid (A), of formula $C_{13}H_{10}ONCl$ on reaction with PCl_5 at 0°C gives compound (B) which may be hydrolyzed to equimolar quantities of *p*-chloroaniline and benzoic acid. Write structure of A and B.

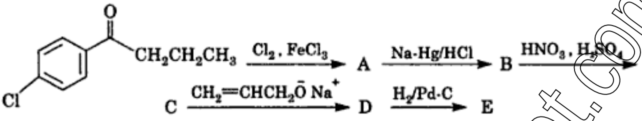
Solution: Compound (A) undergoes the Beckmann rearrangement, therefore it is an oxime with the following structure:



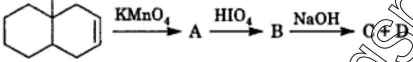
(A) (B)

Problem 17.38:

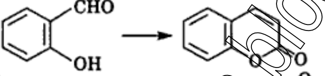
(*a*) Write the structures of the products A to E in the following scheme.



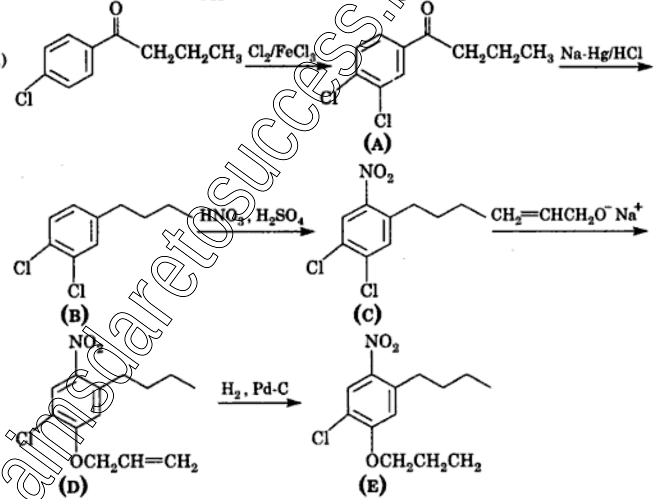
(*b*) Suggest structures A, B, C and D in the following synthetic scheme.



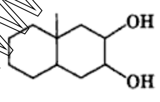
(*c*) Effect the following conversion in not more than four steps:



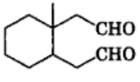
Solution: (*a*)



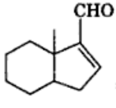
(*b*)



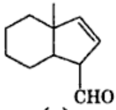
(A)



(B)

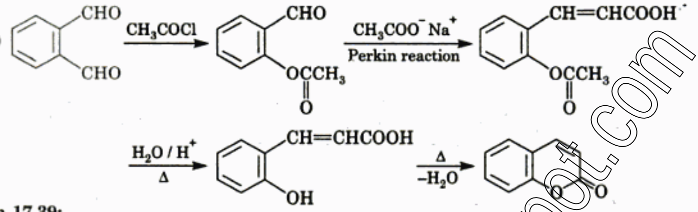


(C)



(D)

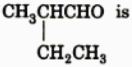
(c)



Problem 17.39:

Select the correct answer.

(a) Correct name of



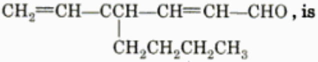
$$CH_3\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCHO$$

is

A. Butan-2-aldehyde B. 2-Ethylpropanal C. 2-Methylbutanal

D. 3-Methyl isobutyraldehyde

(b) 1UPAC name of



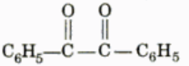
$$CH_2{=}CH{-}C\underset{\displaystyle CH_2CH_2CH_2CH_3}{\underset{|}{C}}H{-}CH{=}CH{-}CHO$$

, is

A. 4-Butyl-2, 5-hexadienal B. 4-Vinyloct-2-en-1-al C. 5-Vinyloct-5-en-8-al

D. 3-Butyl-1, 4-hexadien-8-al

(c) The number of asymmetric carbon atoms created during the complete reduction of

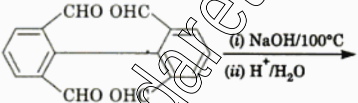


$$C_6H_5{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}C_6H_5$$

are

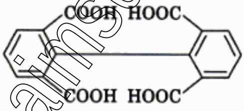
A. 2 B. 3 C. 4 D. 5

(d)

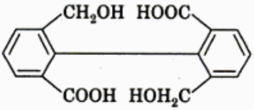


the major product is

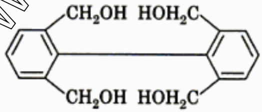
A.



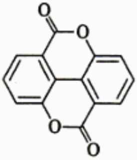
B.



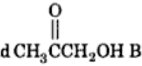
C.

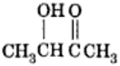


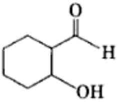
D.

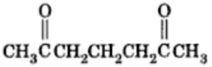


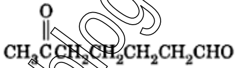
(*d*) Fehling's solution will distinguish between :

A. CH_3CHO and 
$CH_3\overset{\overset{O}{\|}}{C}CH_2OH$ B. CH_3CHO and C_6H_5CHO C. CH_3CHO and HCHO

D. 
$CH_3\overset{\overset{OH}{|}}{CH}\overset{\overset{O}{\|}}{C}CH_3$ and HCHO

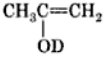
(*e*) Compound  is formed by an intramolecular aldol condensation of:

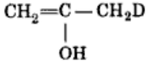
A. 
$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

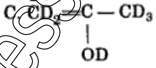
B. 
$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_2CHO$

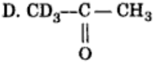
C. $OHCCH_2CH_2CH_2CH_2CH_2CHO$ D. None of these.

(*f*) An enol form of acetone on treatment with D_2O gives:

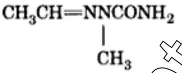
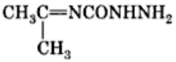
A. 
$CH_3\underset{\underset{OD}{|}}{C}{=}CH_2$

B. 
$CH_2{=}\underset{\underset{OH}{|}}{C}-CH_2D$

C. 
$CD_2{=}\underset{\underset{OD}{|}}{C}-CD_3$

D. 
$CD_3-\underset{\underset{O}{\|}}{C}-CH_3$

(*g*) Compound A, molecular formula C_3H_8O is treated with acidified $K_2Cr_2O_7$ to give 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 $H_2NCONHNH_2$. HCl and sodium acetate gives C. Identify the structure C.

A. 
$CH_3CH{=}N\underset{\underset{CH_3}{|}}{N}CONH_2$ B. $CH_3CH_2CH{=}NCONHNH_2$ C. 
$CH_3\underset{\underset{CH_3}{|}}{C}{=}NCONHNH_2$

D. $CH_3CH_2CH{=}NNHCONH_2$

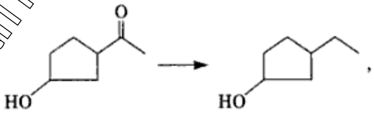
(*h*) Aldehydes and ketones cannot be distinguished by

A. Schiff's test B. Benedict test C. Mollisch test D. Tollens' test

(*i*) When ethanal is heated with Fehling's solution, it gives a precipitate of

A. Cu B. CuO C. Cu_2O D. Cu + CuO + Cu_2O

(*j*) The reagent for the following transformation:



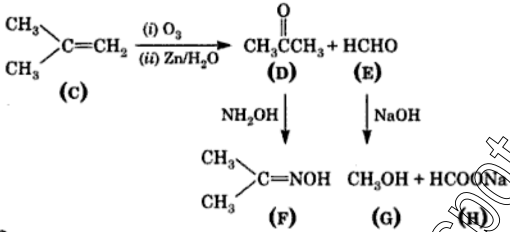
, is

A. Zn/Hg, HCl B. NH_2 , NH_2 , OH^- C. $NaBH_4$ D. H_2 , Ni

(*k*) Which of the following has the most acidic hydrogen?

A. 2, 4-Hexanedione B. 2, 3-Hexanedione C. 2, 5-Hexanedione

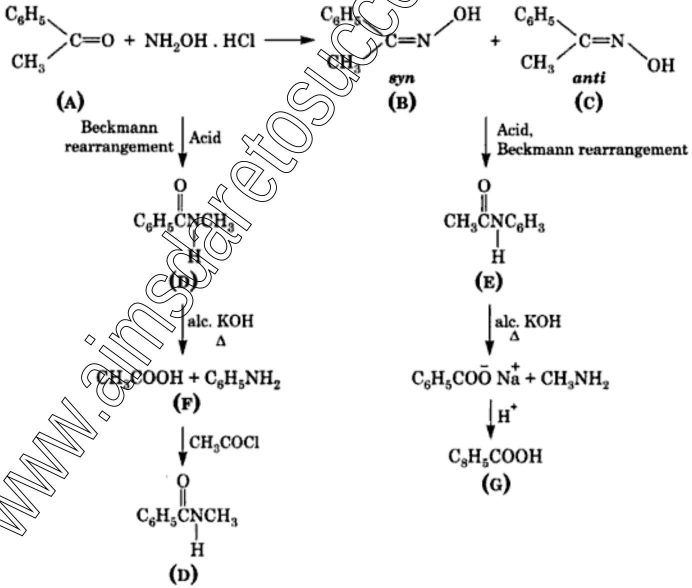
D. 3-Hexanone



Problem 17.42:

Compound A, $C_8H_{18}O$ on treatment with NH_2OH . HCl gives B and C. Both 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_9ON. When D, is boiled with alc. KOH, an oil F, C_6H_7N separates out. F, reacts rapidly with CH_3COCl to give back D. Compound E, on the other hand, on boiling with alkali followed by acidification gives a white solid G, $C_7H_6O_2$. Deduce structures A to G.

Solution: A is a ketone because it reacts with NH_2OH . HCl. Further since B and C are formed in this reaction, A is acetophenone and two oxime isomers are obtained on reaction with hydroxylamine.



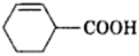
CHAPTER

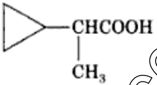
18

Carboxylic Acids

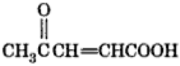
Problem 18.1:

Suggest IUPAC name for each of the following compounds.

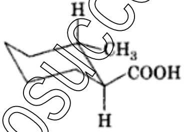
(*a*)


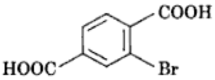
(*b*)


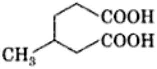
(*c*) $HOOCCH_2CH_2CH_2COOH$

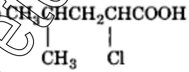
(*d*)


$CH_3\overset{\overset{O}{\|}}{C}CH{=}CHCOOH$

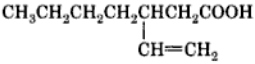
(*e*)


(*f*)


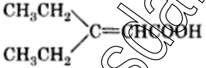
(*g*)


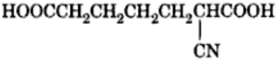
(*h*)


$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2\underset{\underset{Cl}{|}}{C}HCOOH$

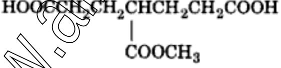
(*i*)


$CH_3CH_2CH_2CH_2\underset{\underset{CH=CH_2}{|}}{C}HCH_2COOH$

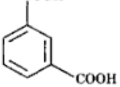
(*j*)


(*k*)


$HOOCCH_2CH_2CH_2CH_2\underset{\underset{CN}{|}}{C}HCOOH$

(*l*)


$HOOCCH_2CH_2\underset{\underset{COOCH_3}{|}}{C}HCH_2CH_2COOH$

(*m*)


Solution: (*a*) 2-Cyclohexenecarboxylic acid (*b*) 2-Cyclopropylpropanoic acid (*c*) 1, 5-Pentanedioic acid (*d*) 4-Oxo-pent-2-enoic acid (*e*) *Trans*-2-methylcyclohexane carboxylic acid (*f*) 2-Bromobenzene-1, 4-dicarboxylic acid (*g*) 3-Methylhexanedioic acid (*h*) 2-Chloro-4-methylpentanoic acid (*i*) 3-Butyl-4-pentenoic acid (*j*) 3-Ethyl-2-pentenoic acid (*k*) 2-Cyanoheptanedioic acid (*l*) 4-Methoxycarbonylheptanedioic acid (*m*) Benzene-1, 3-dicarboxylic acid.

Problem 18.2:

In which solvent would you expect the proportion of acetic acid dimer to be greater in water or carbon tetrachloride?

Solution: In CCl_4, it being a non-polar solvent acetic acid would not ionize.

Problem 18.3:

Match the pK_a values of the following acids:

formic acid, pyruvic acid, levulinic acid, lactic acid:

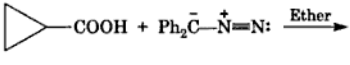
2.5, 4.4, 4.3, 3.9.

Solution: Formic acid 4.3; Pyruvic acid 2.5; Levulinic acid 4.4; Lactic acid 3.9

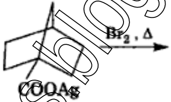
Problem 18.4:

Predict the major organic product of the following reactions:

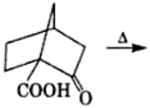
(*a*)



(*b*)



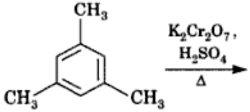
(*c*)



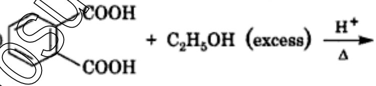
(*d*)

$CH_3-CH(CH_2COOH)_2 + (CH_3CO)_2O \longrightarrow$

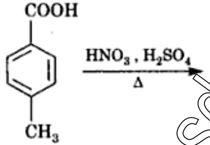
(*e*)



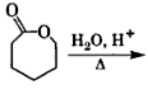
(*f*)



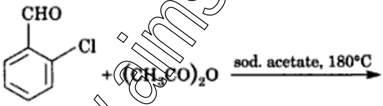
(*g*)



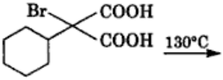
(*h*)



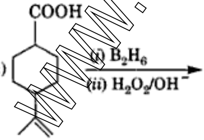
(*i*)



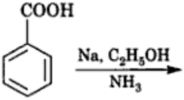
(*j*)



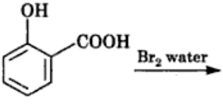
(*k*)

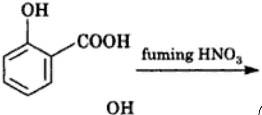


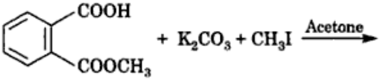
(*l*)

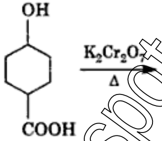


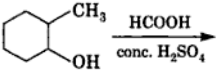
(*m*) $CH_3CH_2CH_2C\equiv CC_6H_5 \xrightarrow[(ii)\ H_2O]{(i)\ O_3}$

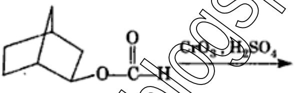
(n) 

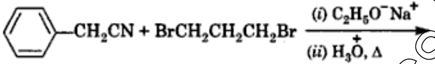
(o) 

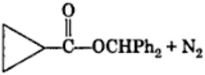
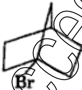
(p) 

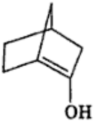
(q) 

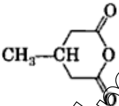
(r) 

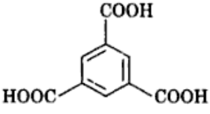
(s) 

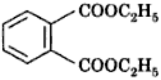
(t) 

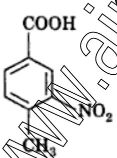
Solution: (a)  + N_2 (b)  (c) No reaction. Since the decarboxylation of an acid proceeds through an enol, presence of a double bond on the bridgehead of the bicyclic ring system would put much strain on the ring.

i.e.  is not formed. Hence decarboxylation not possible.

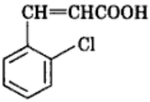
(d) 

(e) 

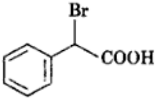
(f) 

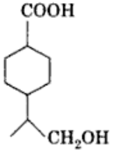
(g) 

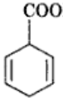
(h) $HO(CH_2)_6COOH$

(i) 

(It is the Perkin reaction.)

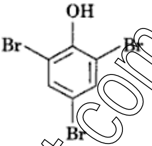
(j) 

(*k*)


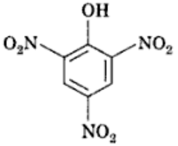
(*l*)


(Birch reduction)

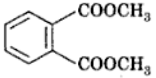
(*m*) $CH_3CH_2CH_2COOH$
$+ C_6H_5COOH$

(*n*)


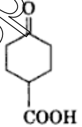
(The -COOH group is replaced by Br)

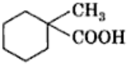
(*o*)


(The -COOH group is replaced by -NO₂)

(*p*)


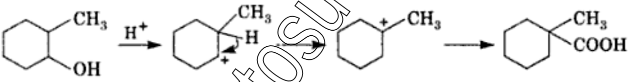
$+ KHCO_3 + KI$

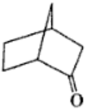
(*q*)


(*r*)


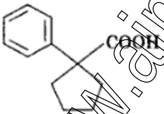
, This is called the Koch-Haas carboxylation reaction. The CO is generated by the dehydration of formic acid with H_2SO_4, same reaction generates a tertiary cation. The reaction is restricted to carboxylation of tertiary carbocations.

Mechanism:



(*s*)


$+ CO_2$ (Carboxylic acids represent the highest oxidation state possible for a carbon atom. Therefore, the oxidation of the compound is relatively uncommon. One important exception is the oxidation of formic acid and its derivatives. Formic acid is easily oxidized.)

(*t*)


Problem 18.5:

Why is the first pK_a of malonic acid (2.85) is much lower than that of acetic acid (4.75)? Whereas the second pK_a (5.70) of malonic acid is much higher than that of acetic acid.

Solution: Because after the removal of a proton, the malonate anion is stabilized by H-bonding as a result loss of second proton becomes difficult.

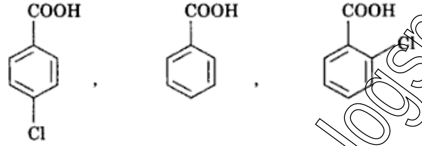
Problem 18.6:

The K_2 ionization constant is greater for fumaric acid than for maleic acid. Why?

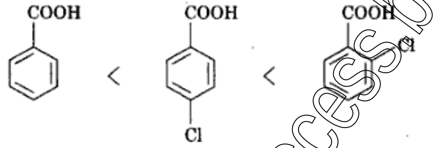
Solution: The second ionizable hydrogen of the maleate ion is involved in H-bonding, thus more energy is required to remove this H because the H-bond has to be broken. But in case of maleate ion there is no H-bond formation.

Problem 18.7:

Rank the following acids in order of their increasing acidity.



Solution:



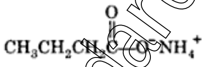
The *ortho* -Cl group withdraws electrons inductively and stabilizes the carboxylate ion.

Problem 18.8:

Draw structures of the following compounds:

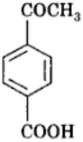
(*a*) Ammonium butanoate (*b*) *p*-Acetoxybenzoic acid (*c*) *trans-1*-Ethylcyclopentanecarboxylic acid (*d*) 3-Phenylpropanoyl chloride (*e*) Silver 3-phenylpropanoate

Solution: (*a*)

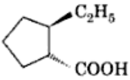


$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}-O^-NH_4^+$

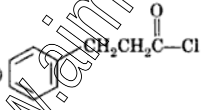
(*b*)



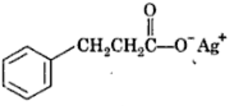
(*c*)



(*d*)



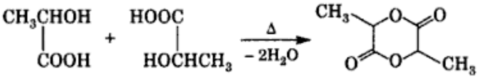
(*e*)



Problem 18.9:

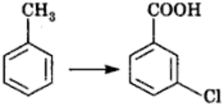
Discuss the action of heat on α-hydroxy carboxylic acids.

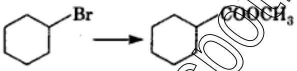
Solution: An α-hydroxy acid is not capable of forming a lactone by itself because of the presence of strain in a three-membered ring lactone. But two molecules undergo intermolecular self-esterification to yield a cyclic product containing two carbonyl groups and is called a *lactide*.

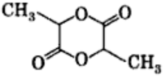


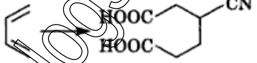
Problem 18.10:

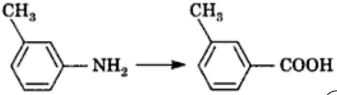
How will you effect the following conversions?

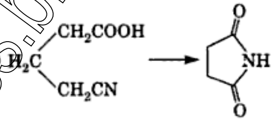
(a)


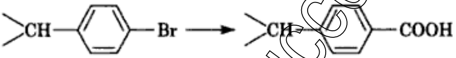
(b)


(c) $CH_3CH_2COOH \longrightarrow$


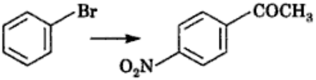
(d)


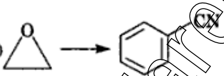
(e)


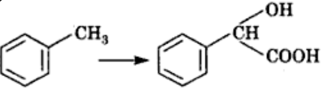
(f)


(g)


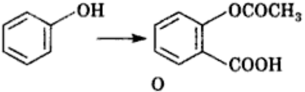
(h) $CH_3CH_2COOH \longrightarrow CH_2{=}CHCOOH$

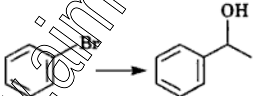
(i)


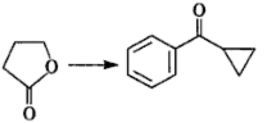
(j)


(k)


(l) $CH_3C{\equiv}CCH_3 \longrightarrow CH_3CH_2COOH$

(m)


(n)


(o)


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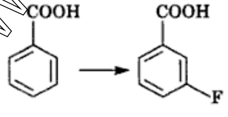
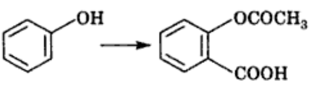
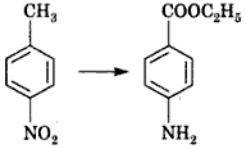
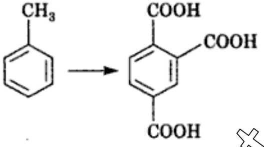


(q)


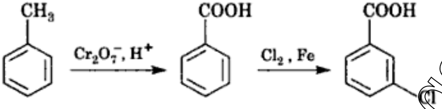
(r)



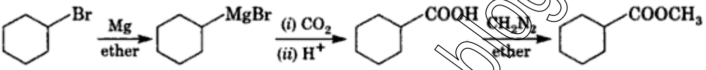
(s)



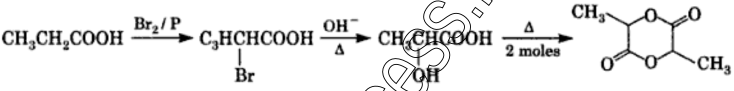
Solution: (a)



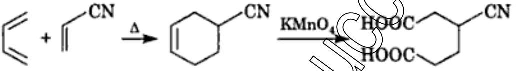
(b)



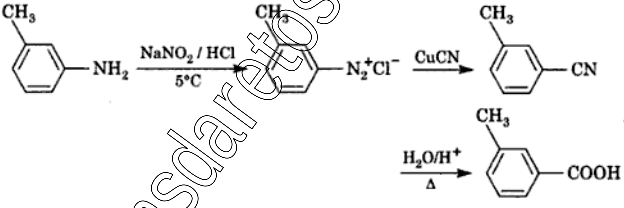
(c)



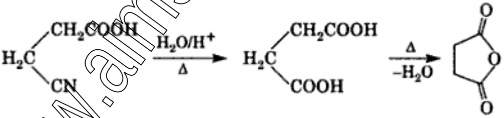
(d)



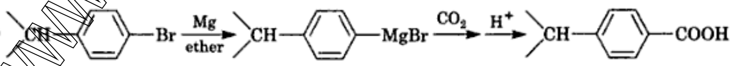
(e)



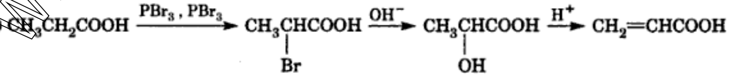
(f)



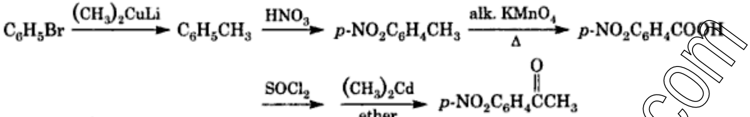
(g)



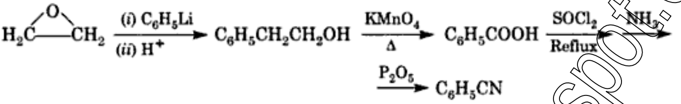
(h)



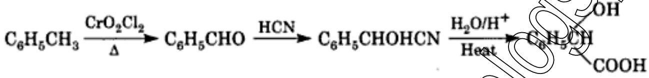
$$CH_3CH_2COOH \xrightarrow{PBr_3\ ,\ PBr_3} \underset{\substack{|\\ Br}}{CH_3CHCOOH} \xrightarrow{OH^-} \underset{\substack{|\\ OH}}{CH_3CHCOOH} \xrightarrow{H^+} CH_2{=}CHCOOH$$

(i)


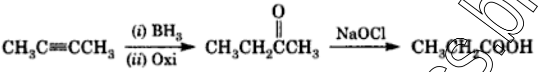
$$C_6H_5Br \xrightarrow{(CH_3)_2CuLi} C_6H_5CH_3 \xrightarrow{HNO_3} p\text{-}NO_2C_6H_4CH_3 \xrightarrow[\Delta]{\text{alk. } KMnO_4} p\text{-}NO_2C_6H_4COOH \xrightarrow{SOCl_2} \xrightarrow[\text{ether}]{(CH_3)_2Cd} p\text{-}NO_2C_6H_4\overset{\overset{O}{\|}}{C}CH_3$$

(j)


$$H_2C\overset{O}{\text{——}}CH_2 \xrightarrow[(ii)\ H^+]{(i)\ C_6H_5Li} C_6H_5CH_2CH_2OH \xrightarrow[\Delta]{KMnO_4} C_6H_5COOH \xrightarrow[\text{Reflux}]{SOCl_2} \xrightarrow{NH_3} \xrightarrow{P_2O_5} C_6H_5CN$$

(k)


$$C_6H_5CH_3 \xrightarrow[\Delta]{CrO_2Cl_2} C_6H_5CHO \xrightarrow{HCN} C_6H_5CHOHCN \xrightarrow[\text{Heat}]{H_2O/H^+} C_6H_5CH\begin{smallmatrix}OH\\COOH\end{smallmatrix}$$

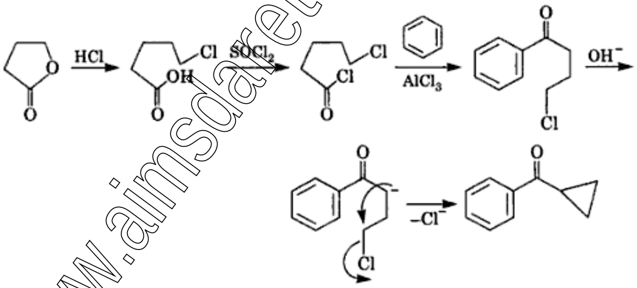
(l)


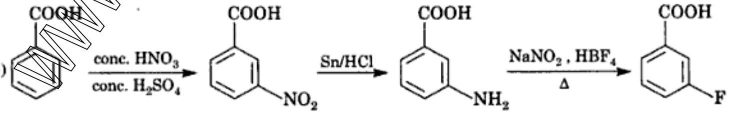
$$CH_3C\equiv CCH_3 \xrightarrow[(ii)\ \text{Oxi}]{(i)\ BH_3} CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{NaOCl} CH_3CH_2COOH$$

(m) $C_6H_5OH + CO_2 \xrightarrow{H^+} o\text{-}HOC_6H_4COOH \xrightarrow[H^+]{(CH_3CO)_2O} o\text{-}OCOCH_3C_6H_4COOH$

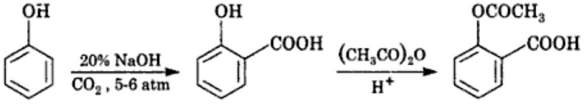
(n)

$$C_6H_5Br \xrightarrow[\substack{(ii)\ CO_2\\(iii)\ H_2O}]{(i)\ \text{Mg/ether}} C_6H_5COOH \xrightarrow[\text{ether}]{LiAlH_4} C_6H_5CH_2OH \xrightarrow[\text{Reflux}]{PCl_5} C_6H_5CH_2Cl \xrightarrow[\substack{(ii)\ CH_3CHO\\(iii)\ H_2O}]{(i)\ \text{Mg/ether}} C_6H_5CH_2CHOHCH_3$$

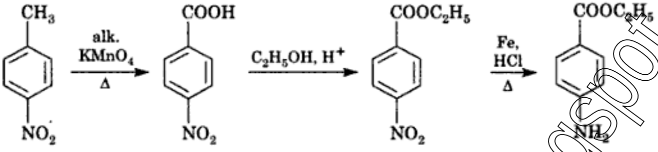
(o)


(p)


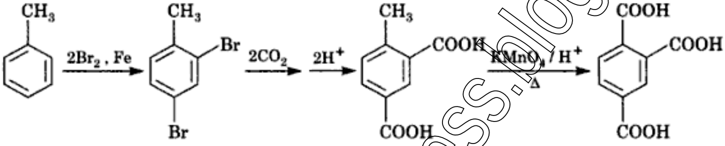
(q)



(r)

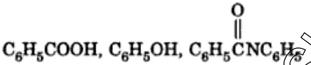


(s)



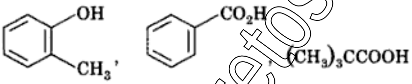
Problem 18.11:

How will you separate a mixture containing the following components?

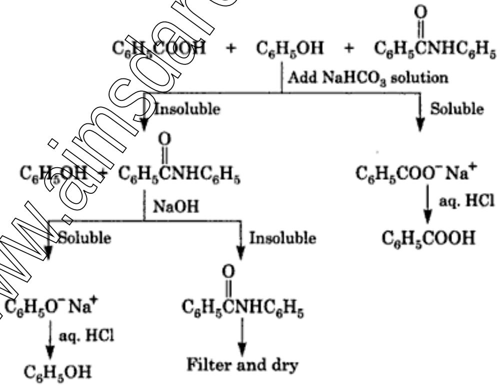
(a) 

C_6H_5COOH, C_6H_5OH, $C_6H_5\overset{\overset{O}{\|}}{C}NC_6H_5$

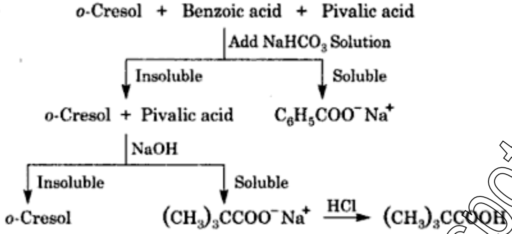
(b)



Solution: (a)

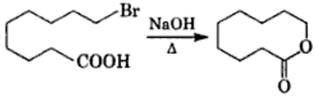


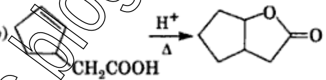
(*b*)



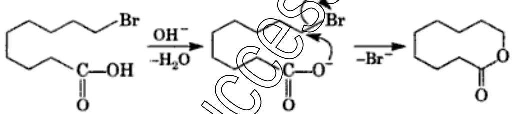
Problem 18.12:

Write a mechanism for each of the following reactions:

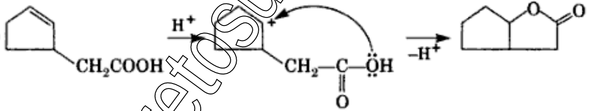
(*a*)


(*b*)


Solution: (*a*)



(*b*)



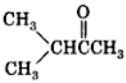
Problem 18.13:

How do you account for the fact that an aromatic carboxylic acid does not form an oxime or a phenyl hydrazone?

Solution: Because of resonance with the ring of the carbonyl group the carbon is not adequately electrophilic.

Problem 18.14:

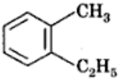
Which ketones of the formula $C_5H_{10}O$ will yield an acid in the haloform reaction?

Solution: Ketones containing a $-\overset{\overset{\large O}{\|}}{C}-CH_3$ grouping : $CH_3CH_2CH_2\overset{\overset{\large O}{\|}}{C}CH_3$ and  $(CH_3)_2CH\overset{\overset{\large O}{\|}}{C}CH_3$

Problem 18.15:

A hydrocarbon with molecular formula C_9H_{12} yields phthalic acid as the only product on oxidation. Write the structural formula of the compound.

Solution: Since phthalic acid is formed, it would be a dialkyl benzene derivative.



Problem 18.16:

Suggest a simple chemical test to distinguish between:

(*a*) Formic and acetic acids (*b*) Lactic and maleic acids (*c*) Crotonic and butyric acids

(*d*) Acetic acid and acetyl chloride

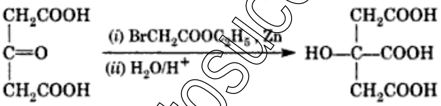
(*e*) Levulinic $(CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2COOH)$ and valeric acids $(CH_3(CH_2)_3COOH)$.

Solution: (*a*) Formic acid reduces aqueous $KMnO_4$ solution. (*b*) Lactic acid responds to iodoform test. (*c*) Crotonic acid decolorizes $KMnO_4$ solution. (*d*) Acetyl chloride evolves heat on adding water. (*e*) Levullinic acid will react with semicarbazide.

Problem 15.17:

How is citric acid prepared ? Discuss its important properties. How does it differ from tartaric acid?

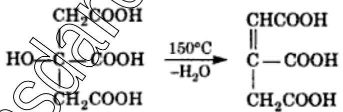
Solution: Citric acid may be obtained from acetonedicarboxylic acid and ethyl bromoacetate by the Reformatsky reaction.



$$\begin{array}{c} CH_2COOH \\ | \\ C{=}O \\ | \\ CH_2COOH \end{array} \xrightarrow[(ii)\ H_2O/H^+]{(i)\ BrCH_2COOC_2H_5,\ Zn} \begin{array}{c} CH_2COOH \\ | \\ HO{-}C{-}COOH \\ | \\ CH_2COOH \end{array}$$

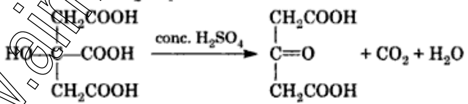
Citric acid undergoes a number of chemical reactions.

(1) On heating at 150°C, it forms aconitic acid by losing elements of water.



$$\begin{array}{c} CH_2COOH \\ | \\ HO{-}C{-}COOH \\ | \\ CH_2COOH \end{array} \xrightarrow[-H_2O]{150°C} \begin{array}{l} CHCOOH \\ \| \\ C{-}COOH \\ | \\ CH_2COOH \end{array}$$

(2) On heating with conc. H_2SO_4, it forms acetonedicarboxylic acid.



$$\begin{array}{c} CH_2COOH \\ | \\ HO{-}C{-}COOH \\ | \\ CH_2COOH \end{array} \xrightarrow{conc.\ H_2SO_4} \begin{array}{c} CH_2COOH \\ | \\ C{=}O \\ | \\ CH_2COOH \end{array} + CO_2 + H_2O$$

Citiric acid has no chiral carbon and therefore has no enantiomers.

Tartaric acid has two chiral carbons and therefore four stereoisomers out of these two are enantiomers and remaining two are identical and *meso*. The *meso* form is distereoisomer with enantiomeric forms.

(*f*) Which is the strongest acid among

A. *o*-Nitrobenzoic acid B. *m*-Nitrobenzoic acid C. *p*-Nitrobenzoic acid

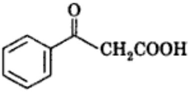
D. *p*-Nitrophenol

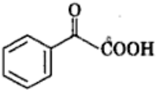
(*g*) Formic acid and acetic acid may be distinguished by reacting with

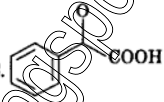
A. Sodium B. Sod. ethoxide C. Dilute acidic $KMnO_4$

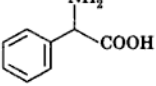
D. 2, 4-$(NO_2)_2\ C_6H_3NHNH_2$

(*h*) Which of the following carboxylic acids undergoes decarboxylation easily?

A. 

B. 

C. 

D. 

(*i*) Benzoic acid and phenol may be distinguished by their reaction with:

A. Aq. NaOH B. Aq. $NaHCO_3$ C. Neutral $FeCl_3$ D. Aq. NH_3

(*j*) The IUPAC name of $CH_2CH_2CH{=\!=}CHCOOH$ is :

A. Pent-3-en-1-oic acid B. Pent-2-en-1-oic acid

C. Pent-2, 3-en-1-oic acid D. Pent-, 3, 4-en-1-oic acid

(*k*) Benzoic acid reacts with conc. HNO_3 and conc. H_2SO_4 to give:

A. *o*-Nitrobenzoic acid B. *m*-Nitrobenzoic acid

C. *p*-Nitrobenzoic acid D. *o*-and *p*-Nitrobenzoic acid

(*l*) Carboxylic acids undergo ionization because of:

A. Hydrogen bonding B. Absence of α-hydrogen

C. High reactivity of α-hydrogen D. Resonance stabilization of the carboxylate ion.

(*m*) 59 g of an amide obtained from a carboxylic acid (RCOOH) on heating with alkali evolves 17 g of NH_3. The acid is:

A. Methanoic acid B. Ethanoic acid C. Propanoic acid D. Benzoic acid

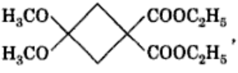
(*n*) *o*-Methoxybenzoic acid is less acidic than salicylic acid because of:

A. Resonance B. Inductive effect C. Hydrogen bond D. None of these

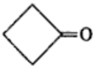
(*o*) Pyruvic acid can be obtained by the oxidation of propanoic acid with

A. $KMnO_4$ B. Ag_2O C. MnO_2 D. SeO_2

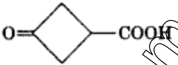
(*p*) The final product on acid hydrolysis and decarboxylation of

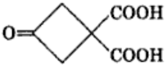


, is

A.


B.


C.


D.


Solution: (*a*) D, $HCOOH \xrightarrow{\text{conc. } H_2SO_4} CO + H_2O$ (Dehydration of formic acid takes place)

(*b*) C, $CH_3CH_2COOH + NaHCO_3 \longrightarrow CH_3CH_2COO^- Na^+ + CO_2 + H_2O$

(*c*) A, Formic acid can be oxidized by acidified $KMnO_4$

$$5HCOOH + 2KMnO_4 + 3H_2SO_4 \longrightarrow 5CO_2 + 8H_2O + K_2SO_4 + 2MnSO_4$$

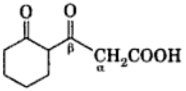
(*d*) C, An attacking base preferentially abstracts an acidic hydrogen thus forming a carboxylate ion. This ion because of the negative charge and resonance does not give the reaction.

(*e*) B, $RCOOH + HN_3 \xrightarrow{\text{conc. } H_2SO_4} RNH_2 + CO_2 + N_2$

This is called the Schmidt reaction.

(*f*) A, (Because of strong inductive electron-withdrawing effect of the *o*-NO_2 group.)

(*g*) C, (Formic acid will undergo oxidation with $KMnO_4$)

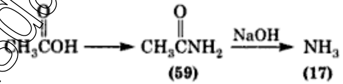
(*h*) A,


(A carboxylic acid can be easily decarboxylated without the use of soda lime, if the acid contains a keto group at the β-position.) (*i*) B, C (*j*) B

(*k*) B, (-COOH group is electron-withdrawing and *m*-directing.)

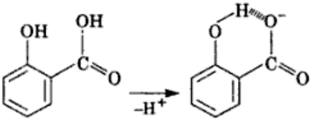
(*l*) D, (the resulting carboxylate ion undergoes resonance stabilization.)

(*m*) B, Ethanoic acid



$$\underset{}{CH_3\overset{O}{\overset{\|}{C}}OH} \longrightarrow \underset{(59)}{CH_3\overset{O}{\overset{\|}{C}}NH_2} \xrightarrow{NaOH} \underset{(17)}{NH_3}$$

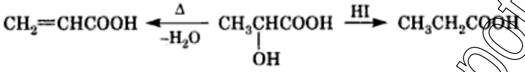
(*n*) C, (the salicylate ion undergoes H-bonding, thereby stabilizing the conjugate base and enhancing acidity.)



$$\text{Molecular formula weight of the acid} = \left[\left(\frac{0.98}{0.54}\times 108\right) - 107\right] \times 1 = 89$$

$$n = \frac{89}{30} \approx 3$$

Molecular formula of acid = $(CH_2O)_n$ or $(CH_2O)_3$ or $C_3H_6O_3$



$$CH_2{=}CHCOOH \xleftarrow[-H_2O]{\Delta} \underset{\displaystyle OH}{CH_3\overset{}{C}HCOOH} \xrightarrow{HI} CH_3CH_2COOH$$

Problem 18.25:

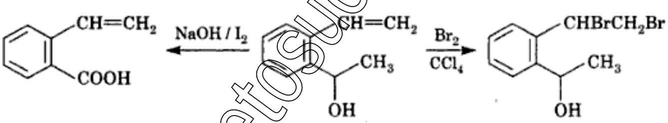
An organic compound A, $C_{10}H_{12}O$ liberated hydrogen on reaction with Na metal. A, also decolorizes Br_2 in CCl_4 to form B, $C_{10}H_{12}OBr_2$. Compound A on treatment with NaOH / I_2 gives an acid C, after acidification. Deduce structures A, B and C.

Solution: A is a benzene derivative

Compound A liberates H_2 on reaction with Na, therefore a -OH group in present in the side-chain.

It decolorizes Br_2 , a C═C is also present.

A gets oxidized on reaction with NaOH / I_2, therefore it contain a $-\overset{\displaystyle O}{\overset{\|}{C}}CH_3$ or a $-\overset{\displaystyle OH}{\overset{|}{C}}HCH_3$ group. Based on these observations the structure of A is:



(A) (B)

Problem 18.26:

An organic compound A, $C_{18}H_{20}O$ on ozonolysis gives B, $C_{10}H_{12}O$ and C, C_8H_8O. Compound B, responds to iodoform reaction and also 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. Compound F, on treatment with HNO_2 followed by oxidation gives phthalic acid. Compound C, on mild oxidation gives G which produces effervescence with $NaHCO_3$. G on treatment with HI gives p-hydroxybenzoic acid and CH_3I.

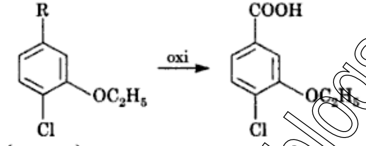
Assign structures A to G with adequate reasoning.

Solution: Compound B gives iodoform reaction and forms an oxime. It is a ketone containing a $-\overset{\displaystyle O}{\overset{\|}{C}}CH_3$ grouping, therefore, B is $\begin{matrix}CH_3\\C_8H_9\end{matrix}\!\!>C{=}O$ (Mole. formula $C_{10}H_{12}O$) and D is $\begin{matrix}CH_3\\C_8H_9\end{matrix}\!\!>C{=}N{-}OH$. D reacts with PCl_5 and gives E $C_8H_{11}N$ a consequence of Beckmann rearrangement.

Problem 18.27:

Two isomeric compounds A, and B, have the same molecular formula $C_{11}H_{13}OCl$. Both are unsaturated and yield the same compound C, on hydrogenation and form 4-chloro-3-ethoxy benzoic acid on vigorous oxidation. A, exists in geometric isomers D, and E, but not B. Give the structures of A to E with proper reasoning.

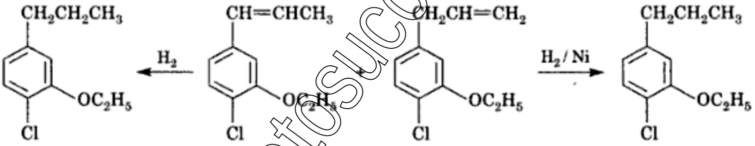
Solution: Since both A and B give 4-chloro-3-ethoxybenzoic acid on vigorous oxidation, therefore A and B are:



(A and B)

Mol. formula is $C_{11}H_{13}OCl$
where $R{=}C_3H_5$

Since both A and B are unsaturated and only A depicts isomerism, therefore a C=C bond is present in two different manners in A and B. Therefore A and B are:



(C) (A) (B)

Problem 18.28:

A 0.450 g sample of aromatic compound A on ignition gives 0.905 g CO_2, 0.185 g H_2O. Also 0.350 g of A, on boiling with HNO_3 and adding $AgNO_3$ solution gives 0.574 g of AgCl. The vapor density of A, is 87.5. Compound A on hydrolysis with $Ca(OH)_2$ yields B, which on mild reduction gives an optically active compound C. On heating C with NaOH / I_2, produce iodoform and D. On treatment of D, with HCl, a solid compound results which is markedly more soluble in hot water than in cold water. Identify compounds A to D.

Solution: $\% \text{ C} = \frac{12}{44} \times \frac{0.905}{0.45} \times 100 = 54.85$; $\% \text{ H} = \frac{2}{18} \times \frac{0.185}{0.45} \times 100 = 4.57$

$$\% \text{ Cl} = \frac{35.5}{143.5} \times \frac{0.574}{0.35} \times 100 = 40.57$$

Empirical Formula

Elements	*Percentage composition*	*At. weight*	*Rel. number of atoms*	*Simplest ratio*
C	54.85	12	$\frac{54.85}{12}$	4
H	4.57	1	$\frac{4.57}{1}$	4
Cl	40.57	35.5	$\frac{40.57}{35.7}$	1

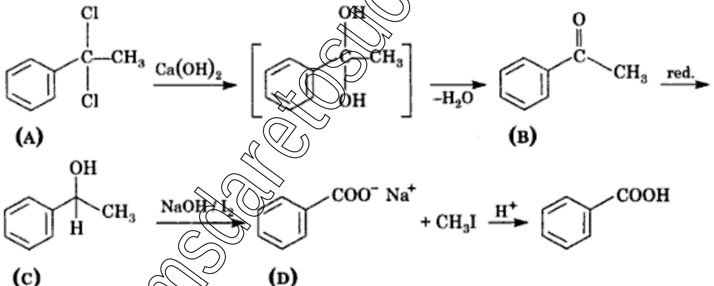
Empirical formula C_4H_4Cl

Molecular weight = 87.2 × 2 = 175

$$n = \frac{175}{\text{E.F. weight}} = \frac{175}{87.5} = 2$$

Therefore, molecular formula = $C_8H_8Cl_2$

From the molecular formula, it is obvious that A is an aromatic compound and the side-chain contains only two carbon atoms. Further, compound C is formed from B by its reduction which is obtained by the hydrolysis of A. Therefore, the two chlorine atoms are attached to the same carbon atom in A. The reaction sequence can thus be written as follows:



Benzoic acid has more solubility in hot than in cold water.

Problem 18.29:

A 1.22 g sample of C_6H_5COOH is added into two solvents and data of ΔT_b and K_b are given as:

(1) in 100 g CH_3COCH_3

$\Delta T_b = 0.17$; $K_b = 1.7$ kg Kelvin/ mol

(2) in 100 g benzene

$\Delta T_b = 0.13$; $K_b = 2.6$ kg Kelvin/mol

Find the molecular weight of C_6H_5COOH in both cases and interpret the result.

Solution:

$$m = \frac{1000 \times K_b \times w}{W \times \Delta T_b}$$

(1)
$$m = \frac{1000 \times 1.7 \times 1.22}{100 \times .17} = 122$$

(2)
$$m = \frac{1000 \times 2.6 \times 1.22}{100 \times .13} = 244$$

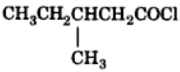
Molecular weight of benzoic acid is twice in benzene than in acetone. Therefore, benzoic acid dimerizes in benzene a non-polar solvent.

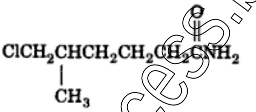
CHAPTER 19

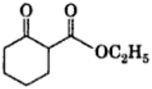
Functional Derivatives of Carboxylic Acids

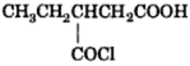
Problem 19.1:

Write a systematic name for the following compounds:

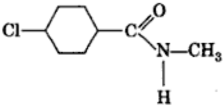
(a)

$CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2COCl$

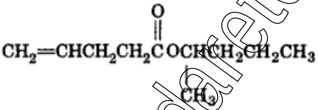
(b)

$ClCH_2\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2CH_2\overset{\substack{O\\ \|}}{C}NH_2$

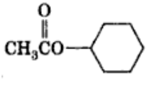
(c)


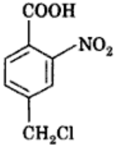
(d)

$CH_3CH_2\underset{\substack{|\\ COCl}}{C}HCH_2COOH$

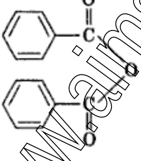
(e) $CH_3CH_2CH{=}CHCOOCH_3$

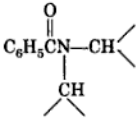
(f)


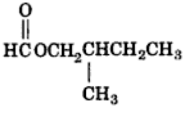
(g)

$CH_2{=}CHCH_2CH_2\overset{\substack{O\\ \|}}{C}O\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2CH_3$

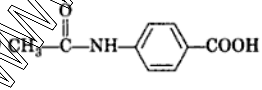
(h)


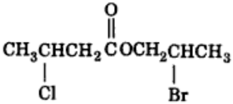
(i)


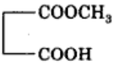
(j)


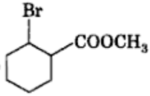
(k)


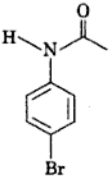
(l)

$H\overset{\substack{O\\ \|}}{C}OCH_2\underset{\substack{|\\ CH_3}}{C}HCH_2CH_3$

(m)


(n)

$CH_3\underset{\substack{|\\ Cl}}{C}HCH_2\overset{\substack{O\\ \|}}{C}OCH_2\underset{\substack{|\\ Br}}{C}HCH_3$

(o)


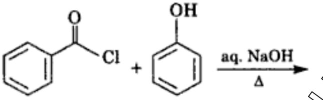
(p)


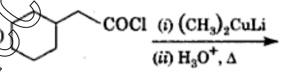
(q)


Solution: (*a*) 3-Methylpentanoyl chloride (*b*) 6-Chloro-5-methylhexanamide (*c*) 2-carboethoxycyclohexanone (*d*) 3-Chloroformylpentanoic acid (*e*) Methyl 2-pentenoate (*f*) 4-Chloro-N-methylcyclohexanecarboxamide (*g*) 1-Methylbutyl 4-pentenoate (*h*) Cyclohexyl ethanoate (*i*) 4-Chloromethyl-6-nitrobenzoic acid (*j*) Benzoic anhydride (*k*) N, N-diisopropyl benzamide (*l*) 2-Methylbutyl formate (*m*) *p*-Acetamidobenzoic acid or 4-(Acetylamino) benzoic (*n*) 2-Bromopropyl-3-chloro butanoate (*o*) Methylhydrogen succinate (*p*) Methyl 2-bromolcyclohexane carboxylate (*q*) N-(*p*-bromophenyl) acetamide

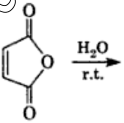
Problem 19.2:

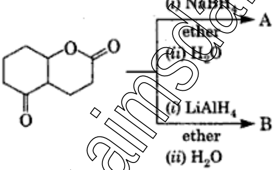
Complete the following reactions:

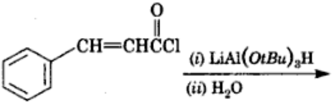
(*a*)


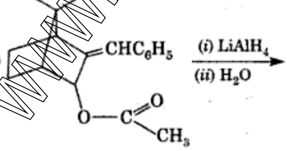
(*b*)


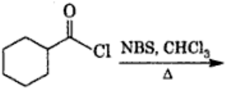
(*c*) $CH_3CH_2COCl + Alc.\ AgNO_3 \xrightarrow{\Delta}$

(*d*)


(*e*)


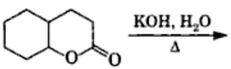
(*f*)


(*g*)


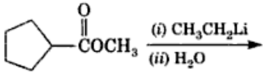
(*h*)


(*i*) $CH_3(CH_2)_3CH_2COOH \xrightarrow[(ii)\ H_2O]{(i)\ Br_2,\ PCl_5}$

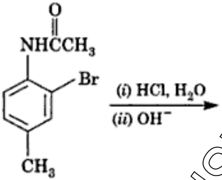
(*j*)



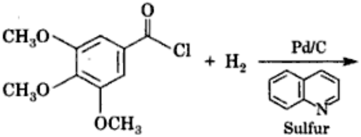
(*k*)



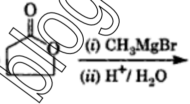
(*l*)



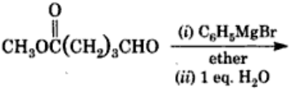
(*m*)



(*n*)

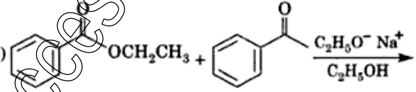


(*o*)

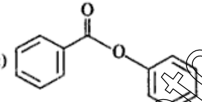


$CH_3O\overset{O}{\overset{\|}{C}}(CH_2)_3CHO \xrightarrow[\text{ether}\ (ii)\ 1\ \text{eq.}\ H_2O]{(i)\ C_6H_5MgBr}$

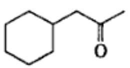
(*p*)



Solution: (*a*)



(*b*)



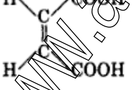
(**Lithium dialkylcuprates are the reagents of choice for preparing ketones.**)

(*c*)

$CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$

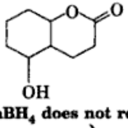
(**Esterification reaction**)

(*d*)



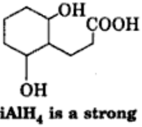
(**Anhydrides hydrolyze under neutral conditions**)

(*e*) A



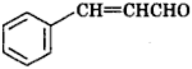
(**NaBH$_4$ does not reduce ester function.**)

B



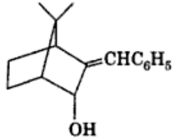
(**LiAlH$_4$ is a strong reducing agent and reduces both the carbonyl and the ester function.**)

(*f*)



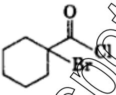
(Lithium *tri-t*-butoxyaluminum hydride has a reduced activity than $LiAlH_4$ as a reducing agent. It is more selective but less reactive.)

(*g*)



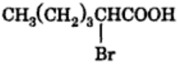
+ CH_3CH_2OH

(*h*)



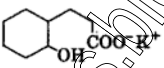
($LiAlH_4$ does not touch a C=C bond.)

(*i*)

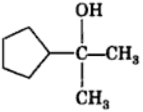


$$CH_3(CH_2)_3\underset{\displaystyle Br}{\underset{|}{C}}HCOOH$$

(*j*)

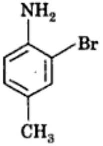


(*k*)

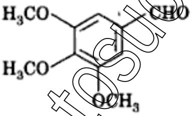


(Both the above reactions illustrate the α-halogenation of acids and acid chlorides)

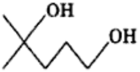
(*l*)



(*m*)



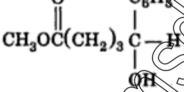
(*n*)



(Amide hydrolysis in alkaline solution.)

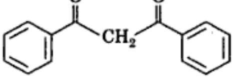
(This is an example of Rosenmund reduction.)

(*o*)



$$CH_3O\overset{\displaystyle O}{\overset{\|}{C}}(CH_2)_3\,\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle C_6H_5}{\overset{|}{C}}}}—H$$

(*p*)



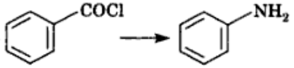
(This is the claisen ester condensation)

(Only the ketone function undergoes reaction because ketones are more reactive than esters toward nucleophilic reagents)

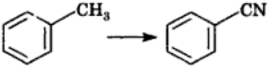
Problem 19.3:

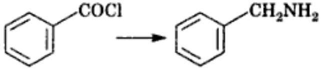
Effect the following conversions:

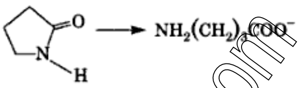
(*a*)

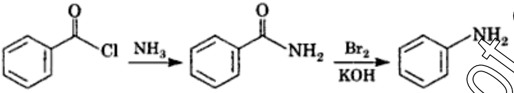


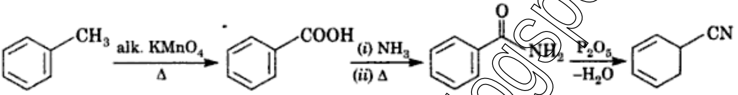
(*b*)

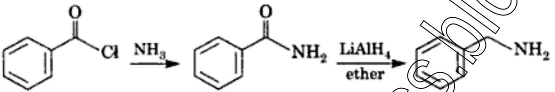


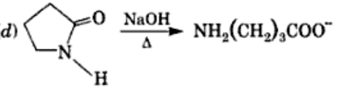
(c)


(d)


Solution: (a)


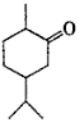
(b)


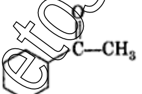
(c)


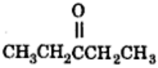
(d)


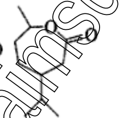
Problem 19.4:

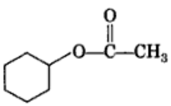
Write the structure of the products of the following ketones in the Baeyer-Villiger oxidation.

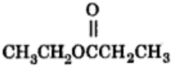
(a)


(b)


(c)

$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$

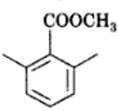
Solution: (a)


(b)


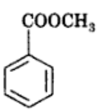
(c)

$CH_3CH_2O\overset{O}{\overset{\|}{C}}CH_2CH_3$

Problem 19.5:

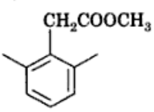
Rank the following esters in order of facile hydrolysis. Explain.



A

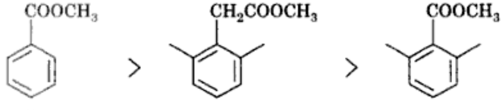


B



C

Solution:

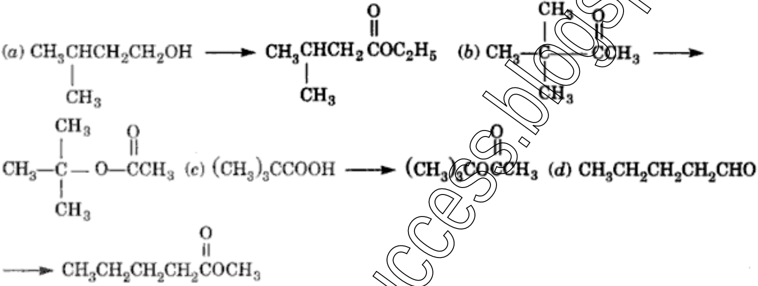


B C A

The reason is steric hindrance to hydrolysis by the *ortho* methyl groups. **C is more reactive** than A because of the presence of a methylene group **which reduces steric effect.**

Problem 19.6:

Suggest methods for the following conversions:



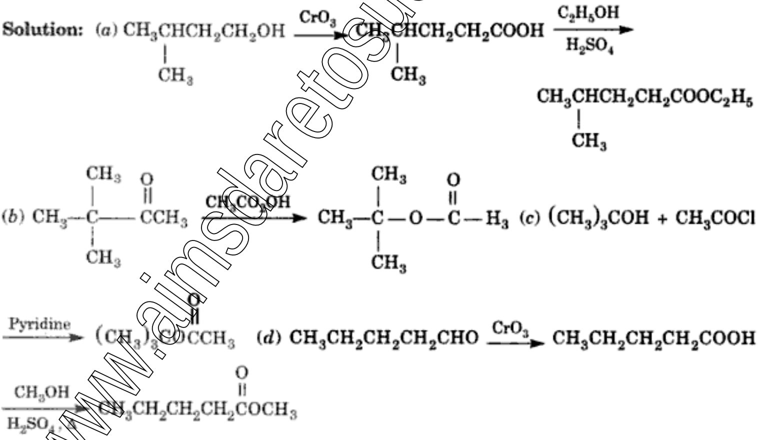
(a) $CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2OH \longrightarrow CH_3\underset{CH_3}{\underset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}OC_2H_5$

(b) $CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-O-\overset{O}{\overset{\|}{C}}CH_3$

(c) $(CH_3)_3CCOOH \longrightarrow (CH_3)_3CO\overset{O}{\overset{\|}{C}}CH_3$

(d) $CH_3CH_2CH_2CH_2CHO \longrightarrow CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3$

Solution:



(a) $CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2OH \xrightarrow{CrO_3} CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2COOH \xrightarrow[H_2SO_4]{C_2H_5OH} CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2COOC_2H_5$

(b) $CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{CH_3CO_3H} CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-O-\overset{O}{\overset{\|}{C}}-H_3$

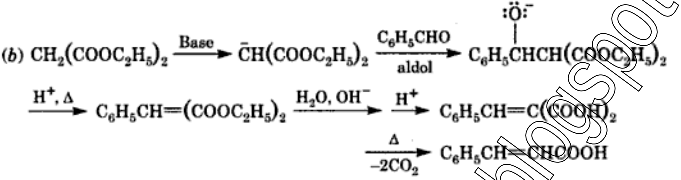
(c) $(CH_3)_3COH + CH_3COCl \xrightarrow{Pyridine} (CH_3)_3CO\overset{O}{\overset{\|}{C}}CH_3$

(d) $CH_3CH_2CH_2CH_2CHO \xrightarrow{CrO_3} CH_3CH_2CH_2CH_2COOH \xrightarrow[H_2SO_4,\,\Delta]{CH_3OH} CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3$

Solution: (*a*) $CH_2(COOC_2H_5)_2 \xrightarrow{\text{Base}} \bar{C}H(COOC_2H_5)_2 \xrightarrow{(CH_3)_2CHCH_2Br}$

$$(CH_3)_2CHCH_2CH(COOC_2H_5)_2 \xrightarrow{H_2O,\ OH^-} \xrightarrow{H^+} (CH_3)_2CHCH_2CH(COOH)_2$$

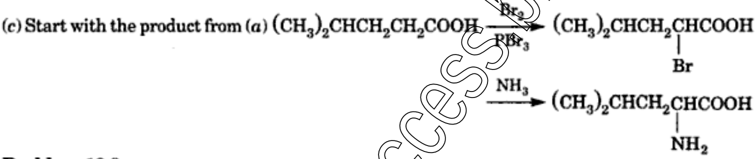
$$\xrightarrow[-CO_2]{\Delta} \underset{\textbf{Isocaproic acid}}{(CH_3)_2CHCH_2CHCOOH}$$



(*b*) $CH_2(COOC_2H_5)_2 \xrightarrow{\text{Base}} \bar{C}H(COOC_2H_5)_2 \xrightarrow[\text{aldol}]{C_6H_5CHO} C_6H_5\overset{:\ddot{O}:^-}{C}HCH(COOC_2H_5)_2$

$$\xrightarrow{H^+,\ \Delta} C_6H_5CH{=}(COOC_2H_5)_2 \xrightarrow{H_2O,\ OH^-} \xrightarrow{H^+} C_6H_5CH{=}C(COOH)_2$$

$$\xrightarrow[-2CO_2]{\Delta} C_6H_5CH{=}CHCOOH$$



(*c*) Start with the product from (*a*) $(CH_3)_2CHCH_2CH_2COOH \xrightarrow[PBr_3]{Br_2} (CH_3)_2CHCH_2\underset{Br}{C}HCOOH$

$$\xrightarrow{NH_3} (CH_3)_2CHCH_2\underset{NH_2}{C}HCOOH$$

Problem 19.9:

Indicate the product or products of the reaction (if any) of propanenitrile with the following:

(*a*) $LiAlH_4$ in ether, then water (*b*) CH_3OH, H^+ (*c*) 2H, Ni (*d*) C_6H_5MgBr and H^+ (*e*) $NaBH_4$ and H_2O (*f*) Alc. NaOH, followed by acidification.

Solution: (*a*) $CH_3CH_2CH_2NH_2$ (*b*) $CH_3CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$ (*c*) $CH_3CH_2CH_2NH_2$ (*d*) $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$ (*e*) No reaction (*f*) $CH_3CH_2COOH + NH_4^+$

Problem 19.10:

Write short notes on the following:

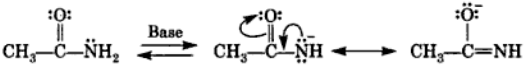
Esterification of an acid, waxes, synthetic detergents, acidity of amide group, saponification and Rosenmund reduction.

Solution: Esterification of an acid. The formation of an ester from a carboxylic acid using an alcohol and acid catalyst is called *esterification*.

Waxes. *Waxes* are esters of long chain fatty acids with long chain alcohols. They occur in nature.

Synthetic Detergents. *Detergents* are the sodium salts of sulfonic acids. They also possess the same structural features as soaps.

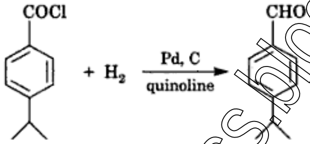
Acidity of Amides. The N—H bond of an amide is acidic. The resulting anion is stabilized by resonance similar to an enolate anion. An amide is as acidic as the O—H hydrogen of an alcohol.



Acyl Group. The $R-\overset{O}{\overset{\|}{C}}-$ group (*i.e.* C═O with an alkyl or aryl group as one of the substituents is called an *acyl group*.

Saponification. The basic hydrolysis of an ester to an alcohol and the corresponding carboxylate ion is termed *saponification*.

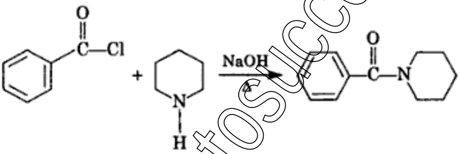
Rosenmund Reduction. The reduction of an acid chloride to an aldehyde by hydrogenation using a poisoned palladium catalyst.



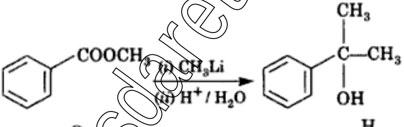
Problem 19.11:

Write a mechanism for each of the following reactions:

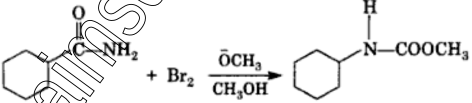
(*a*)



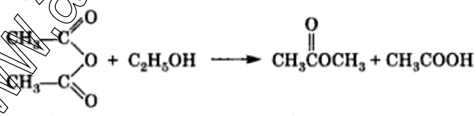
(*b*)



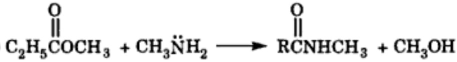
(*c*)



(*d*)

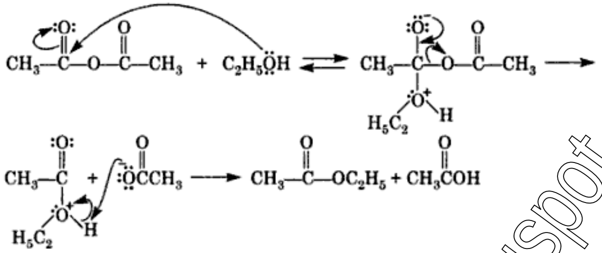


(*e*)

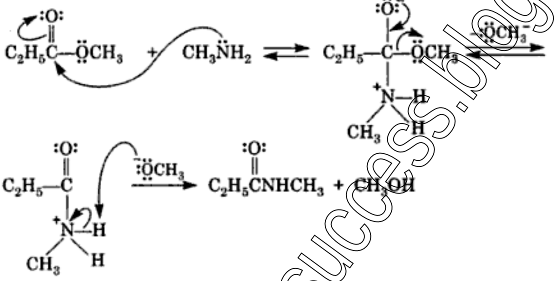


$$C_2H_5\overset{O}{\overset{\|}{C}}OCH_3 + CH_3\ddot{N}H_2 \longrightarrow R\overset{O}{\overset{\|}{C}}NHCH_3 + CH_3OH$$

(*d*)



(*e*)

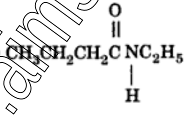


Problem 19.12:

Write a structural formula for each of the following compounds:

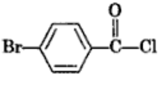
(*a*) N-Ethylbutanamide (*b*) *p*-Bromobenzoyl chloride (*c*) Propionic anhydride (*d*) *n*-Hexyl hexanoate (*e*) 2, 3-Dimethyl succinimide (*f*) *m*-Cyanotoluene (*g*) Cyclohexane carboxamide (*h*) Ethyl butyrate (*i*) Isopropyl butyrate (*j*) α-Bromopropionitrile (*k*) 2-Naphthyl hexanoate (*l*) 2-Isopropyl heptanenitrile (*m*) Cyclopentanecarbonitrile (*n*) Isobutyric acetic anhydride (*o*) Ethyl-2-(4-methylcyclohexyl) propionate (*p*) Cyclopropanecarboxylic acid chloride (*q*) N-Phenylcyclopentane carboxamide (*r*) 9-Hydroxynonanoic acid lactone (*s*) 4-Methyl phalic anhydride.

Solution: (*a*)

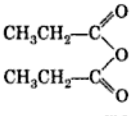


$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}\underset{\underset{H}{|}}{N}C_2H_5$

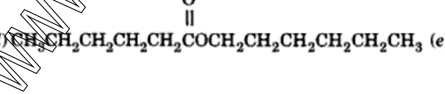
(*b*)



(*c*)

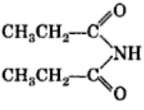


(*d*)

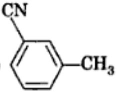


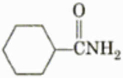
$CH_3CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_2CH_2CH_2CH_2CH_3$

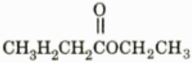
(*e*)



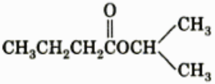
(*f*)



(*g*) 

(*h*) 

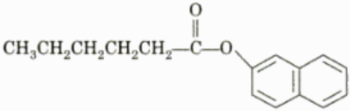
$CH_3H_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$

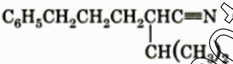
(*i*) 

$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OCH(CH_3)_2$

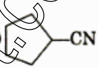
(*j*) 

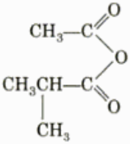
$CH_3\underset{Br}{\underset{|}{C}}HCN$

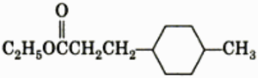
(*k*) 

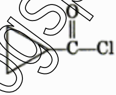
(*l*) 

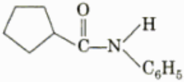
$C_6H_5CH_2CH_2CH_2\underset{CH(CH_3)_2}{\underset{|}{C}}HC{\equiv}N$

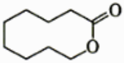
(*m*) 

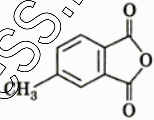
(*n*) 

(*o*) 

(*p*) 

(*q*) 

(*r*) 

(*s*) 

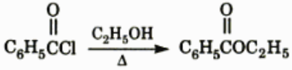
Problem 19.13:

Show how each of the following conversion could be accomplished ?

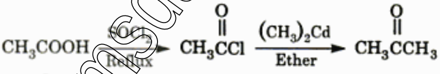
(*a*) Acetyl chloride to acetic anhydride (*b*) Benzoyl chloride to ethyl benzoate (*c*) Acetic acid to acetone (*d*) Ethyl acetate to 3-methyl-3-pentanol (*e*) Trimethylacetic acid to *t*-butyl isocyanate (*f*) Ethyl propionate to propionitrile (*g*) Propionitrile to ethylamine

Solution: (*a*) 

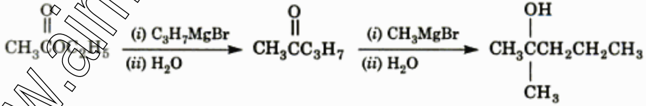
$CH_3\overset{O}{\overset{\|}{C}}Cl \xrightarrow[\Delta]{CH_3COO^- Na^+} (CH_3CO)_2O$

(*b*) 

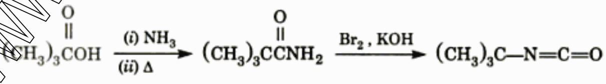
$C_6H_5\overset{O}{\overset{\|}{C}}Cl \xrightarrow[\Delta]{C_2H_5OH} C_6H_5\overset{O}{\overset{\|}{C}}OC_2H_5$

(*c*) 

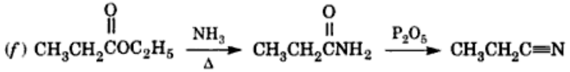
$CH_3COOH \xrightarrow[\text{Reflux}]{SOCl_2} CH_3\overset{O}{\overset{\|}{C}}Cl \xrightarrow[\text{Ether}]{(CH_3)_2Cd} CH_3\overset{O}{\overset{\|}{C}}CH_3$

(*d*) 

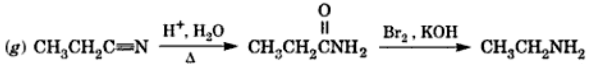
$CH_3\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow[(ii)\ H_2O]{(i)\ C_3H_7MgBr} CH_3\overset{O}{\overset{\|}{C}}C_3H_7 \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} CH_3\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}CH_2CH_2CH_3$

(*e*) 

$(CH_3)_3\overset{O}{\overset{\|}{C}}OH \xrightarrow[(ii)\ \Delta]{(i)\ NH_3} (CH_3)_3\overset{O}{\overset{\|}{C}}CNH_2 \xrightarrow{Br_2,\ KOH} (CH_3)_3C{-}N{=}C{=}O$



$$(f)\ CH_3CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow[\Delta]{NH_3} CH_3CH_2\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{P_2O_5} CH_3CH_2C{\equiv}N$$

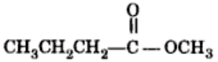


$$(g)\ CH_3CH_2C{\equiv}N \xrightarrow[\Delta]{H^+,\ H_2O} CH_3CH_2\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{Br_2\ ,\ KOH} CH_3CH_2NH_2$$

Problem 19.14:

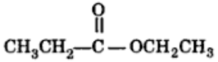
Write the structural formulas for all the esters of the formula $C_5H_{10}O_2$. Write their IUPAC names also.

Solution:



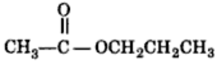
$$CH_3CH_2CH_2{-}\overset{O}{\overset{\|}{C}}{-}OCH_3$$

Methyl butanoate



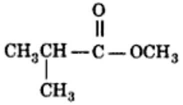
$$CH_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}OCH_2CH_3$$

Ethyl propanoate



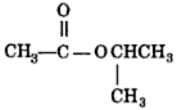
$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}OCH_2CH_2CH_3$$

Propyl ethanoate



$$CH_3\underset{CH_3}{\underset{|}{C}}H{-}\overset{O}{\overset{\|}{C}}{-}OCH_3$$

Methyl 2-methylpropanoate



$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}O\underset{CH_3}{\underset{|}{C}}HCH_3$$

Isopropyl ethanoate

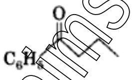
Problem 19.15:

Write the produts of butanoyl chloride with the following reagents.

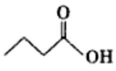
(*a*) Benzene + $AlCl_3$ (*b*) Water (*c*) Isopropyl alcohol (*d*) Aniline

(*e*) Dimethylamine (*f*) Sodium acetate and heat (*g*) Trimethylamine

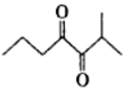
Solution: (*a*)



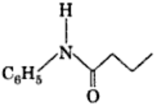
(*b*)



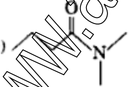
(*c*)



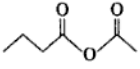
(*d*)



(*e*)



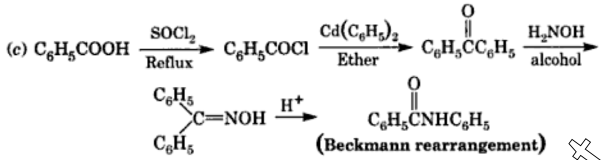
(*f*)



(*g*) No reaction.

Problem 19.16:

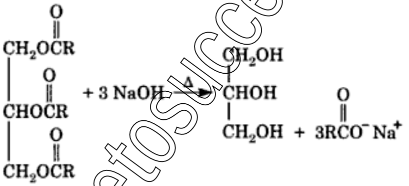
An ester $C_6H_{12}O_2$ was hydrolyzed on heating with water to give an acid, A, and an alcohol B. Oxidation of B, with chromic acid produced A. What is the structure of the original ester? Write equations for all the reactions.



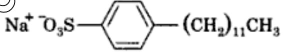
Problem 19.22:

What are vegetable oils and how do they differ from mineral oils? Starting with a suitable mixture of oils, give a detailed account for the manufacture of soap? Write a short note on synthetic detergents. What are surfactants? Are soaps and detergents classified as surfactants? What is a micelle ?

Solution: The most important of natural esters are the animals and vegetable oils. These are esters of glycerol with long chain fatty acids. The vegetable oils in particular are liquids and contain unsaturated fatty acids such as soyabean oil, peanut oil, corn oil and coconut oil. Their principal use is as food. They are transformed to solid fats by hydrogenation. The mineral oils are obtained from petroleum and consist of a mixture of saturated and unsaturated hydrocarbons such as kerosene oil and petrol. These are insoluble in water and are non-edible. For the preparation of soap, a fat is boiled with sodium hydroxide in an iron vessel till saponification is complete.



The mixture is treated with sodium chloride and precipitated soap is separated. Synthetic detergents are closely related to soaps. They possess same structural features as soaps, *viz.*, anionic group and a long chain organic group. Among the most important detergents are the sodium salts of sulfonic acid. The following compound is widely used as a laundry detergents.



Detergents can be used even in hard water as they do not form the insoluble white precipitates. *Surfactants* are molecules with two structural parts that interact with ester in opposing ways. Soaps and detergents are classified as surfactants. Surfactants in aqueous solution form micelles of spherical aggregates of 50-150 surfactant molecules.

Problem 19.23:

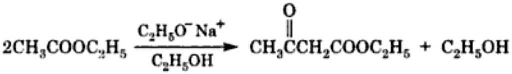
(*a*) Briefly state how ethyl acetoacetate is prepared.

(*b*) How will you prove the existence of the keto and enol forms in the ester solution?

(*c*) Making use of the ester show how can you prepare:

(*i*) succinic acid (*ii*) isobutyric acid (*iii*) methyl ethyl ketone.

Solution: (*a*) Ethyl acetoacetate may be prepared by treatment of two molecules of ethyl acetate with sodium ethoxide as catalyst *via* the Claisen condensation.



$$2CH_3COOC_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5O^-Na^+} CH_3\overset{O}{\overset{\|}{C}}CH_2COOC_2H_5 + C_2H_5OH$$

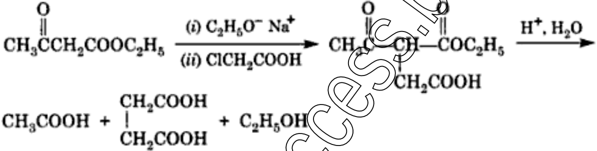
(*b*) Acetoacetic ester exists in solution as a mixture of two forms–a ketonic and an enolic:

$$CH_3\overset{O}{\overset{\|}{C}}CH_2COOC_2H_5 \qquad CH_3\overset{OH}{\overset{|}{C}}{=}CHCOOC_2H_5$$

The change of one form of acetoacetic ester into the other is termed as a tautomeric change.

Their separate existence in solution can be proved by *p.m.r.* spectroscopy which distinguishes between keto and enol tautomers. Furthermore, the enolic form of ethyl acetoacetic ester reacts rapidly with bromine water but the keto form is relatively unreactive. The enolic form of ethyl acetoacetate is lower boiling than the keto form.

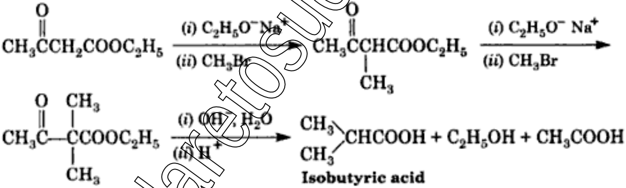
(*c*) (*i*)



$$CH_3\overset{O}{\overset{\|}{C}}CH_2COOC_2H_5 \xrightarrow[(ii)\ ClCH_2COOH]{(i)\ C_2H_5O^-\ Na^+} CH_3\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_2COOH}{|}}{CH}-\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow{H^+,\ H_2O}$$

$$CH_3COOH + \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} + C_2H_5OH$$

(*ii*)

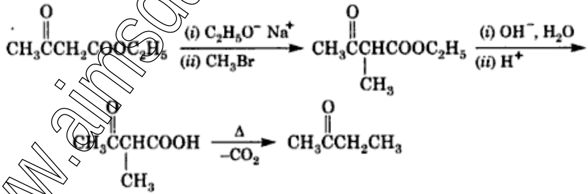


$$CH_3\overset{O}{\overset{\|}{C}}CH_2COOC_2H_5 \xrightarrow[(ii)\ CH_3Br]{(i)\ C_2H_5O^-Na^+} CH_3\overset{O}{\overset{\|}{C}}\underset{\underset{CH_3}{|}}{C}HCOOC_2H_5 \xrightarrow[(ii)\ CH_3Br]{(i)\ C_2H_5O^-\ Na^+}$$

$$CH_3\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}COOC_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ OH^-,\ H_2O} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHCOOH + C_2H_5OH + CH_3COOH$$

Isobutyric acid

(*iii*)



$$CH_3\overset{O}{\overset{\|}{C}}CH_2COOC_2H_5 \xrightarrow[(ii)\ CH_3Br]{(i)\ C_2H_5O^-\ Na^+} CH_3\overset{O}{\overset{\|}{C}}\underset{\underset{CH_3}{|}}{C}HCOOC_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ OH^-,\ H_2O}$$

$$CH_3\overset{O}{\overset{\|}{C}}\underset{\underset{CH_3}{|}}{C}HCOOH \xrightarrow[-CO_2]{\Delta} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$$

Problem 19.24:

(*a*) What is "*active methylene*" group? Explain.

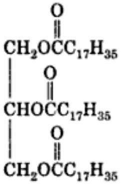
(*b*) How will you prepare:

(*i*) Adipic acid from malonic ester (*ii*) Crotonic acid from acetoacetic ester?

Problem 19.27:

What are fats and oils? What is the importance of hydrogenation and hydrolysis of fats and oils? Explain with example.

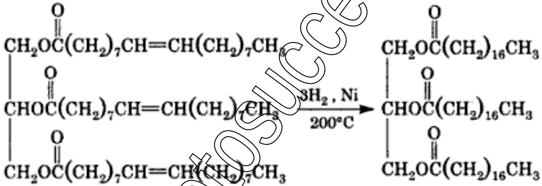
Solution: Fats and oils are the esters of glycerol (1, 2, 3-propanetriol) with long chain fatty acids. The esters from stearic acid and glycerol has the following structure



$$\begin{array}{l} CH_2O\overset{O}{\overset{\parallel}{C}}C_{17}H_{35} \\ | \\ CHO\overset{O}{\overset{\parallel}{C}}C_{17}H_{35} \\ | \\ CH_2O\overset{O}{\overset{\parallel}{C}}C_{17}H_{35} \end{array}$$

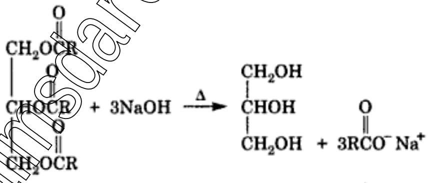
Glycerol tristearate (or Tristearin)

Hydrogenation of oils and fats is necessary in many ways. For example, vegetable oils possess colors and odor and they become viscous and black on keeping. Furthermore food cooked in oils emits odor after it is left for a few days. These drawbacks are not found in hardened oils. Triolein is converted to tristearin by hydrogenation.



$$\begin{array}{l} CH_2O\overset{O}{\overset{\parallel}{C}}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ | \\ CHO\overset{O}{\overset{\parallel}{C}}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ | \\ CH_2O\overset{O}{\overset{\parallel}{C}}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \end{array} \xrightarrow[200°C]{3H_2,\ Ni} \begin{array}{l} CH_2O\overset{O}{\overset{\parallel}{C}}(CH_2)_{16}CH_3 \\ | \\ CHO\overset{O}{\overset{\parallel}{C}}(CH_2)_{16}CH_3 \\ | \\ CH_2O\overset{O}{\overset{\parallel}{C}}(CH_2)_{16}CH_3 \end{array}$$

Hydrolysis of a fat by sodium hydroxide yields a soap.



$$\begin{array}{l} CH_2O\overset{O}{\overset{\parallel}{C}}R \\ | \\ CHO\overset{O}{\overset{\parallel}{C}}R \\ | \\ CH_2O\overset{O}{\overset{\parallel}{C}}R \end{array} + 3NaOH \xrightarrow{\Delta} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3R\overset{O}{\overset{\parallel}{C}}O^- Na^+$$

A fat Soap

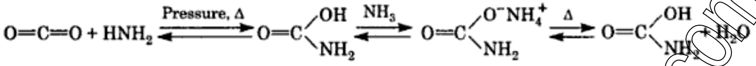
Problem 19.28:

(*a*) What is the natural source of urea? How is it synthesized? What are its important uses?

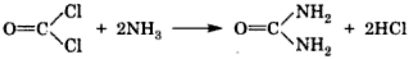
(*b*) Explain what happens when urea is:

(*i*) heated alone (*ii*) treated with alkaline hypobromite solution (*iii*) treated with malonic ester (*iv*) treated with ice-cold nitrous acid (*v*) treated with hydrazine.

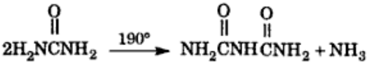
Solution: (*a*) The natural source of urea is urine. On commercial scale urea is prepared by heating a mixture of ammonia and carbon dioxide under pressure.



A laboratory preparation of urea requires the reaction between phosgene ($COCl_2$) and NH_3.

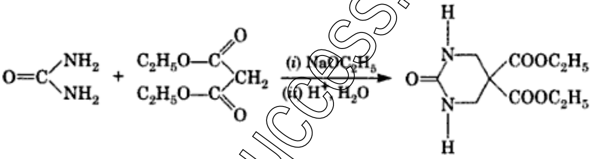


Urea is used as fertilizer, in the preparation of barbiturates and in the formation of urea-formaldehyde resin.

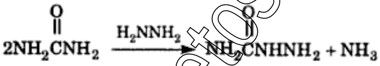
(*b*) (*i*) 

$$2H_2N\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{190°} NH_2\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}NH_2 + NH_3$$

(*ii*) $NH_2CONH_2 + 3NaOBr \longrightarrow 3NaBr + 2H_2O + CO_2 + N_2$

(*iii*) 

(*iv*) $H_2NCONH_2 + 2HNO_2 \longrightarrow 3H_2O + 2N_2 + CO_2$

(*v*) 

$$2NH_2\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{H_2NNH_2} NH_2\overset{O}{\overset{\|}{C}}NHNH_2 + NH_3$$

Problem 19.29:

Calculate the saponification number of tristearin of 90% purity.

Solution: Mol. weight of tristearin = 890

According to the hydrolysis reaction, 3 moles of KOH (3 × 56 = 168) are required for complete saponification.

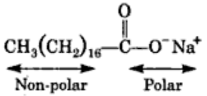
$$\text{Saponification No.} = \frac{168}{890} \times 100 = 188.7$$

$$\text{Saponification No. of 90\% purity} = \frac{188.7}{100} \times 90 = 170$$

Problem 19.30:

Discuss the cleaning action of soap.

Solution: Cleaning Action of Soap. The mechanism of the cleaning action of soap is related to its chemical structure. A soap molecule consists of two parts, mainly a polar, salt-like carboxylate function and a non-polar, long alkyl chain.



$CH_3(CH_2)_{16}-\overset{\overset{O}{\|}}{C}-O^-Na^+$

The polar part is hydrophilic (water soluble) whereas the non-polar portion is hydrophobic (water insoluble or oil soluble). A typical soap molecule sodium stearate has both an oil soluble and water soluble portions. A sodium salt of a smaller carboxylic acid is soluble in water but if this hydrocarbon residue is long then the hydrocarbon portion causes the soap to become insoluble.

There are several theories to explain the cleaning action of soap. Soap greatly reduces the surface tension of water. Thus soap is able to enter into tiny cracks and crevices. Soap also has the ability to emulsify fats and oils and thus greatly assists in their removal.

According to another theory the charged carboxyl group at the end of the soap chain enables it to dissolve in water. When soap dissolves, it does so in the form of spherical clusters called *micelles*. The non-polar hydrocarbon chain mixes well with the greasy substances.

When soap water comes in contact with grease, the non-polar chain dissolves grease which is also non-polar. This leaves the grease surrounded by an outer layer of groups which are attached towards water. The forces between water and grease are much increased so that the latter is lifted off the surface of water in the form of small globules and can be washed away. The layer of negatively charged groups causes the globules to repel one another so that they do not coagulate and redeposit on the surface of the cloth.

Problem 19.31:

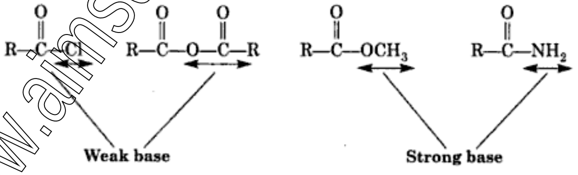
The acetoacetic ester synthesis gives best yields when primary alkyl halides are used for alkylation, secondary give low yield while tertiary halides practically give no alkylation product. Explain.

Solution: Reactivity is similar to any S_N2 displacement reaction, with primary alkyl halides substitution is highly favorable. With secondary halides, elimination competes with substitution. However, elimination is the exclusive course with tertiary halides.

Problem 19.32:

Why are acid chlorides and anhydrides more reactive in hydrolysis than esters or amides?

Solution: The chlorides and carboxylate ions are weaker bases than the methoxide and amide ions. The former are thus good leaving groups.



Problem 19.33:

Arrange the following compounds in increasing ease of hydrolysis:

$$CH_3COOC_2H_5\ ,\ (CH_3CO)_2O,\ CH_3CONH_2\ ,\ CH_3COCl$$

Solution: $CH_3CONH_2 < CH_3COOC_2H_5 < (CH_3CO)_2O < CH_3COCl$

Hydrolysis parallels the ease of the leaving group.

Problem 19.34:

Which is a stronger acid? Why?

(*a*) Formic acid or acetic acid (*b*) Benzoic acid or an aliphatic acid.

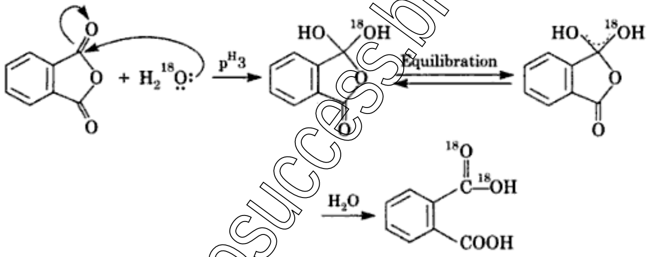
Solution: (*a*) Formic acid is stronger than acetic acid. In acetic acid the $-CH_3$ group donates electrons and unstabilizes the acetate ion.

(*b*) Benzoic acid is stronger than an aliphatic acid because the phenyl group inductively stabilizes the benzoate ion, by electron withdrawl.

Problem 19.35:

Hydrolysis of phthalic anhydride in $H_2{}^{18}O$ at pH = 3 gives phthalic acid. Show the distribution of labelled oxygen in the product.

Solution:

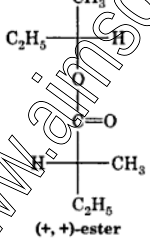


In the product there is an equivalent labelling in the carboxyl group.

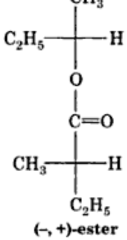
Problem 19.36:

A racemic mixture of (±)-2-phenylpropionic acid on esterification with (+)-2-butanol gives two esters. Write the correct stereochemistry of the esters.

Solution:



(+, +)-ester



(–, +)-ester

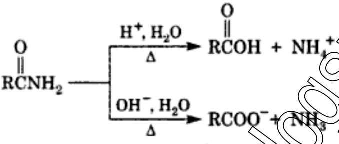
This is a technique for the resolution of isomers. The racemic mixture is combined, with an enantiomerically pure chiral compound (2-butanol) called a resolving agent. This results in the formation of diastereoisomers which have different properties.

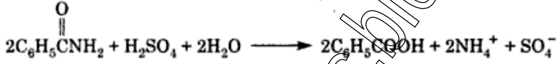
Problem 19.37:

Write a suitable mechanism for each of the following reactions:

(*a*) Acid hydrolysis of an amide (*b*) Hofmann rearrangement (*c*) Esterification of a carboxylic acid (*d*) The Baeyer–Villiger oxidation (*e*) Hydrolysis of an ester in the presence of an acid and a base (*f*) Claisen condensation.

Solution: (*a*) An amides may be hydrolyzed in the presence of either an acid or a base leading to the formation of the parent acid.



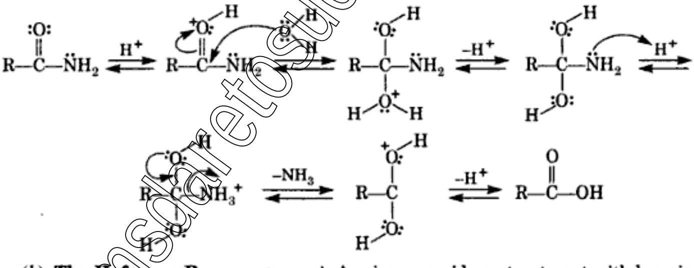


$$2C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}NH_2 + H_2SO_4 + 2H_2O \longrightarrow 2C_6H_5COOH + 2NH_4^+ + SO_4^-$$

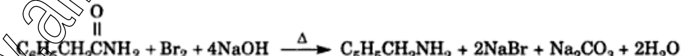
Mechanism

Acid hydrolysis:

For the acid hydrolysis of an amide the oxygen atom is protonated in contrast to the nitrogen atom because the former is more electronegative and also yields the most stable conjugate acid. Water acts as a nucleophile and ammonia is the leaving group.



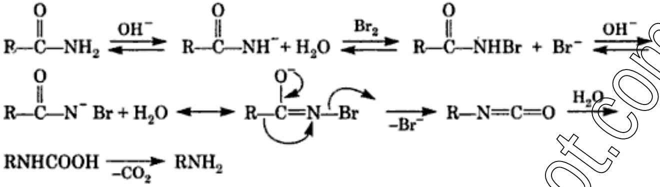
(*b*) **The Hofmann Rearrangement.** A primary amide on treatment with bromine in the presence of aqueous base forms an amine. The reaction is called the *Hofmann rearrangement*.



$$C_6H_5CH_2\overset{\overset{\displaystyle O}{\|}}{C}NH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} C_5H_5CH_2NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

Phenylacetamide

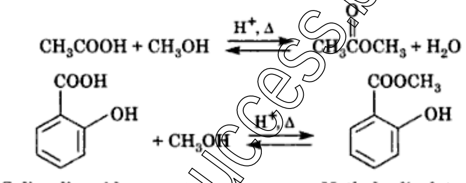
Mechanism. The first two steps are the base-catalyzed bromination of the amide. The N-bromamide is more acidic than the starting amide and forms the corresponding anion which is stabilized by resonance. A migration of the alkyl group takes place to nitrogen with the simultaneous expulsion of the bromide ion. This results in an isocynate intermediate. This is hydrolyzed to carbamic acid which is easily decarboxylated to an amine.



$$RNHCOOH \xrightarrow[-CO_2]{} RNH_2$$

The resulting amine has one carbon atom less than the amide. Acetamide undergoes this reaction but formamide does not.

(*c*) **Esterification of Carboxylic Acids.** A direct reaction between a carboxylic acid and an alcohol under the catalytic effect of sulfuric acid on heating yields an ester. This is a reversible reaction and is known as the *Fischer esterification*. No ester formation takes place unless the mixture is heated.

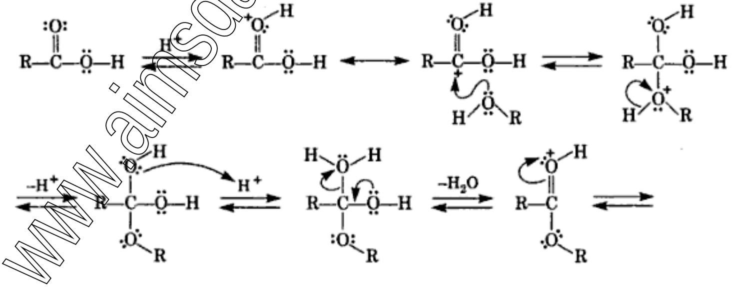


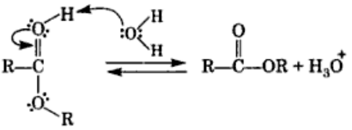
$$CH_3COOH + CH_3OH \underset{}{\overset{H^+,\Delta}{\rightleftharpoons}} CH_3COOCH_3 + H_2O$$

Salicyclic acid **Methyl salicylate**

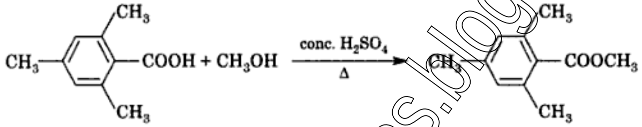
The disadvantage of this method is that the equilibrium is reached slowly and yield of the ester is often low.

Mechanism. A preliminary equilibrium protonation of the oxygen of the carbonyl takes place followed by the nucleophilic attack of an alcohol molecule to form a tetrahedral intermediate. Then a proton transfer and loss of a water molecule forms an intermediate which loses a proton and yields the ester.



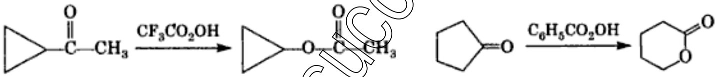


A secondary alcohol may be used similarly, a tertiary alcohol dehydrates readily in the presence of a mineral acid whereas phenols react very slowly. To prepare an ester from a tertiary alcohol or a phenol, the acid chloride is refluxed with alcohol along with an organic base, usually N, N-dimethylaniline. Sterically hindered acids require more drastic conditions for esterification. Mesitoic acid is esterified with CH_3OH in the presence of conc. sulfuric acid.

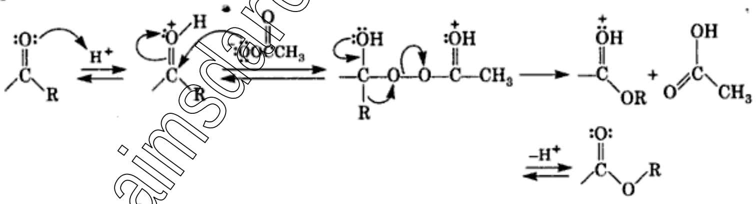


Mesitoic acid **Methyl mesitoate**

(*d*) **The Baeyer-Villiger Reaction.** Treatment a ketone with a peroxy acid affords an ester. This is called the *Baeyer–Villiger reaction.* This is represented by the following examples.



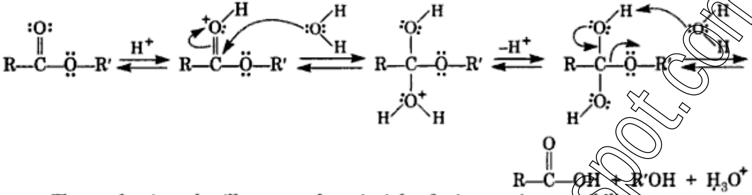
Mechanism. An acid catalyzed attack by the peroxy acid on the ketone carbonyl group yields an addition intermediate. This undergoes an ionic cleavage of the oxygen-oxygen bond. Simultaneously a 1, 2-alkyl shift from carbon to oxygen occurs which yields the ester after proton transfer.



Expansion of the ring takes place in the Beyer-Villiger oxidation, in the case of cyclic ketones.

(*e*) Hydrolysis of Esters

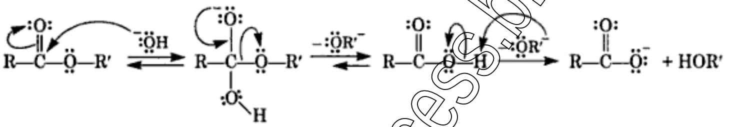
Acid hydrolysis



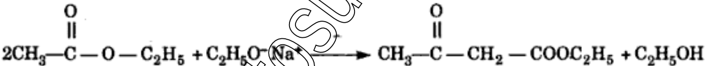
The mechanism also illustrates the principle of microscopic reversibility.

Base hydrolysis

The hydrolysis may also be accomplished with an aqueous base and the process is known as *saponification* (Latin, *sapon*, soap). The mechanism involves the following sequence reactions:

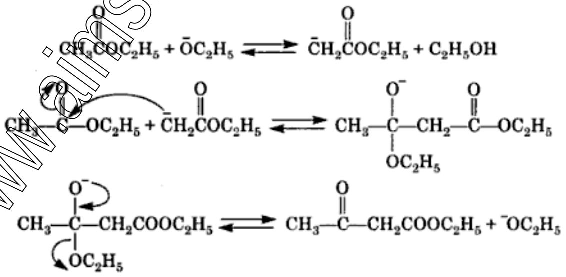


(*f*) **Acetoacetic.** Acetoacetic ester or ethyl acetoacetate is obtained by the self-condensation of ethyl acetate in the presence of excess sodium ethoxide. The process is known as the *Claisen ester condensation.*



$$2CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5+C_2H_5O^-Na^+\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOC_2H_5+C_2H_5OH$$

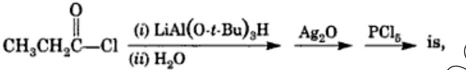
Mechanism. The mechanism is similar to the aldol condensation. Ethoxide ion being a strong base abstracts a proton from the ester molecule to form a resonance stabilized enolate anion. This ion makes a nucleophilic attack subsequently on the carbonyl carbon of a second molecule of the ester. Then a subsequent ejection of the ethoxide ion leads to the product. Acetoacetic ester is converted to its enolate ion in the presence of excess base. The ester is obtained by acidification.



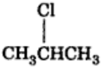
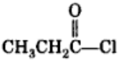
(*d*) Which of the following cannot undergo Claisen condensation?

A. $C_6H_5CH_2COOC_2H_5$ B. $C_6H_{11}CH_2COOC_2H_5$ C. $CH_3(CH_2)_3COOC_2H_5$
D. $C_6H_5COOC_2H_5$

(*e*) The end product in the following sequence of reactions



$$CH_3CH_2\overset{O}{\overset{\|}{C}}—Cl \xrightarrow[(ii)\ H_2O]{(i)\ LiAl(O\text{-}t\text{-}Bu)_3H} \xrightarrow{Ag_2O} \xrightarrow{PCl_5} \text{is,}$$

A. $CH_3CH_2CH_2Cl$ B.  $CH_3\overset{Cl}{\overset{|}{C}}HCH_3$ C.  $CH_3CH_2\overset{O}{\overset{\|}{C}}—Cl$ D.  $CH_3\overset{O}{\overset{\|}{C}}CH_3$

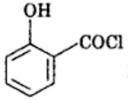
(*f*) Which of the following ester is obtained by esterification of propan-2-ol with propanoic acid ?

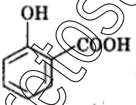
A. $CH_3CH_2COOCH(CH_3)_2$ B. $(CH_3)_2CHCOOCH_3$ C. $CH_3COOCH_2CH_3$
D. $(CH_3)_2CHCOOCH_2CH_3$

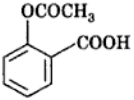
(*g*) Reaction of ethyl formate with excess CH_3MgBr followed by hydrolysis gives
A. Ethanal B. Isopropyl alcohol C. Propanal D. *n*-Propyl alcohol

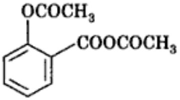
(*h*) Identify Z in the reactions

$$C_6H_6 \xrightarrow[\Delta]{H_2SO_4} W \xrightarrow[(ii)\ H^+]{(i)\ NaOH\ fusion} X \xrightarrow[(ii)\ H^+]{(i)\ CO_2\ ,\ KOH} Y \xrightarrow{CH_3COCl} Z$$

A. 

B. 

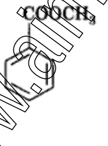
C. 

D. 

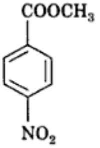
(*i*) The following reaction takes place $CH_3COOH + C_2H_5OH \xrightarrow{?} CH_3COOC_2H_5 + H_2O$ in the presence of

A. Heat and acid B. Heat alone C. Acid alone D. Base alone

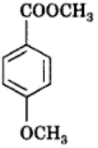
(*j*) The correct decreasing order of alkaline hydrolysis is:



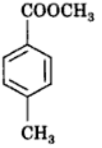
I



II



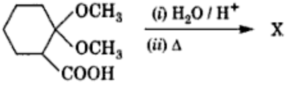
III

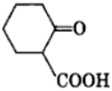
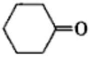
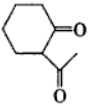
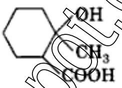


IV

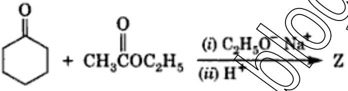
A. I > II > III > IV B. III > I > IV > II C. II > III > I > IV
D. II > I > III > IV

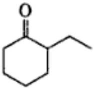
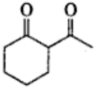
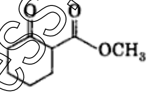
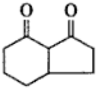
(*k*) Identify X in the following reaction:



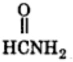
A. 
B. 
C. 
D. 

(*l*) Assign correct structure to Z in the following reaction:

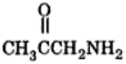


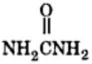
A. 
B. 
C. 
D. 

(*m*) Which of the following will give the Hoffmann reaction?

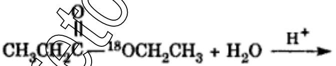
A. 
$HC(=O)NH_2$

B. 
$CH_3C(=O)NH_2$

C. 
$CH_3C(=O)CH_2NH_2$

D. 
$NH_2C(=O)NH_2$

(*n*) In the following hydrolysis reaction:

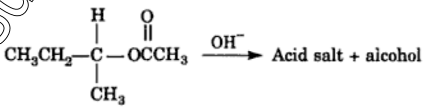


$$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}^{18}OCH_2CH_3 + H_2O \xrightarrow{H^+}$$

The ^{18}O is contained in

A. CH_3CH_2OH B. CH_3CH_2COOH C. Both A and B D. H_2O

(*o*) Select the correct statement in the hydrolysis of the following chiral ester:

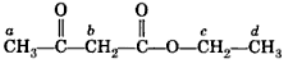


$$CH_3CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}O\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \xrightarrow{OH^-} \text{Acid salt + alcohol}$$

A. Configuration is retained about C B. Configuration is inverted about C

C. Configuration is lost about C D. None of the above is correct

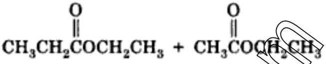
(*p*) In the following compound, the most acidic hydrogen is



$$\overset{a}{CH_3}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{b}{CH_2}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\overset{c}{CH_2}{-}\overset{d}{CH_3}$$

A. *a* B. *b* C. *c* D. *d*

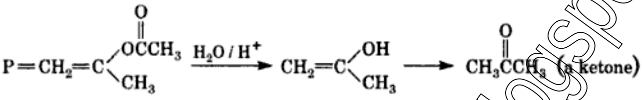
(*q*) In the following claisen condensation,



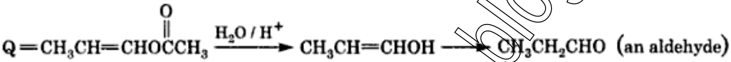
$CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3 + CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3 \xrightarrow[C_2H_5OH]{C_2H_5O^- Na^+}$ the number of products obtained would be :

A. 1 B. 2 C. 3 D. 4

Solution: (*a*) B, a secondary amine is most basic (*b*) C (*c*) C



$P = CH_2{=}C(OCOCH_3)CH_3 \xrightarrow{H_2O / H^+} CH_2{=}C(OH)CH_3 \longrightarrow CH_3COCH_3$ (a ketone)

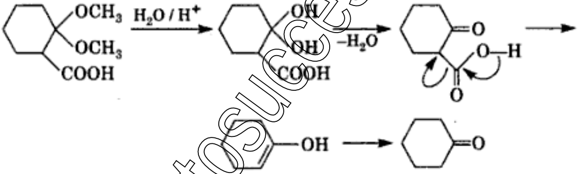


$Q = CH_3CH{=}CHOCOCH_3 \xrightarrow{H_2O / H^+} CH_3CH{=}CHOH \longrightarrow CH_3CH_2CHO$ (an aldehyde)

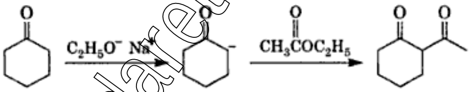
(*d*) D, contains no α-hydrogen (*e*) C (*f*) A (*g*) B (*h*) C (*i*) A

(*j*) D, *p*-NO_2 group is a strong electron-withdrawing group and facilitates hydrolysis.

(*k*) B,



(*l*) B,



(*m*) B (*n*) A, During hydrolysis an acyl-oxygen fission of the ester takes place.

(*o*) A, Acyl-oxygen fission. (*p*) B, flanked by two carbonyl groups. (*q*) D, One product each from self-condensation. Two products from cross-condensation as each ester contains an α-H atom.

Problem 19.42:

An aromatic compound contains 69.4% C, 5.8% H. A sample of 0.303 g of this compound was analyzed for nitrogen by Kjeldahl's method. The ammonia gas evolved was absorbed in 50 ml of 0.05 M H_2SO_4. The excess acid required 25 ml of 0.1 M NaOH solution for neutralization. Deduce the molecular formula of the compound if the molecular weight is 121. Draw a structure for its isomer also.

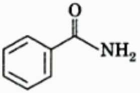
Solution: Percentage of N = $\frac{1.4 \times 0.1 \times (50 - 25)}{0.303}$ = 11.55%

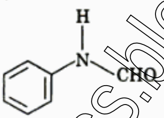
Empirical Formula

Element	*Percentage Composition*	*Atomic Weight*	*Relative number of atoms*	*Simplest ratio*
C	69.4	12	5.78	7
H	5.8	1	5.8	7
N	11.55	14	0.82	1
O	13.25	16	0.82	1

Empirical formula of the compound is C_7H_7NO. **Empirical formula weight is 121.**

Since empirical formula weight is equal to the **molecular formula weight the empirical** formula is equal to molecular formula, ***i.e.***, C_7H_7NO. **Structure of compound and its isomer is:**





Problem 19.43:

Identify the ester in the following sequence **of reactions:**

$$(A) \xrightarrow{PCl_5} (B) + (C)$$

$$(B) \xrightarrow[BaSO_4]{H_2/Pd} (D) \xrightarrow{LiAlH_4} \begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!\!>\!CHCH_2OH \xleftarrow{AqKOH} (C)$$

Solution: Assume the ester is $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR'$.

Now $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR' \xrightarrow{PCl_5} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl + R'Cl + POCl_3$

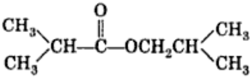
(B) undergoes the Rosenmund **reduction, thus it is an acyl halide.**

$$\underset{(B)}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl} \xrightarrow[BaSO_4]{H_2/Pd} \underset{(D)}{RCHO} \xrightarrow{LiAlH_4} RCH_2OH$$

Since $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!\!>\!CHCH_2OH$ **is obtained on reduction, therefore R is** $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!\!>\!CH{-}$

Accordingly R′ is $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!\!>\!CH$- **and R′Cl is** $\underset{(C)}{\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!\!>\!CHCH_2Cl}$

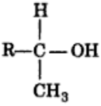
Hence (A) is



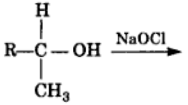
Problem 19.44:

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. Assign structures to A and B. Show the reactions involved.

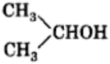
Solution: Since the alcohol is oxidized by NaOCl to an acid it would have the structure.



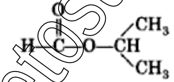
(B)

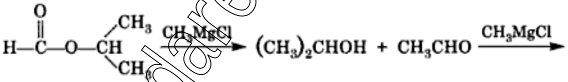


$RCOO^-$. Since $RCOO^-$ is acetic acid, therefore B is



An ester reacts with Grignard reagent to give two products–an aldehyde or ketone and an alcohol. The aldehyde or ketone further reacts to give an alcohol. Therefore A is



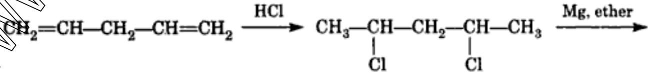


$$(CH_3)_2CHOH + (CH_3)_2CHOH \xrightarrow{NaOCl} CH_3CH_3 + CH_3COO^-Na^+ \xrightarrow{H^+} CH_3COOH$$

Problem 19.45:

1, 4-Pentadiene reacts with excess of HCl to give compound A which upon reaction with excess Mg in dry ether forms B. Compound B, on treatment with ethyl acetate followed by dilute acid yields C. Identify the structures A, B and C.

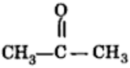
Solution:



$$CH_2{=}CH{-}CH_2{-}CH{=}CH_2 \xrightarrow{HCl} CH_3{-}\underset{Cl}{CH}{-}CH_2{-}\underset{Cl}{CH}{-}CH_3 \xrightarrow{Mg,\ ether}$$

to Tollens' reagent and also does not reduce Fehling's solution but forms a 2, 4-dinitrophenylhydrazone. Propose structures A to E and show the reactions.

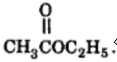
Solution: Molecular formula of E is C_3H_6O. It does not react with Tollens' reagent or Fehling's solution but forms a 2, 4-dinitrophenyl hydrazone. Therefore, it is a ketone and it is acetone,



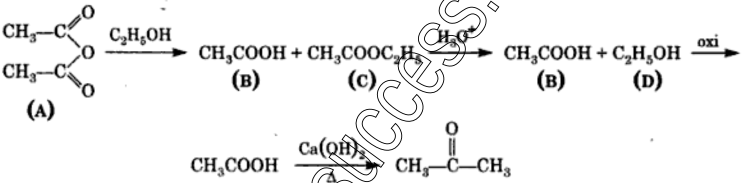
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(E)

E is formed from B on heating with $Ca(OH)_2$, B is CH_3COOH. B is obtained from D on oxidation, thus D is ethyl alcohol, C_2H_5OH.

C gives D on hydrolysis, therefore D is  $CH_3\overset{\overset{\displaystyle O}{\|}}{C}OC_2H_5$.

Now a compound which forms an acid and an ester on reaction with C_2H_5OH is an anhydride. Therefore A is acetic anhydride.



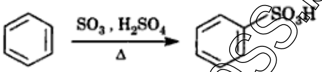
CHAPTER

20

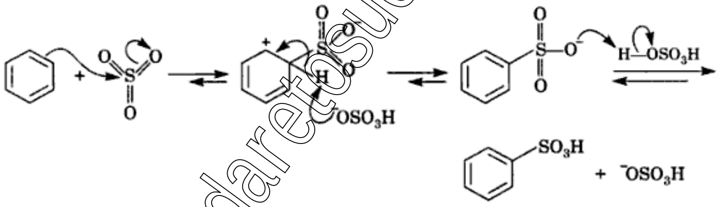
Sulfonic Acids, Their Derivatives and Drugs

Problem 20.1:

Write a mechanism for the following sulfonation reaction:

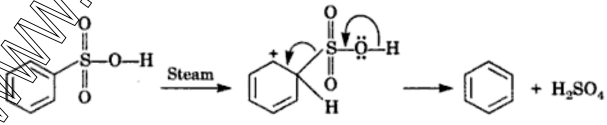


Solution: The mechanism for the sulfonation of benzene involves sulfur trioxide, a fuming liquid that reacts violently with water to give H_2SO_4. The source of SO_3 for sulfonation is usually a solution of SO_3 in conc. H_2SO_4 called *fuming sulfuric* acid or *oleum*.



It should be noted that the intermediate in sulfonation mechanism unlike other electrophilic reactions is neutral. It is a reversible reaction. The -SO_3H (Sulfonic acid) group is replaced by a hydrogen when sulfonic acid is heated with steam. Because of the reversibility of the reaction, desulfonation is also possible. Reversibility is a consequence of the weak C—S bond.

Desulfonation mechanism:



The reverse process for benzenesulfonic acid would occur by initial protonation of the carbon bearing the -SO_3H group to generate the same intermediate that is produced in sulfonation. Loss of -SO_3H group would then yield benzene.

Problem 20.2:

Write the products of benzenesulfonic acid with the following:

(*a*) C_2H_5OH (*b*) NaOH (cold) (*c*) NaOH (*aq*) (*d*) Br_2 . Fe (*e*) $NaHCO_3$ (*aq*) (*f*) dil H_2SO_4, heat (*g*) CH_3Cl, $AlCl_3$ (*h*) fuming sulfuric acid and heat (*i*) H_2O (*j*) $Ba(OH)_2$

Solution: (*a*) No reaction (*b*) $C_6H_5SO_3^-\ Na^+$ (*c*) $C_6H_5SO_3^-\ Na^+$ (*d*) *m*-$BrC_6H_4SO_3H$ (*e*) CO_2, $C_6H_5SO_3^-\ Na^+$ (*f*) C_6H_6 (desulfonation) (*g*) No reaction (*h*) *m*-$C_6H_4(SO_3H)_2$ (*i*) $C_6H_5SO_3^-$ and H_3O^+ (*j*) $(C_6H_5SO_3^-)_2\ Ba^{++}$

Problem 20.3:

Outline a synthesis of the following compounds starting from benzene or toluene and any other reagent.

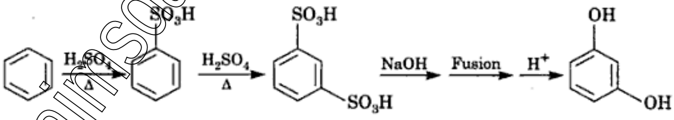
(*a*) Phenol (*b*) *p*-Cresol (*c*) Phenyl *p*-toluenesulfonate (*d*) Resorcinol

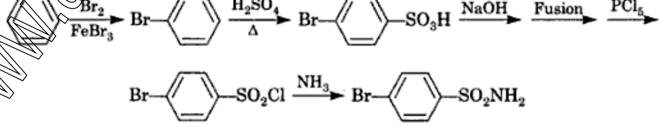
(*e*) *p*-Bromobenzenesulfonamide

Solution: (*a*) $C_6H_6 \xrightarrow[\Delta]{\text{conc. } H_2SO_4} C_6H_6SO_3H \xrightarrow{NaOH} C_6H_5SO_3^-\ Na^+ \xrightarrow[NaOH]{\text{Fuse with}} \xrightarrow{H^+} C_6H_5OH$

(*b*) $C_6H_5CH_3$ same as in (*a*)

(*c*)


(*d*)


(*e*)


Problem 20.4:

Write the major product obtained from the sulfonation of the following compounds.

(*a*) Chlorobenzene (*b*) Anisole (*c*) Toluene (*d*) *p*-Nitrotoluene (*e*) *p*-Xylene

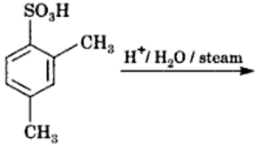
(*f*) Nitrobenzene (*g*) *m*-Xylene

Solution: (*a*) *o, p* (*b*) *p* (*c*) *o, p* (*d*) *o* (*e*) *o* (*f*) *m* (*g*) *o.*

Problem 20.5:

Complete the following reactions:

(*a*)

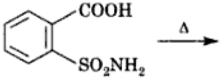


(*b*) $C_6H_5SO_3H + NaHCO_3 \longrightarrow$

(*c*) $C_6H_5SO_2Cl + N(CH_3) \longrightarrow$

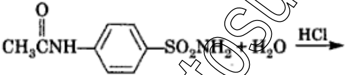
(*d*) $C_6H_5NO_2$ + Oleum $\xrightarrow{\Delta}$

(*e*)

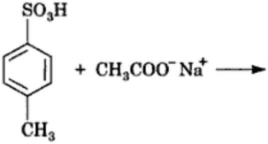


(*f*) $C_6H_5CH_3 + ClSO_3H \longrightarrow$

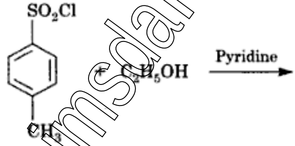
(*g*)



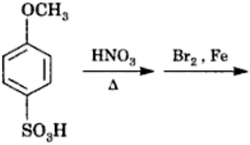
(*h*)



(*i*)

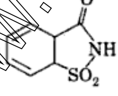


(*j*)

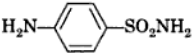


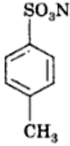
Solution: (*a*) *m*-Xylene (*b*) $C_6H_5SO_3^-Na^+$ (*c*) No reaction (*d*) *m*-Nitrobenzenesulfonic acid

(*e*)

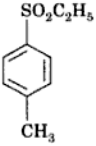


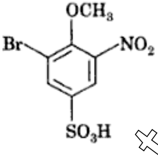
(*f*) *o*-Tolylsulfonic acid (*g*) CH_3COOH +



(h) 

+ CH_3COOH

(i) 

(j) 

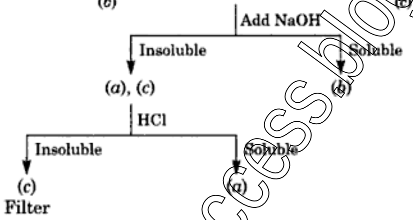
Problem 20.6:

Explain how would you proceed to separate mixture containing the following?

(*a*) Aniline (*b*) *p*-Methylbenzenesulfonamide (*c*) N, N-Dimethylbenzenesulfonamide

Solution: Aniline + *p*-Methylbenzenesulfonamide + N, N-Dimethylbenzenesulfonamide

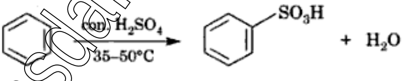
(*a*) (*b*) (*c*)



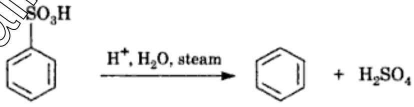
Problem 20.7:

Discuss the general methods for the preparation of aromatic sulfonic acids. Explain how (*a*) benzene (*b*) phenol and (*c*) benzoic acid may be prepared from it.

Solution: The aromatic sulfonic acids can be prepared by treatment of benzene with sulfuric acid (H_2SO_4), chlorosulfonic acid $(ClSO_3H)$ or fuming sulfuric acid $(H_2SO_4 + SO_3)$, also known as oleum.

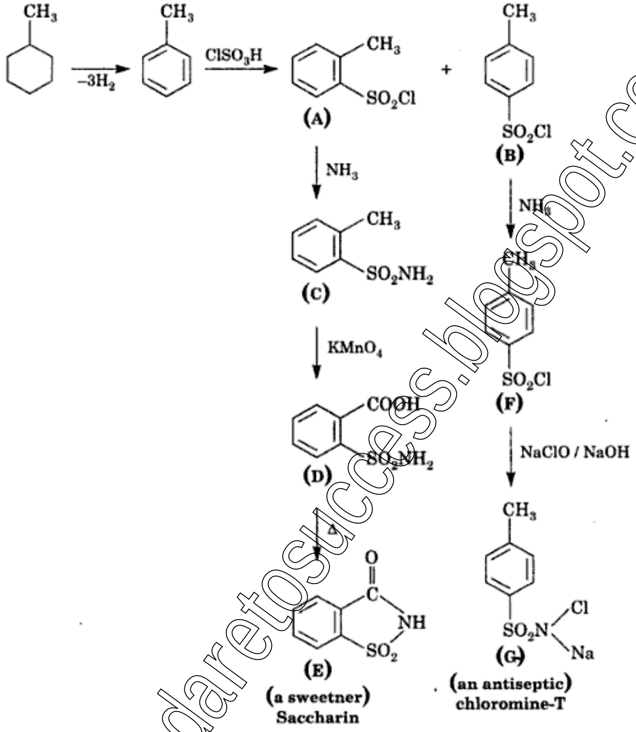


(*a*) Benzene can be prepared by heating benzenesulfonic acid at 100-175°C with aqueous sulfuric acid (desulfonation reaction).



(*b*) Phenol can be prepared by fusing benzene sulfonic acid with NaOH.

$$C_6H_5SO_3^- Na^+ + NaOH \xrightarrow{\Delta} C_6H_5O^- Na^+ \xrightarrow{H^+} C_6H_5OH$$



Problem 20.15:

A compound A, of molecular formula C_8H_{10} gives a single monosulfonated product B, on reacting with conc. sulfuric acid. The sodium salt of B, on fusion with sodium hydroxide and subsequent acidification yields a substituted phenol (C). Write the structures of A, B and C.

Solution:

Probloem 20.16:

Compound A, C_7H_8 , on sulfonation with conc. sulfuric acid yields two monosulfonated isomeric products B and C. The potassium salt of B, with KCN gives D, C_8H_7N which on hydrolysis forms an acid E, $C_8H_8O_2$. Identify the compounds A to E.

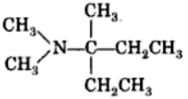
CHAPTER

21

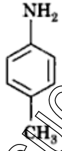
Amines and Nitro Compounds

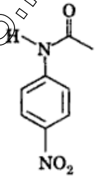
Problem 21.1:

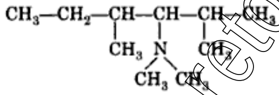
Write systematic name for the following compounds:

(a) 

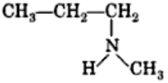
$(CH_3)_2N-\underset{CH_2CH_3}{\overset{CH_3}{C}}-CH_2CH_3$

(b) 

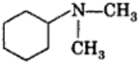
(c) 

(d) 

$CH_3-CH_2-\underset{CH_3}{CH}-\underset{\underset{CH_3\quad CH_3}{N}}{CH}-\underset{CH_3}{CH}-CH_3$

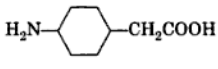
(e) 

$CH_3-CH_2-\underset{\underset{H\quad CH_3}{N}}{CH_2}$

(f) 

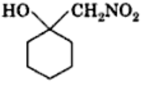
(g) 

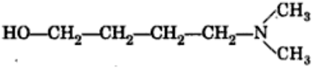
$H_2N-CH_2-CH=CH-CH_2-CH\begin{matrix}Cl\\ Cl\end{matrix}$

(h) 

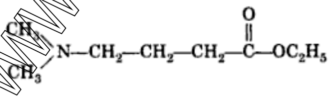
(i) 

$CH_2=CH-N\begin{matrix}CH_3\\ CH_3\end{matrix}$

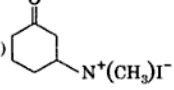
(j) 

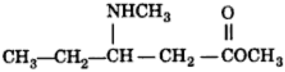
(k) 

$HO-CH_2-CH_2-CH_2-CH_2-N\begin{matrix}CH_3\\ CH_3\end{matrix}$

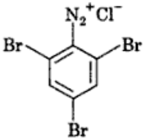
(l) 

$\begin{matrix}CH_3\\ CH_3\end{matrix}N-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$

(m) 

(*n*) 

$$CH_3-CH_2-\overset{\overset{\displaystyle NHCH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{||}}{C}OCH_3$$

(*o*) 

Solution: (*a*) 3, N, N-trimethyl-3-pentanamine (*b*) 4-Methylaniline (*c*) N-acetyl *p*-nitroaniline (*d*) 2, 4-N, N-tetramethyl-3-hexanamine (*e*) N-methyl propanamine (*f*) N, N-dimethyl cyclohexamine (*g*) 1-Amino-5, 5-dichloro-2-pentene (*h*) 4-Aminocyclohexaneacetic acid (*i*) N, N-dimethylethenamine (*j*) 3-Nitromethylcyclohexanol (*k*) 4-Dimethylamino-1-butanol (*l*) Ethyl 4-dimethylamino butyrate (*m*) 3-Oxocyclohexyltrimethylammonium iodide (*n*) Methyl 3-(methylamino) pentanoate (*o*) 2, 4, 6-Tribromobenzenediazonium chloride.

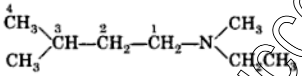
Problem 21.2:

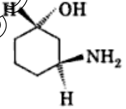
Write structures for the following compounds:

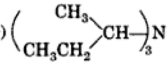
(*a*) 3, N-dimethyl-N-ethylbutanamine (*b*) *trans*-3-Aminocyclohexanol

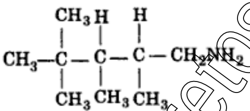
(*c*) Tri, sec. butylamine (*d*) 2, 3, 4, 4-Tetramethylpentanamine

(*e*) 2, 2′-Dichlorodiethylamine

Solution: (*a*) 

(*b*) 

(*c*) 

(*d*) 

$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-CH_2NH_2$$

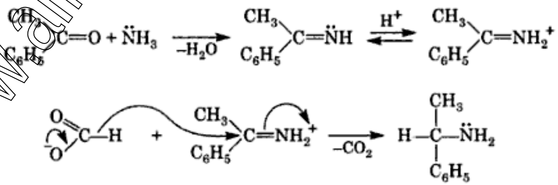
(*e*) $ClCH_2-CH_2-NH-CH_2-CH_2Cl$

Problem 21.3:

Suggest a suitable mechanism for the Leuckart reaction for the formation of an amine between acetophenone and ammonium formate.

Solution: Mechanism

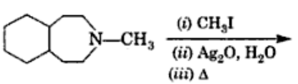
$$HCO_2^-\,NH_4^+ \overset{\Delta}{\rightleftharpoons} HCOOH + NH_3$$



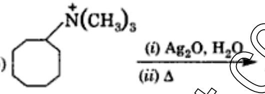
Problem 21.7:

Write the product of exhaustive methylation of the following amines.

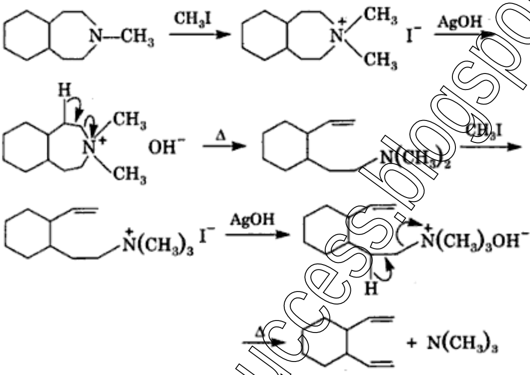
(a)



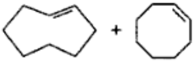
(b)



Solution: (a)



(b)

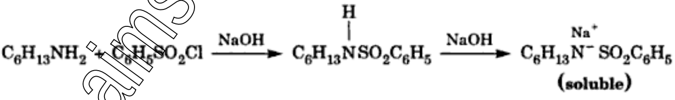


Problem 21.8:

An amine has the molecular formula $C_6H_{15}N$. How can you tell if it is primary, secondary or tertiary?

Solution: The Hinsberg test can be employed for this purpose. The molecular formula of the amine is $C_6H_{15}N$.

A primary amine would be $C_6H_{13}NH_2$:



$$C_6H_{13}NH_2 + C_6H_5SO_2Cl \xrightarrow{NaOH} C_6H_{13}\overset{H}{\overset{|}{N}}SO_2C_6H_5 \xrightarrow{NaOH} \underset{\textbf{(soluble)}}{C_6H_{13}\overset{Na^+}{N^-}\,SO_2C_6H_5}$$

The sulfonamide salt is soluble in water.

A secondary amine would be: $C_6H_{14}NH$

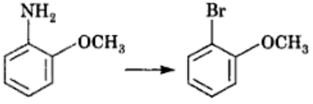
$$C_6H_{14}NH + C_6H_5SO_2Cl \xrightarrow{NaOH} \underset{\textbf{(insoluble)}}{C_6H_{14}\ddot{N}SO_2C_6H_5}$$

Since it lacks a hydrogen on the nitrogen atom it cannot form a sod. salt, instead it precipitates out in the form of an oil.

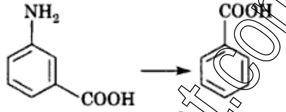
Problem 21.11:

Suggest appropriate reagents for the following reactions:

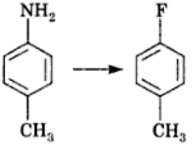
(a)



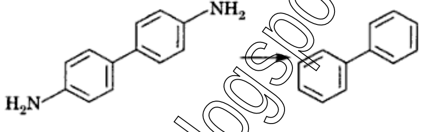
(b)



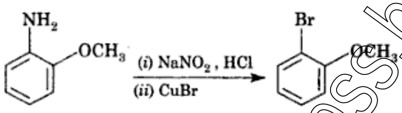
(c)



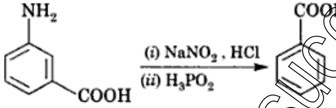
(d)



Solution: (a)



(b)



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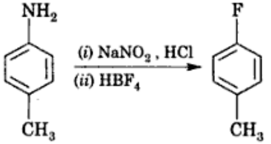
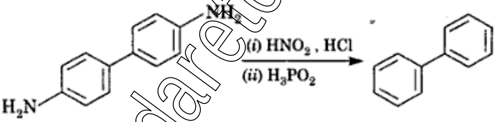


(d)



Problem 21.12:

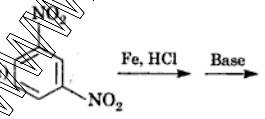
Why does the diazo coupling often necessitate basic conditions?

Solution: Because deprotonation of the phenolic group to phenoxide ion in the substrate activates the ring toward electrophilic attack.

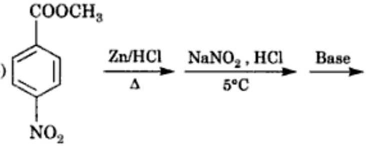
Problem 21.13:

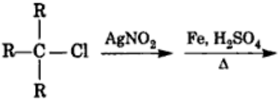
Fill in the missing compounds:

(a)



(b)



(c)


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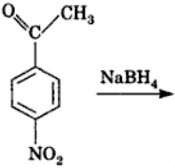

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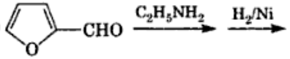
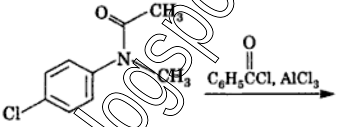
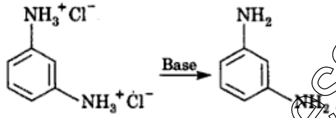


(f)


Solution: (a)


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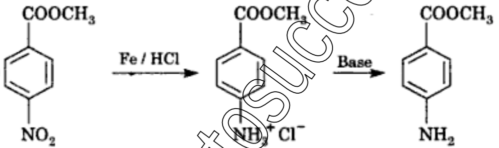

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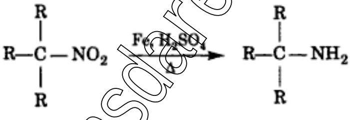
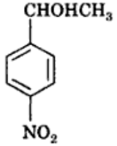
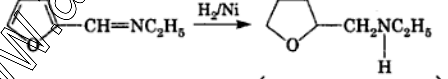
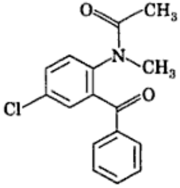


(d)


(e)


(Reductive amination)

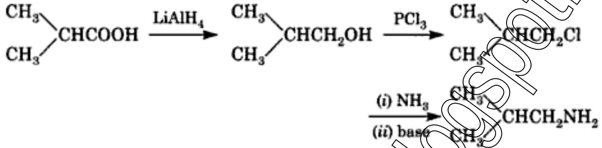
(f)


Problem 21.14:

Make the following conversions:

(*a*) Isobutyric acid to isobutylamine (*b*) Nitrobenzene to benzoic acid (*c*) Aniline to *p*-bromoaniline (*d*) Ethylamine to ethyl alcohol (*e*) N, N-Dimethyl-4-pentene to 1, 4-pentadiene (*f*) Aniline to *s*-tribromoaniline (*g*) Propene to isopropylamine (*h*) Ethyl chloride to *n*-propylamine (*i*) Aniline to sulfanilamide (*j*) Cyclohexanone to cyclohexylamine

Solution: (*a*)

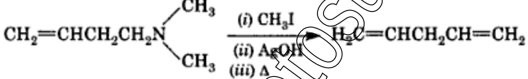


(*b*) $C_6H_5NO_2 \xrightarrow[\Delta]{Fe,\ HCl} C_6H_5NH_2 \xrightarrow[5°C]{NaNO_2,\ HCl} C_6H_5N_2^+\,Cl^- \xrightarrow{CuCN} C_6H_5CN \xrightarrow[\Delta]{H_2O,\ H^+} C_6H_5COOH$

(*c*) $C_6H_5NH_2 \xrightarrow{(CH_3CO)_2O} C_6H_5NHCOCH_3 \xrightarrow{Br_2}$ *p*-Bromoacetamide $\xrightarrow[\Delta]{H_2O,\ H^+}$ *p*-Bromoaniline

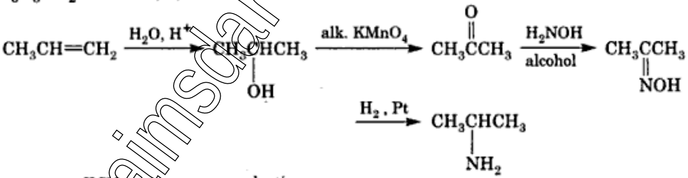
(*d*) $C_2H_5NH_2 \xrightarrow[H_2O]{NaNO_2,\ HCl/5°C} C_2H_5OH$

(*e*)



(*f*) $C_6H_5NH_2 \xrightarrow{Br_2}$ 2, 4, 6-Tribromoaniline

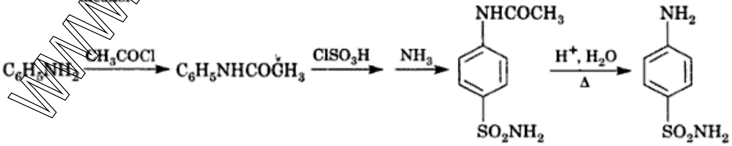
(*g*)



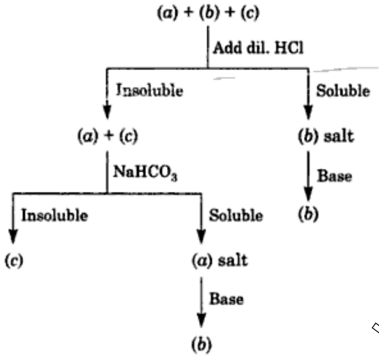
$CH_3CH{=}CH_2 \xrightarrow{H_2O,\ H^+} CH_3\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow{alk.\ KMnO_4} CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[alcohol]{H_2NOH} CH_3\underset{NOH}{\underset{\|}{C}}CH_3 \xrightarrow{H_2,\ Pt} CH_3\underset{NH_2}{\underset{|}{C}}HCH_3$

(*h*) $C_2H_5Cl \xrightarrow[alcohol]{KCN} C_2H_5CN \xrightarrow{reduction} C_2H_5CH_2NH_2$

(*i*)

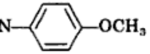


(*b*)



Problem 21.18:

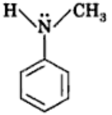
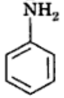
Write products for the reaction of benzenediazonium sulfate with the following reagents: (*a*) CuCl (*b*) H_3PO_2 (*c*) KI (*d*) Anisole (*e*) CuCN (*f*) Hot dil H_2SO_4 (*g*) HF, BF_3 (*h*) CuBr

Solution: (*a*) C_6H_5Cl (*b*) C_6H_6 (*c*) C_6H_5I (*d*) $C_6H_5N{=}N$––OCH_3 (*e*) C_6H_5CN (*f*) C_6H_5OH (*g*) C_6H_5F (*h*) C_6H_5Br

Problem 21.19:

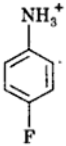
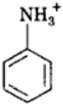
Offer plausible explanation for the following observations:

(*a*) Methylethyl-*n*-propylamine cannot be resolved into its optical isomers. (*b*) Methyl alcohol is less basic than methylamine. (*c*) Diethylamine is more basic than triethylamine. (*d*) The sulfonamide of a secondary amine is insoluble in NaOH. (*e*) Acetanilide reacts with bromine moderately than does aniline. (*f*) The reaction of nitrous acid with a secondary amine stops at the nitrosamine stage. (*g*) It is not desirable to nitrate aniline directly to prepare nitroanilines. (*h*) Amongst the three isomers of nitrophenol, *o*-nitrophenol is the least soluble in water. (*i*) $(SiH_3)_3\ddot{N}$ is a weaker base than $(CH_3)_3\ddot{N}$ (*j*) The order of decreasing basicity of the following amines is:

$(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 >$  > 

(*k*) Anhydrous $CaCl_2$ cannot be used as a drying agent for amines and alcohols.

(*l*) 1-Nitropropane and 2-nitropropane are not functional isomers.

(m)  is more acidic than 

(n) The sulfonamide obtained between the reaction of dimethylamine and the Hinsberg reagent is insoluble in NaOH solution.

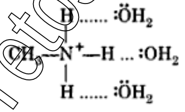
Solution: (a) Because the molecule can flip and the two forms are superimposable. (b) Nitrogen is less electronegative than oxygen, thus methylamine has a larger tendency to donate electrons. (c) Amines are derivatives of NH_3. The basicity of an amine often depends on the groups substituted on the nitrogen atom. Protonated amines like carbocations are stabilized by substitution of alkyl group on the positively charged nitrogen atom. Thus a primary amine is more basic than NH_3 and a secondary amine is more basic than a primary one but triethylamine is slightly less basic.

	NH_4^+	$C_2H_5NH_3^+$	$(C_2H_5)_2NH_2^+$	$(C_2H_5)_3NH^+$
pK_a	1.20	10.62	10.95	10.64

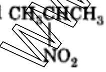
than diethylamine. In the gas phase (no solvent), triethylamine is more basic than others because of the inductive stabilization of the amine by alkyl groups.

$$(C_2H_5)_3\overset{+}{N}H > (C_2H_5)_2\overset{+}{N}H_2 > C_2H_5\overset{+}{N}H_3 > \overset{+}{N}H_4$$

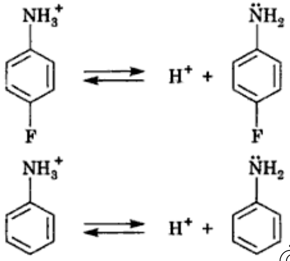
However in solution the basicity order is different because the solvent also plays a part. A simple explanation is that the conjugate acid ammonium ion in solution is stabilized not only by alkyl groups but also by hydrogen bond formation with the solvent. A primary ammonium salt has three hydrogen bonds and a tertiary ammonium salt will have only one. Furthermore,



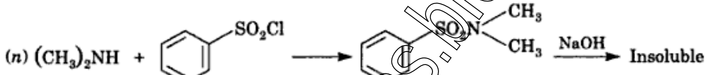
there is probably some steric hindrance to hydrogen bonding in a tertiary ammonium ion. These effects work in opposite direction because more the alkyl groups lesser will be the H-bonds. As a result the secondary amine is more basic because it has more hydrogen bonds than tertiary amine and also two alkyl groups to stabilize the ion.

(d) Does not possess a hydrogen atom to form the sodium salt. (e) The amide group is only moderately activating compared to $-NH_2$ (f) Does not have a hydrogen atom (g) It can undergo oxidation to *p*-quinone. (h) Because of the occurrence of intramolecular H-bond in the *ortho*-isomer. (i) Because CH_3 is a better electron donor group inductively than SiH_3. (j) The aliphatic amines are stronger bases than aromatic amines. The electron donation capacity of the latter amines are decreased because of the resonance between the electrons on the nitrogen atom and the benzene ring. (k) $CaCl_2$ reacts with both amines and alcohols. (l) $CH_3CH_2CH_2NO_2$ and  $CH_3\underset{NO_2}{CH}CH_3$, are instead positional isomers.

(*m*)



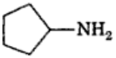
The conjugate base *p*-fluoroaniline is a weaker base than aniline because of the inductive electron-withdrawing effect of the fluoro group.

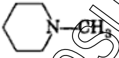


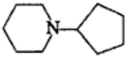
The secondary amine sulfonamide lacks an acidic hydrogen and is thus unable to react with NaOH.

Problem 21.20:

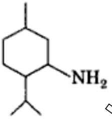
What products(s) would be obtained from each when subjected to Hofmann degradation?

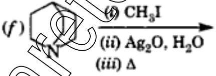
(*a*)


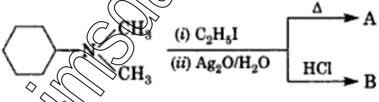
(*b*)


(*c*)


(*d*) $(CH_3)_3CNH_2$

(*e*)


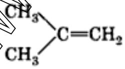
(*f*)


(*g*)


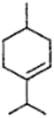
Solution: (*a*)

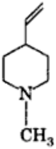
(*b*)

(*c*) Cyclopentene +2, 4-Pentadiene + 1, 3-Pentadiene

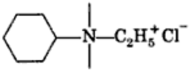
(*d*)


$(CH_3)_2C{=}CH_2$

(*e*)


(*f*)


(*g*) A,

, B,


Problem 21.21:

What products would be obtained in the reduction of the following compounds with $LiAlH_4$?

(*a*) Methyl cyanide (*b*) Isopropyl cyanide (*c*) Methyl isocyanide (*d*) Isopropyl isocyanide

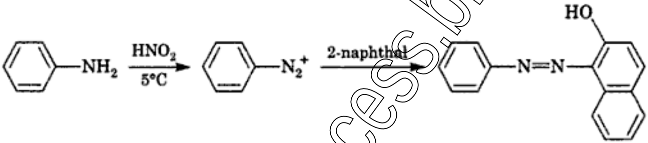
Solution: (*a*) Ethylamine (*b*) Isobutylamine (*c*) Dimethylamine (*d*) Isopropylmethylamine

Problem 21.22:

Write equations for simple chemical tests that would distinguish between:

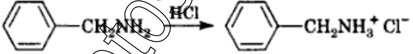
(*a*) Aniline and cyclohexylamine (*b*) Benzylamine and benzamide (*c*) Propylamine and methylethylamine (*d*) N-methylaniline and toluidine (*e*) Aniline and phenol (*f*) Pyridine and benzene (*g*) Propylamine and allylamine (*h*) Aniline hydrochloride and o-chloroaniline (*i*) Aniline and acetamide

Solution: (*a*) Aniline reacts with HNO_2 at 5°C to give a stable diazonium salt that couples with 2-naphthol yielding an intense colored azo compound.



Cyclohexylamine under the same conditions produces an unstable diazonium salt that decomposes rapidly and gives no color with 2-naphthol (rather gives an alcohol)

(*b*) Benzylamine dissolves in HCl at room temperature.



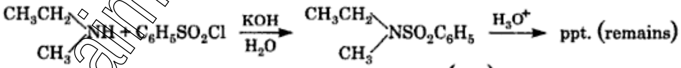
With benzamide there is no such reaction.

(*c*) The Hinsberg test:

$$CH_3CH_2CH_2NH_2 + C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH} CH_3CH_2CH_2N^- K^+ SO_2C_6H_5$$

(Soluble)

$$\longrightarrow CH_3CH_2CH_2NHSO_2C_6H_5$$

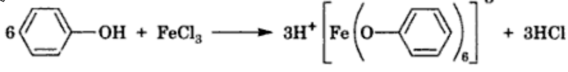


$$\overset{CH_3CH_2}{\underset{CH_3}{>}}NH + C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH} \overset{CH_3CH_2}{\underset{CH_3}{>}}NSO_2C_6H_5 \xrightarrow{H_3O^+} \text{ppt. (remains)}$$

Insoluble (ppt.)

(*d*) Hinsberg test as in (C).

(*e*) Phenol produces a color with neutral $FeCl_3$ solution.



$$(a)\ C_6H_5N_2^+Cl^- \xrightarrow[\text{Cu powder}]{NaNO_2} C_6H_5NO_2 \quad (b)\ C_6H_5N_2^+Cl^- \xrightarrow[\text{conc. HCl}]{SnCl_4,} C_6H_5NHNH_2 + HCl$$

$$(c)\ C_6H_5N_2^+Cl^- \xrightarrow{KI} C_6H_5I + N_2 + KCl$$

Problem 21.27:

An organic compound A, C_4H_9I reacts with silver nitrite to give mostly B, $C_4H_9O_2$. Compound B does not dissolve in alkali and also gives no reaction with nitrous acid. Reduction of B, gives another compound C, which can also be obtained from A and potassium phthalimide. Compound C, reacts with nitrous acid to give a tertiary alcohol D, $C_4H_{10}O$. Identify the compounds A, B, C and D stating the reactions involved.

Solution: Since compound B gives no reaction with nitrous acid, compound A is a tertiary iodide. The sequence of reactions is as follows:

$$\underset{\textbf{(A)}}{(CH_3)_3CCl} \xrightarrow{AgNO_2} \underset{\textbf{(B)}}{(CH_3)_3CNO_2} \xrightarrow{\text{red}} \underset{\textbf{(C)}}{(CH_3)_3CNH_2} \xrightarrow{HNO_2} \underset{\textbf{(D)}}{(CH_3)_3COH}$$

Problem 21.28:

What are amines? How may primary, secondary and tertiary amines be identified? Give the structural formulas and names of isomeric amines of molecular formula $C_4H_{11}N$.

Solution: Amines are nitrogen containing compounds which may be considered as derivatives of ammonia in which hydrogen atoms have been replaced by alkyl or aryl groups. Primary, secondary and tertiary amines are identified by the Hinsberg test. This test involves the reaction of an amine with benzenesulfonyl chloride in the presence of aqueous sodium hydroxide. A primary amine forms a soluble sulfonamide while a secodary amine forms an insoluble sulfonamide but a tertiary amine does not undergo any reaction because it does not possess a replaceable hydrogen atom.

Primary:

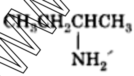
$$RNH_2 + C_6H_5SO_2Cl \longrightarrow RNHSO_2C_6H_5 \xrightarrow{NaOH} \underset{\textbf{Soluble}}{R{-}\overset{Na^+}{\bar{N}}O_2C_6H_5}$$

Secondary: $R_2NH + C_6H_5SO_2Cl \longrightarrow R_2NSO_2C_6H_5 \xrightarrow{NaOH}$ Insoluble

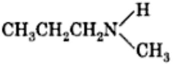
Tertiary: $R_3N + C_6H_5SO_2Cl \longrightarrow$ No reaction

Structure and names of isomers of $C_4H_{11}N$:

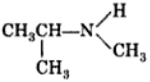
$CH_3CH_2CH_2CH_2NH_2$ *n*-Butanamine



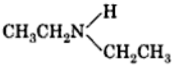
$CH_3CH_2\underset{NH_2}{\underset{|}{C}}HCH_3$ 2-Butanamine



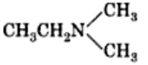
$CH_3CH_2CH_2N(H)(CH_3)$ N-Methylpropanamine



$CH_3CH(CH_3)-N(H)(CH_3)$ N-Methyl-2-propanamine



$CH_3CH_2N(H)(CH_2CH_3)$ N-Ethylethanamine



$CH_3CH_2N(CH_3)(CH_3)$ N, N-Dimethylethanamine

Problem 21.29:

Give the reaction of HNO_2 with the following amines:

(*a*) Aniline (*b*) N-Methylaniline (*c*) N, N-Dimethylaniline

Solution: (*a*) Phenyl diazonium salt (*b*) N-Nitroso-N-methylaniline (*c*) *p*-Nitroso-N, N-dimethylaniline

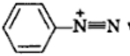
Problem 21.30:

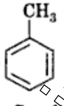
Consider: *o*-toluidine, ethylamine, butylamine and pentamethylenediamine.

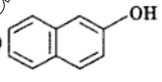
(*a*) Which would be made by reduction of butanonitrile? (*b*) Which would reat with HCl in the ratio of one mole of the compound and two moles of HCl? (*c*) Which would be converted into a diazonium salt? (*d*) Which would be among the products of the reaction of chlorothane and ammonia?

Solution: (*a*) Butylamine (*b*) Pentamethylenediamine (*c*) *o*-Toluidine (*d*) Ethylamine

Problem 21.31:

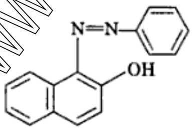
Give the structures of the products of the reaction of  with

(*a*) 

(*b*) 

Solution: Coupling is an electrophilic aromatic substitution reaction in which the terminal N is the electrophile.

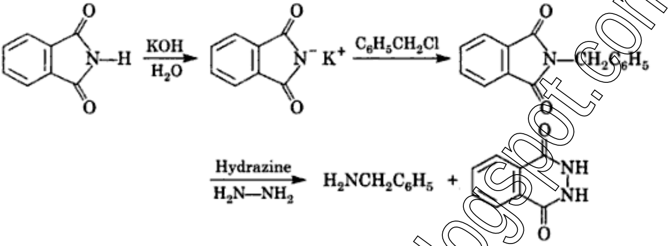
(*a*) Toluene does not couple with the diazonium ion as the ring is not sufficiently activated.

(*b*) 

Problem 21.32:

Suggest a preparation of benzylamine using the Gabriel synthesis.

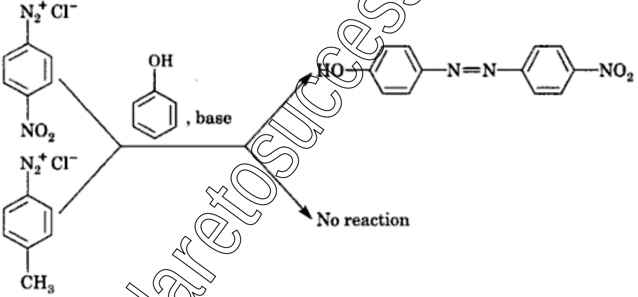
Solution:



Problem 21.33:

Assume a solution containing 1 g molecular weight each of *p*-toluenediazonium chloride and *p*-nitrophenyldiazonium chloride was added to an alkaline solution containing 1 g molecular weight of phenol. Predict the product of the reaction. Explain.

Solution:

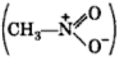


The phenoxide ion is more likely to be attacked by *p*-nitrobenzendiazonium chloride as the electron-withdrawing nitro group makes the diazonium ion less stable and thus more reactive than the other ion.

Problem 21.34:

Explain the observation that nitromethane does not have a high solubility in hydrocarbons.

Solution: Nitromethane is highly polar molecule and thus does not dissolve in non-polar hydrocarbons.



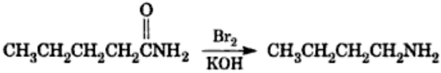
$$\left(CH_3—\overset{+}{N}{\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O^-}}\right)$$

Problem 21.35:

Show how *n*-butylamine can be prepared from each of the following:

(*a*) *n*-Bromobutane (*b*) 1-Nitrobutane (*c*) Butyraldehyde (*d*) Butyronitrile
(*e*) *n*-Pantanamide (*f*) 1-Pentanol (*h*) Propanol

Solution: (*a*) $CH_3CH_2CH_2CH_2Br \xrightarrow[C_2H_5OH]{KCN} CH_3CH_2CH_2CH_2CN \xrightarrow[\text{Partial hydrolysis}]{H_2O/H^+}$



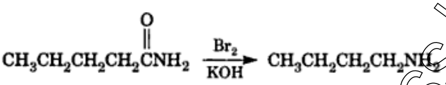
$CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2 \xrightarrow[KOH]{Br_2} CH_3CH_2CH_2CH_2NH_2$

(*b*) $CH_3CH_2CH_2CH_2NO_2 \xrightarrow[\text{3 moles}]{H_2/Pt} CH_3CH_2CH_2CH_2NH_2$

(*c*) $CH_3CH_2CH_2CHO \xrightarrow{H_2NOH} CH_3CH_2CH_2CH{=}NOH \xrightarrow[C_2H_5OH]{Na} CH_3CH_2CH_2CH_2NH_2$

(*d*) $CH_3CH_2CH_2CH_2CN \xrightarrow[\text{2 moles}]{H_2/Pt} CH_3CH_2CH_2CH_2NH_2$

(*e*)



$CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2 \xrightarrow[KOH]{Br_2} CH_3CH_2CH_2CH_2NH_2$

(*f*) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{KMnO_4} CH_3CH_2CH_2CH_2COOH \xrightarrow{SOCl_2}$

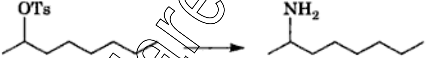
$CH_3CH_2CH_2CH_2COCl \xrightarrow{NH_3} CH_3CH_2CH_2CH_2CONH_2 \xrightarrow[KOH]{Br_2} CH_3CH_2CH_2CH_2NH_2$

(*h*) $CH_3CH_2CH_2OH \xrightarrow{HBr} CH_3CH_2CH_2Br \xrightarrow[C_2H_5OH]{KCN} CH_3CH_2CH_2CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2NH_2$

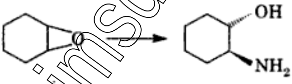
Problem 21.36:

Effect the following conversions:

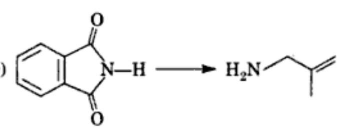
(*a*)



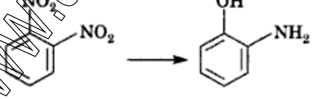
(*b*)



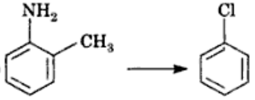
(c)

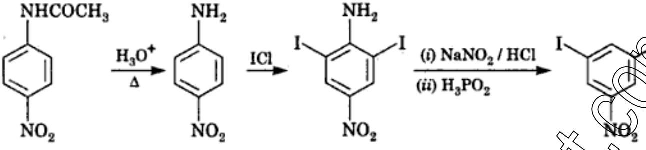


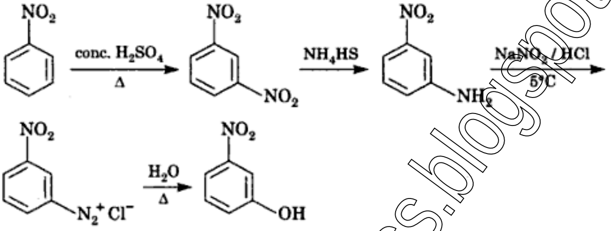
(*d*)

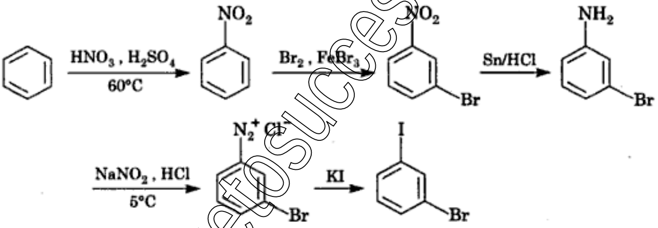


(*e*)



(*i*)


(*j*)


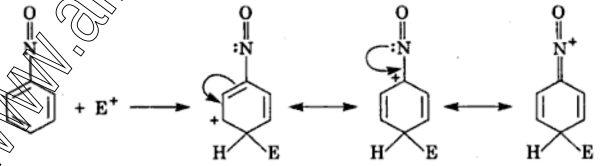
(*k*)


Problem 21.37:

Account for the fact that a nitroso (-N=O) group activates ortho- and *para*- positions towards both electrophilic and nucleophilic aromatic substitutions.

Solution: A nitroso group is capable of dispersing either positive or negative charge developing in the transition state during electrophilic or nucleophilic substitution by resonance.

Electrophilic substitution:



(*c*) In the reaction of *p*-chlorotoluene with KNH_2 in liq NH_3, the major product is:

A. *o*-Toluidine B. *m*-Toluidine C. *p*-Toluidine D. *p*-Chloroaniline

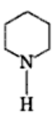
(*d*) The strongest base amongest the following is:

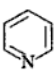
A. $CH_3CH_2CH_2NH_2$ B. $CH_2{=}CHCH_2NH_2$ C. $CH{\equiv}CCH_2NH_2$ D. $C_6H_5NH_2$

(*e*) Maximum basicity in the gas phase of the following amines is:

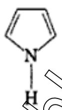
A. $CH_3CH_2NH_2$ B. $(CH_3CH_2)_2NH$ C. $(CH_3CH_2)_3N$ D. NH_3

(*f*) In the compounds:


I


II


III

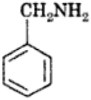

IV

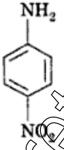
the order of basicity is:

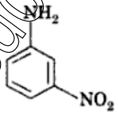
A. IV > I > III > II B. I > III > II > IV

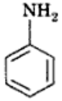
C. III > I > IV > II D. II > I > III > IV

(*g*) Among the following the strongest base is

A. 

B. 

C. 

D. 

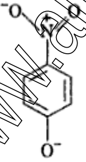
(*h*) In amines, the hybridization state of N is:

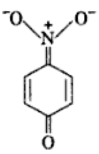
A. *sp* B. sp^2 C. sp^3 D. sp^3d

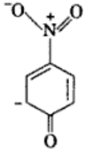
(*i*) Allyl cyanide $CH_2{=}CH{-}CH_2{-}C{\equiv}N$ has bonds:

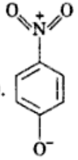
A. 9σ, 4π B. 9σ, 3π C. 8σ, 5π D. 8σ, 3π

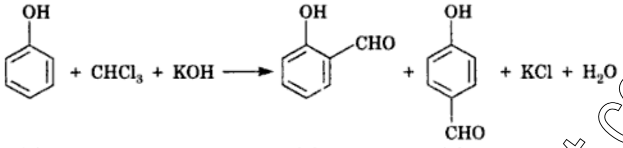
(*j*) The most unlikely representation of resonance structure of *p*-nitrophenoxide ion is

A. 

B. 

C. 

D. 

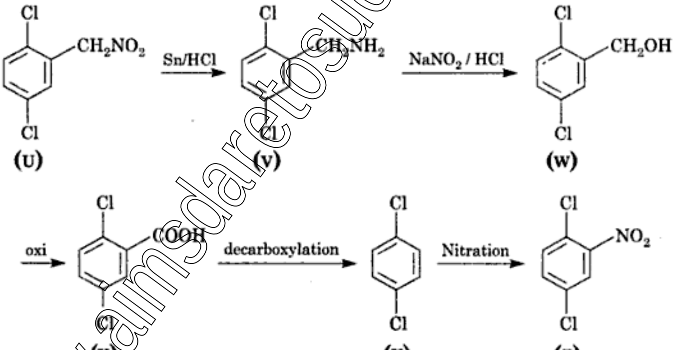


(B) (D) (E)

Problem 21.45:

An aromatic compound U, $C_7H_5NO_2Cl_2$ on reduction in the presence of Sn/HCl produces V, which on subsequent reaction with $NaNO_2$/HCl yields W. Compound V, does not form a dye with β-naphthol. But W, gives red color with ceric ammonium nitrate and on oxidation gives an acid X, having an equivalent weight 191. Decarboxylation of X, gives Y, which on nitration yields a single mononitro derivative Z. Deduce structures u to Z and show the sequence of reactions.

Solution: Compound V, reacts with $NaNO_2$/HCl and it is a product of reduction of U, therefore, V has a $-NH_2$ group while U is a nitro compound. Furthermore, V on reaction with $NaNO_2$/HCl gives W, and does not form a dye with β-naththol, therefore, $-NH_2$ group is not directly linked to the benzene ring but in the side-chain. This is also confirmed by the ceric ammonium nitrate test which is given by phenol and not alcohols. In U, the two Cl are present *para* to each other because Y gives a single mononitro product Z. The sequence of reactions can be expressed as follows:



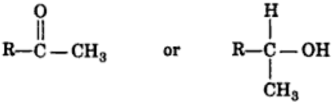
Problem 21.46:

An organic compound A, reacts with Br_2/KOH to give B. Compound B, on reaction with nitrous acid gives C, which on treatment with Br_2/KOH give D. Compound B, reacts with D in the presence of KOH to give an unpleasant smell. Compound D, yields ethyne on heating with silver powder. Assign structures A to D with proper reasoning.

Solution: Compound D, gives ethyne on heating with silver powder, therefore, D is bromoform.

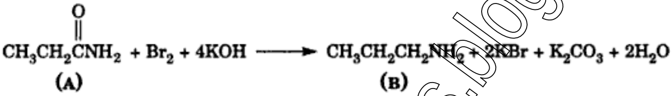
$$\underset{(\text{D})}{2CHBr_3} + 6\ Ag \xrightarrow{\Delta} CH{\equiv}CH + 6AgBr$$

D, is obtained by treatment of C with Br_2/KOH, therefore, C is either



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 \quad \text{or} \quad R{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}OH$$

But C is obtained form B on treatment with HNO_2, therefore, B is ethanol (R=H) and C, is ethylamine. Also B, is obtained from A, with Br_2/KOH, therefore, A is propanamide. The reactions are the following:



$$\underset{(\text{A})}{CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}NH_2} + Br_2 + 4KOH \longrightarrow \underset{(\text{B})}{CH_3CH_2CH_2NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

$$CH_3CH_2NH_2 + HNO_2 \longrightarrow \underset{(\text{C})}{CH_3CH_2OH} + N_2 + H_2O$$

$$CH_3CH_2OH + 4Br_2 + 6KOH \longrightarrow CHBr_3 + HCOO^-K^+ + 5KBr + 5H_2O$$

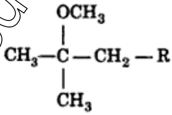
Compound B, reacts with D in the presence of KOH in a carbylamine reaction.

$$\underset{(\text{B})}{CH_3CH_2NH_2} + \underset{(\text{D})}{CHBr_3} + 3KOH \longrightarrow CH_3CH_2NC + 3KBr + 3H_2O$$

Problem 21.47:

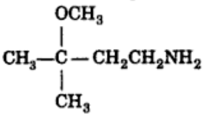
One mole of each of bromo derivative of A and NH_3 react to give one mole of an organic compound B. Compound B, reacts with CH_3I to yield C. Both B and C react with HNO_2 to give compounds D, and E, respectively. D, on oxidation and subsequent decarboxylation gives 2-methoxy-2-methylpropane. Deduce structures A to E with adequate reasoning.

Solution: 2-Methoxy-2-methtylpropane is obtained on oxidation of D, followed by decarboxylation, therefore, the structure of D is



$$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OCH_3}{|}}{C}}{-}CH_2{-}R$$

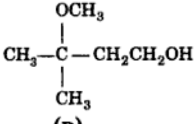
D, is also obtained from B on reaction with HNO_2, therefore, B is an amine. Also B is obtained from the bromo derivative A and NH_3 therefore, B is :



$$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OCH_3}{|}}{C}}{-}CH_2CH_2NH_2$$

(B)

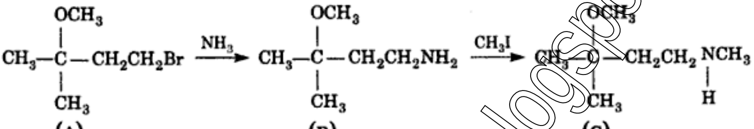
and D, is (R = -CH$_2$OH)



$$CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_2CH_2OH$$

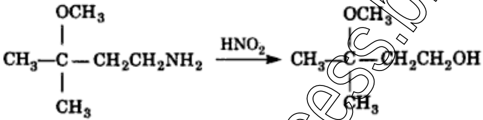
(D)

The reactions are as follows:



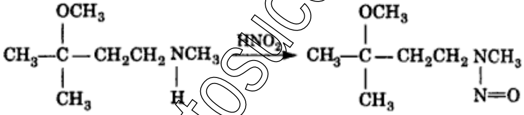
$$CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_2CH_2Br \xrightarrow{NH_3} CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_2CH_2NH_2 \xrightarrow{CH_3I} CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_2CH_2\underset{H}{N}CH_3$$

(A) (B) (C)



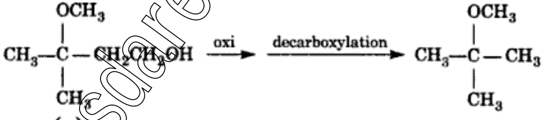
$$CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_2CH_2NH_2 \xrightarrow{HNO_2} CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_2CH_2OH$$

(B) (D)



$$CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_2CH_2\underset{H}{N}CH_3 \xrightarrow{HNO_2} CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_2CH_2\underset{N=O}{N}CH_3$$

(C)



$$CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_2CH_2OH \xrightarrow{oxi} \xrightarrow{decarboxylation} CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-CH_3$$

(D)

Problem 21.48:

An organic compound A, composed of C, H and O gives characteristic color with ceric ammonium nitrate. Treatment of A, with PCl$_5$ gives B, which reacts with KCN to form C. Reduction of C, with warm Na/C$_2$H$_5$OH produces D, which on heating gives E with the evolution of NH$_3$. Pyridine is obtained on treatment of E, with nitrobenzene. Give the structures of A to E with proper reasoning.

Solution: Compound A, gives a color with ceric ammonium nitrate, so it is an alcohol. Now A reacts with PCl$_5$ to give B which reacts with KCN to yield C. Therefore, B and C are chloride and cyanide respectively. C is reduced to an amine since D on heating gives E and evolves

CHAPTER

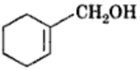
22

Organometallic Compounds

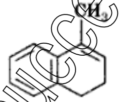
Problem 22.1:

Show how will you synthesize the following using an appropriate Grignard reagent ?

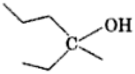
(a)



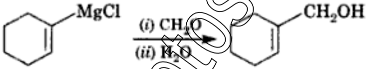
(b)



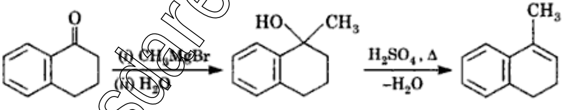
(c)



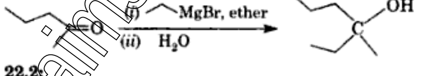
Solution: (a)



(b)



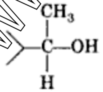
(c)



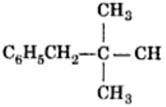
Problem 22.2:

Propose a synthesis for each of the following alcohols using two different Grignard reagents:

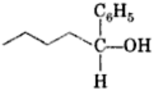
(a)



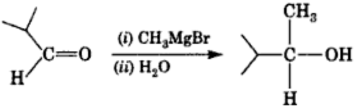
(b)

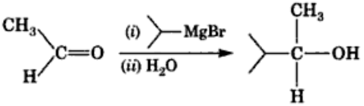

$C_6H_5CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH$

(c)

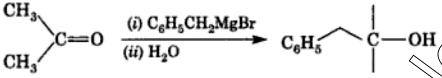


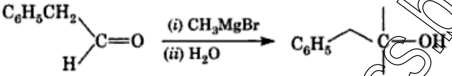
Solution: (*a*)



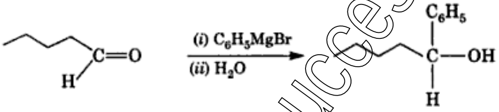


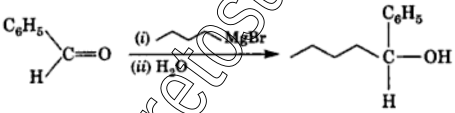
(*b*)





(*c*)



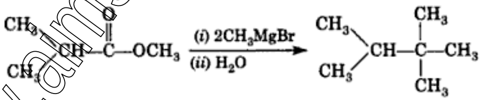


Problem 22.3:

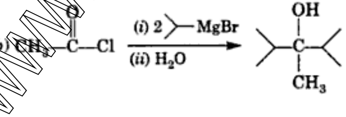
Show how would you use the addition of a Grignard reagent to an acid chloride and an ester to obtain the following alcohols:

(*a*) 2,3-Dimethyl-2-butanol (*b*) 2,3,4-Trimethyl-3-pentanol

Solution: (*a*)

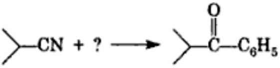


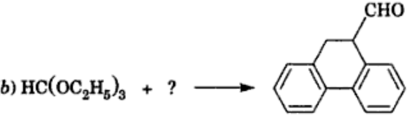
(*b*)

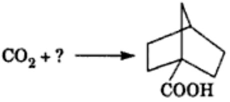


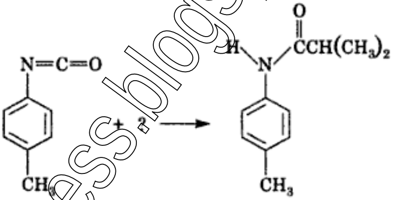
Problem 22.4:

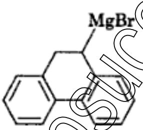
Suggest a suitable Grignard reagent to complete the following reactions:

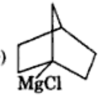
(*a*)


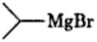
(*b*)


(*c*)


(*d*)


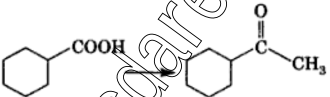
Solution: (*a*) C_6H_5MgBr (*b*)


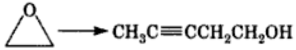
(*c*)


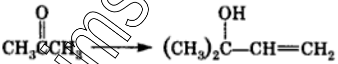
(*d*)


Problem 22.5

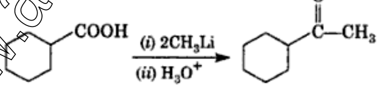
Effect the following conversions using appropriate organolithium reagents:

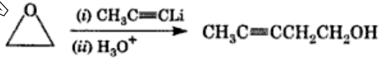
(*a*)


(*b*)


(*c*)


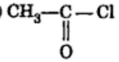
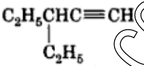
$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow (CH_3)_2\overset{OH}{\overset{|}{C}}-CH=CH_2$$

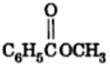
Solution: (*a*)


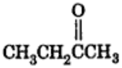
(*b*)


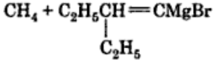
Problem 22.9:

Methylmagnesium bromide is combined with each of the following compounds and then with water. What products are obtained in each case?

(*a*) HBr (dry) (*b*)  $CH_3-C(=O)-Cl$ (*c*) CH_3CH_2CN (*d*) H_2CO (*e*)  $C_2H_5CH(C_2H_5)C\equiv CH$

(*f*)  $C_6H_5C(=O)OCH_3$ (*g*) C_2H_5OH (*h*) 

Solution: (*a*) CH_4 (*b*) $(CH_3)_3COH$ (*c*)  $CH_3CH_2C(=O)CH_3$ (*d*) CH_3CH_2OH

(*e*)  $CH_4 + C_2H_5CH(C_2H_5)-C\!=\!CMgBr$ (*f*) $C_6H_5COH(CH_3)_2$ (*g*) CH_4 (*h*) 2-Methylcyclopentanol.

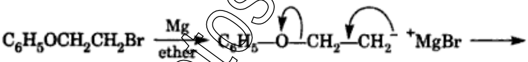
Problem 22.10

Suggest a mechanism for each of the following reactions:

$$(a)\ C_6H_5OCH_2CH_2MgBr \xrightarrow[-MgBr^+]{} C_6H_5O^- + H_2C{=}CH_2$$

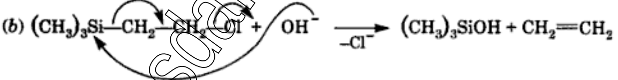
$$\xrightarrow{H_2O} C_6H_5OH + CH_2{=}CH_2 + Mg(OH)Br$$

$$(b)\ (CH_3)_3SiCH_2CH_2Cl + OH^- \xrightarrow[-Cl^-]{} (CH_3)_3SiOH + H_2C{=}CH_2$$

Solution: (*a*) 

$$C_6H_5OCH_2CH_2Br \xrightarrow[ether]{Mg} C_6H_5-O-CH_2-CH_2^-\ {}^+MgBr \longrightarrow$$

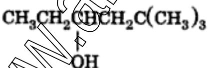
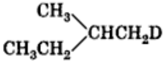
$$C_6H_5O^- + H_2C{=}CH_2 + MgBr^+ \xrightarrow{H_2O} C_6H_5OH + H_2C{=}CH_2 + Mg(OH)Br$$

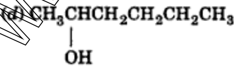
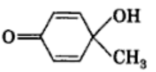
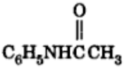
(*b*) 

$$(CH_3)_3Si-CH_2-CH_2-Cl + OH^- \xrightarrow[-Cl^-]{} (CH_3)_3SiOH + CH_2{=}CH_2$$

Problem 22.11:

Synthesize the following compounds starting from suitable reagents:

(*a*)  $CH_3CH_2CH(OH)CH_2C(CH_3)_3$ (*b*) $p\text{-}CH_3C_6H_4COOH$ (*c*) 

(*d*)  $CH_3CH(OH)CH_2CH_2CH_2CH_3$ (*e*)  (*f*)  $C_6H_5NHC(=O)CH_3$

Problem 22.17:

Give, in each case, write the reagent you would use to convert isopropyl magnesium bromide to the following compounds:

(*a*) $(CH_3)_2CHI$ (*b*) $[(CH_3)_2CH]_3P$ (*c*) $(CH_3)_2CHCOOH$ (*d*) $(CH_3)_2CHD$

(*e*) $(CH_3)_2CHCH{=}CH_2$ (*f*) $(CH_3)_2CHCH_2OH$

Solution: (*a*) I_2 (*b*) PCl_3 (*c*) CO_2 (*d*) D_2O (*e*) $CH_2{=}CHCH_2Br$ (*f*) HCHO

Problem 22.18:

How can Grignard reagents be prepared? What special precautions are to be taken into consideration? How can a Grignard reagent be used to prepare (*a*) propionic acid, (*b*) *n*-butyl alcohol, (*c*) trimethylcarbinol, (*d*) propionaldehyde.

Solution: A Grignard reagent can be prepared in a three-necked flask equipped with a mechanical stirrer, condenser and a dropping funnel. The reaction is initiated by treating magnesium turnings with an organic halide in ether. The reaction is carried out with complete exclusion of moisture.

(*a*) $CH_3CH_2MgBr \xrightarrow{CO_2} \xrightarrow{H_2O} CH_3CH_2COOH$

(*b*) $CH_3CH_2CH_2MgBr + H_2CO \xrightarrow{\text{ether}} \xrightarrow{H_2O} CH_3CH_2CH_2CH_2OH$

(*c*) $CH_3MgBr + CH_3COCH_3 \xrightarrow{\text{ether}} \xrightarrow{H_2O} (CH_3)_3COH$

(*d*) $CH_3CH_2MgBr + HC(OC_2H_5)_3 \xrightarrow{\text{ether}} \xrightarrow{H_2O} CH_3CH_2CHO$

Problem 22.19:

Offer explanation for the following:

(*a*) Why should Grignard reagent be prepared with the exclusion of moisture?

(*b*) Can an ester be used to prepare a ketone via the Grignard reaction?

(*c*) Does ferrocene display aromatic behavior?

Solution: (*a*) Because water gives rise to a hydrocarbon on reaction with a Grignard reagent.

(*b*) No, because a Grignard reagent reacts faster with the initially formed ketone.

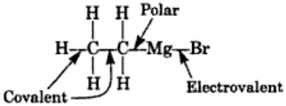
(*c*) Yes.

Problem 22.20:

Draw a formula for a Grignard reagent prepared from ethyl bromide showing

(*a*) An electrovalent bond (*b*) A polar bond (*c*) A covalent bond.

Solution:

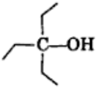


Problem 22.22:

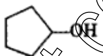
From what alkene and by which method would you prepare the following alcohol essentially free of constitutional isomers?

(*a*)

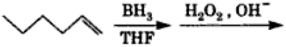
(*b*)



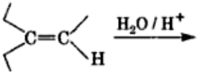
(*c*)



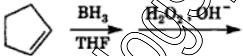
Solution: (*a*)



(*b*)



(*c*)



CHAPTER

23

Heterocyclic Compounds

Problem 23.1:

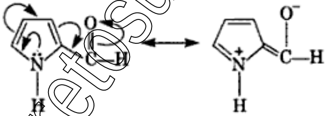
Why is pyrrole less basic than a secondary aliphatic amine ?

Solution: The lone pair on nitrogen in pyrrole forms a part of the aromatic sextet and are involved in resonance with the ring. These electrons are thus not available for donation as in a secondary amine.

Problem 23.2:

Why does pyrrole-2-carbaldehyde not undergo the Perkin reaction ?

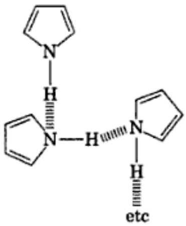
Solution: Pyrrole-2-carbaldelyde undergoes resonance with the ring. The nucleoplihicity of the carbonyl group thus diminishes for attack by the anion.



Problem 23.3:

Why does furan have a lower boiling point than pyrrole ?

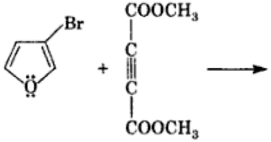
Solution: Pyrrole has a high boiling point because it is involved in intermolecular H-bond formation.



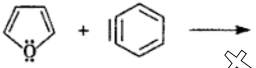
Problem 23.4:

Write the structures of the following Diels-Alder adducts :

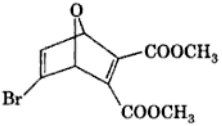
(*a*)



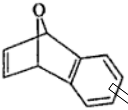
(*b*)



Solution: (*a*)



(*b*)



Problem 23.5:

Monobromination of thiophene-3-carboxylic acid gives only one product. What is its structure and why is it the only product formed ?

Solution: The hetero atom in the five-membered heterocyclic rings direct substitution to the 2-position. When substituents are already present on the ring than the usual directing effect as expected from benzene applies. In thiophene-3-carboxylic acid, the thiophene ring tends to substitute at the 2-position.

The -COOH group directs the incoming electrophile to the *meta*-position (as in benzene derivatives.

Note than we count around the ring of a heterocyclic compound, not through the hetero atom when using *o*, *m*- and *p*-analogy.

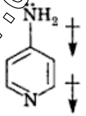
Thus both the effects superimpose on each other and the resultant product formed is 5-bromo-3-thiophenecarboxylic acid.

Problem 23.6:

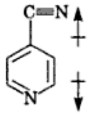
Which of the following pyridines have a larger dipole moment and why ?

4-Aminopyridine or 4-cyanopyridine ?

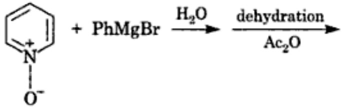
Solution:

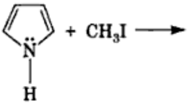


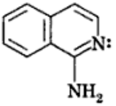
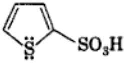
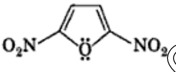
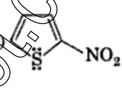
(4.4 D)

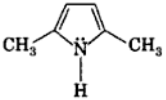
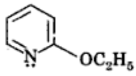
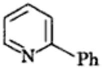


(1.6 D)

(h) 

(i) 

Solution: (a)  (b)  (c)  (d) 

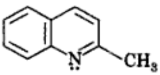
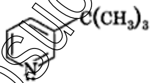
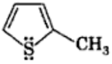
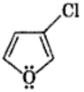
(e)  (f)  (g)  (h) 

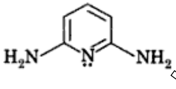
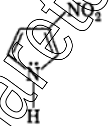
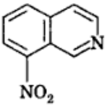
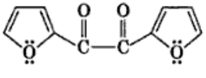
(i) N.R. because the HN: grouping is not nucleophilic.

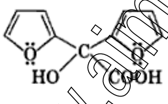
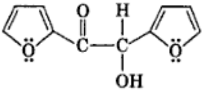
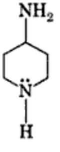
Problem 23.14:

Write structure formula for the following compounds:

(a) 2-Methylquinoline (b) β-t-Butylpridine (c) α-Methylthiophene (d) β-Chlorofuran (e) 2, 5-Diaminopridine (f) 3-Nitropyrrole (g) 8-Nitroisoquinoline (h) Furil (i) Furilic acid (j) Furoin (k) 4-Aminopiperidine

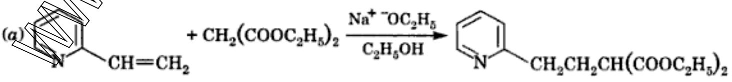
Solution: (a)  (b)  (c)  (d) 

(e)  (f)  (g)  (h) 

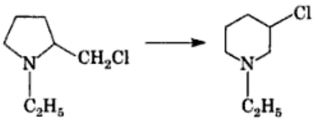
(i)  (j)  (k) 

Problem 23.15:

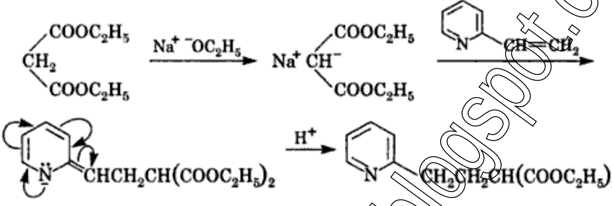
Propose mechanisms for the following reactions:

(a) 

(*b*)



Solution: (*a*)



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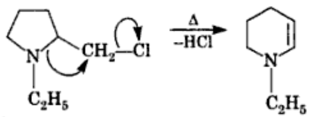
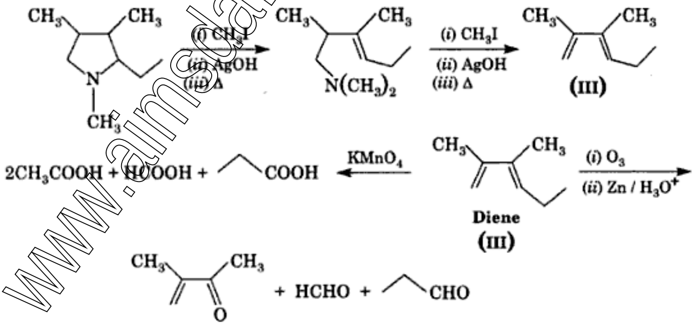


Problem 23.16:

A tertiary amine $C_9H_9N_7$, was subjected to Hofmann degradation to give an unsaturated amine. This amine on further Hofmann degradation yielded a diene C_8H_{14} and a tertiary amine. Oxidation of the diene with $KMnO_4$ led to formic, propionic and acetic acids in a molar ratio of 1 : 1 : 2. Ozonolysis of the diene lead to a mixture of HCHO, CH_3CH_2CHO and 2, 3-butadiene. Write the structures of all the unknown compounds.

Solution: A double bond is created in Hofmann degradation at position α-to nitrogen. Since two Hofmann degradations yield a diene, it follows that nitrogen forms a part of ring. Oxidation and ozonolysis tests suggest that the structural formula of diene is (III)



Problem 23.17:

Why does an electrophilic attack in quinoline take place on the benzene ring ?

Solution: Because the benzene ring has more electron density and the condensed pyridine ring is electron deficient.

Problem 23.18:

Although the 1- and 3-positions are both *ortho* to a 2-substituent in the naphthalene series, the two positions exhibit different chemical properties. Illustrate how a similar difference exists in the isoquinoline series, using an appropriate reaction. Offer an explanation for the difference.

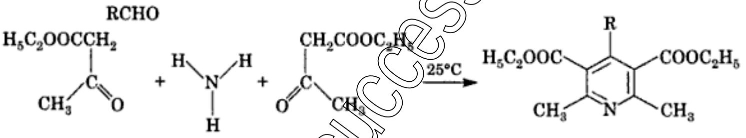
Solution: Position-1 is more reactive compared to position-3.

Problem 23.19:

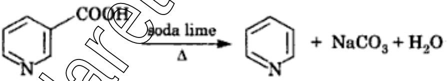
Describe two methods for the synthesis of pyridine. Compare and contrast its properties with that of benzene. Give the chief uses of pyridine.

Solution: Two methods for synthesis of pyridine are the :

(*i*) The Hantzsch synthesis : This involves the condensation of a β-ketone ester with an aldehyde in the presence of ammonia.



(*ii*) A laboratory preparation of pyridine includes the distillation of nicotinic acid with soda-lime (CaO + NaOH)



The electrophilic attack on pyridine takes place only under drastic conditions in contrast to benzene, in which this reaction takes place rather readily. This is due to the electron deficient pyriding ring. A nucleophilic attack on pyridine ring takes place with relative ease because of the dipolar resonating structures. Pyridine is used as a solvent because of its high solvation properties, as catalyst in acylation, in denaturing alcohol and in the manufacture of dyes.

Problem 23.20:

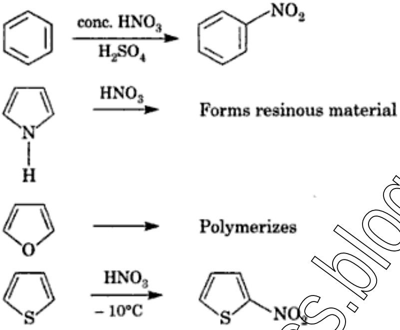
Compare the basicity of pyridine with that of pyrrole and justify your conclusion on the basis of their structures.

Solution: Pyrrole (pK_a 0.4) is virtually non-basic while pyridine (pK_a 5.2) is weakly basic though both are aromatic. The resonance energy of pyrrole is 21 kcal/mol and that of pyridine is 32 kcal/mol. The difference in basicity of the two aromatic systems is attributed to the fact that in pyrrole the electron pair on nitrogen atom is resonated with ring and thus not available for donation. In contrast pyridine has an aromatic sixtet and the extra electron pair on nitrogen atom is not conjugated with ring and thus available for protonation.

Problem 23.23:

Compare the action of nitric acid on benzene, pyrrole, furan and thiophene.

Solution:



Benzene and thiophene are more aromatic, therefore, can undergo electrophilic substitution with a strong acid.

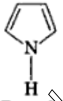
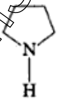
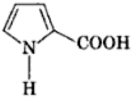
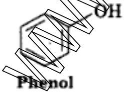
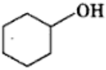
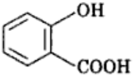
Problem 23.24:

Point out the differences and similarities in the properties of pyrrole and phenol.

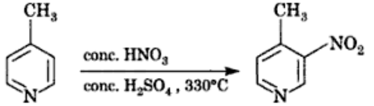
Solution: Differences :

Compound	*Basicity / acidity*	*Electrophilic substitution*	*Friedel-Crafts reaction*
Pyrrole	Virtually non-basic	Undergoes the reaction under milder conditions	Needs no catalyst
Phenol	Acidic	Normal reaction	Needs a catalyst

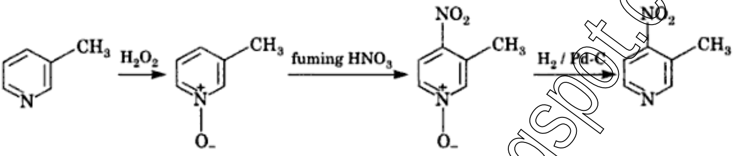
Similarities :

Compounds	*H_2, Ni*	*Kolbe reaction*	*Diazo coupling*
 Pyrrole			Couples with $C_6H_5N_2^+Cl^-$
 Phenol			Also couples with diazonium salt.

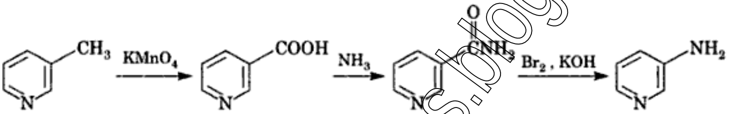
Solution: (*a*)



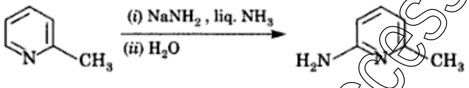
(*b*)



(*c*)



(*d*)



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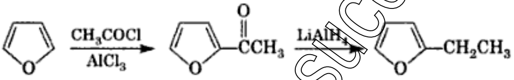

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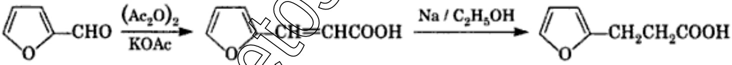
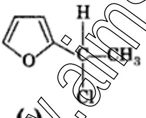
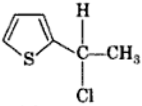


Problem 23.31:

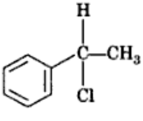
Rank the following compounds in order of decreasing reactivity towards S$_N$1 reaction. Explain your choice.



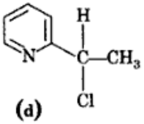
(a)



(b)



(c)



(d)

Solution: $c > b > d > a$

In case of compound (*c*) the carbocation is stabilized by resonance with the benzene ring. In other three cases the reactivity towards S$_N$1 reaction is decreased depending upon the electron-withdrawing effect of the heteroatom which is of the following order O > N > S.

Problem 23.32:

Rank the following in order of increasing reactivity towards nitration (HNO_3, H_2SO_4). Explain.

Quinoline, pyridine and quinoline-N-oxide.

Solution: The order of increasing reactivity is

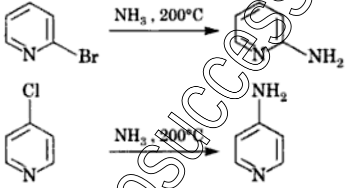
Pyridine < Quinoline < Quinoline-N-oxide

Pyridine is least reactive because it is highly deactivated towards electrophilic attack due to presence of the electronegative nitrogen atom. In quinoline the attack takes place on the benzene ring. Quinoline-N-oxide is most reactive because of the activating effect of the N–oxide group.

Problem 23.33:

Halogen located at the 2-or 4-positions in pyridine is highly reactive towards nucleophilic displacement. Account for this reactivity.

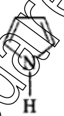
Solution: A halogen substituted pyridine resembles a halobenzene containing electron-withdrawing group. Therefore, the attack of nucleophile is easier on the halopyridine ring.

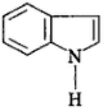


Problem 23.34:

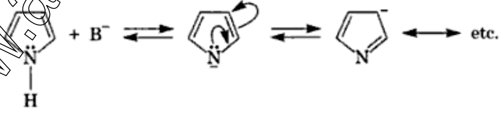
Pyrrole and indole are weak acids. Explain.

Solution:





Both pyrrole and indole have pk_a values of about 17.5 and are about as acidic as alcohols. The greater acidity of these two compounds is a consequence of the resonance stabilization of the conjugate base.

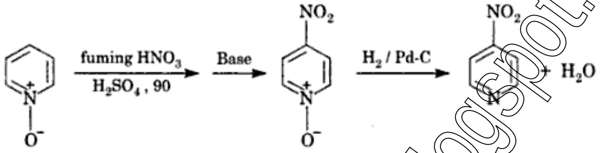


These are acidic enough to behave as acids towards basic organometallic compounds (RMgX).

Problem 23.35:

Electrophilic substitution of pyridine takes place predominantly at the 4-position. How can one obtain 4-pyridine derivatives ?

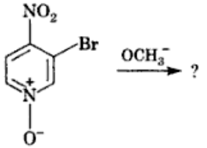
Solution: Pyridine N-Oxide is the compound to obtain 4-substituted derivatives of pyridine. The chemistry of pyridine N-oxide is similar to phenol. This compound undergoes useful aromatic substitution reactions and the N-oxide is finally removed.



Problem 23.36:

Nitro and halogen substituents can be displaced from pyridine N-oxide by reaction with nucleophiles. Which of the two would react more rapidly ?

(*a*)



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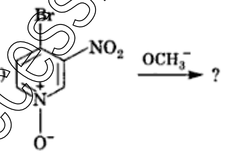
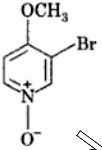
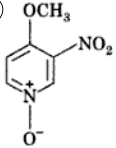


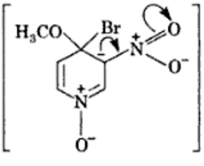
Solution: (*a*)



(*b*)



Compound (*b*) will react faster because the negative charge on the intermediate will be stabilized with the -NO_2 group.



CHAPTER

24

Carbohydrates

Problem 24.1:

Describe each of the following terms :

Mutarotation, a glycoside, a reducing sugar, pyranose, hemiacetal, amylose, anomers, glucoside, alditol, epimers and furanose.

Solution: Mutarotation. A change in optical rotation with time of a sugar in its hemiacetal form when it equilibrates with the other form to give an equilibrium mixture with an average value of optical rotation is called *mutarotation*.

A glycoside. A cyclic acetal or ketal form of sugar is called a *glycoside*. These are non-reducing sugars and stable to base. Glycosides are generally pyranosides and furnosides.

A reducing sugar. Any sugar that responds positively to Tollens' test (silver ammonia complex) $[Ag(NH_3)^+]$ is reducing.

Pyranose. A cyclic form of a sugar (hemiacetal or hemiketal) that has six-membered ring is a *pyranose*.

Hemiacetal. The product of addition of an alcohol molecule to an aldehyde catalyzed by acid is called *hemiacetal*. *i.e.* an -OH and -OC_2H_5 groups are attached to the same carbon atom.

Amylose. Starch is a mixture of two types of glucose polymers. If the glucose residues are linked by α-1, 4-linkages then it is called *amylose*.

Anomers. The α- and β-forms of D-glucose are optical isomers, they are diastereoisomers but not enantiomers because the α-form of glucose in not the mirror image of the β-form. They are known as *anomers*. They differ only in the configuration about the C—1 chiral carbon atom.

Glucoside. A glycoside (acetal) formed from D-glucose on treatment with methanol and HCl is called *glucoside*.

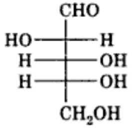
Epimers. Two diastereoisomeric sugars differing only in the configuration at a single chiral carbon atom are called *epimers*. Thus D(+)-glucose is a C—4 epimer of D(+)-glucose ; D(+)-glucose is also a C—2 epimer of D(+)-mannose.

Alditol. A polyalcohol formed by reduction of the carboxyl group of a monosaccharide is called an *alditol*. For example, D(+)-glucose on reduction $(NaBH_4)$ yields an alditol (D-glucitol). Similarly D(+)-fructose on reduction results in D-glucitol.

Problem 24.2:

D-arabinose (a pentose) is *levo* rotatory. Draw its structure.

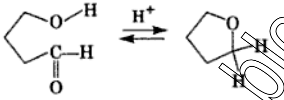
Solution: D indicates the absolute configuration as for D-(+)-glyceraldehyde. It is *levo* because it rotates the plane of polarized light to the left.



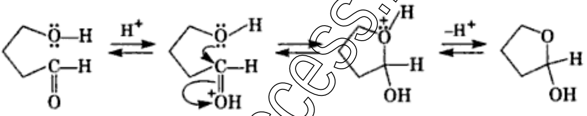
D-(–)-Arabinose

Problem 24.3:

Show the formation of the hemiacetal from 4-hydroxypentanal.



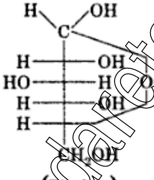
Solution:



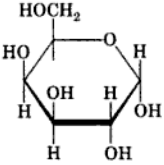
Problem 24.4:

Draw Fischer projection and Haworth representation of α-D-glucopyranose.

Solution:



(Fischer)



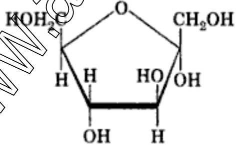
(Haworth)

In the Haworth formula the substituents are placed on a simple planar hexagon.

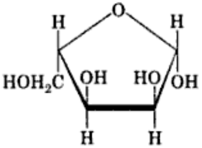
Problem 24.5:

Name the following structures:

(*a*)



(*b*)



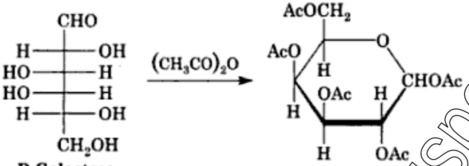
Solution: (*a*) α-D-fructofuranose (*b*) β-L-ribofuranose

Problem 24.6:

Write the reaction of D-Galactose with each of the following reagents:

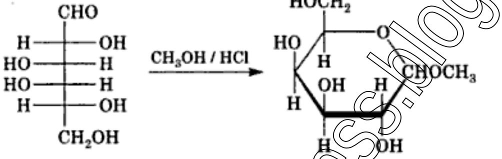
(*a*) $(CH_3CO)_2O$ (*b*) CH_3OH/HCl (*c*) $(CH_3)_2SO_4$, NaOH

Solution: (*a*)

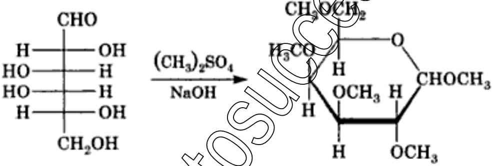


D-Galactose

(*b*)



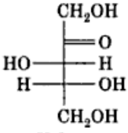
(*c*)



Problem 24.7:

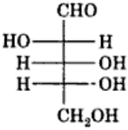
Define each of the following and give a specific example and write the structural formula : A ketose, pentose, osazone, disaccharide, hexose, and a deoxy sugar.

Solution: Ketose. A monosaccharide containing a keto group.



Xylose

Pentose. A monosaccharide containing five carbon atoms.



D-(–)-Arabinose

3. **Presence of an Aldehyde Group.** The presence of an aldehyde function has been based on several chemical reactions:

(*a*) Glucose reacts with HCN and H_2NOH in the same manner as aldehydes do.

(*b*) The aldehyde group is oxidized by bromine water to a carboxyl function.

(*c*) Glucose also responds to Fehling and Tollens tests.

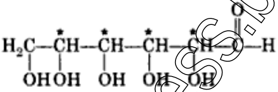
The formation of an acid further indicates that the aldehyde group is present at the terminal carbon atom since only an aldehyde can be easily oxidized to an acid.

4. With acetic anhydride, glucose yields a pentaacetate derivative.

$$\underset{\textbf{Glucose}}{C_6H_7O(OH)_5} + 5(CH_3CO)_2O \longrightarrow \underset{\textbf{Glucose pentaacetate}}{C_6H_7O(CH_3COO)_5} + 5CH_3COOH$$

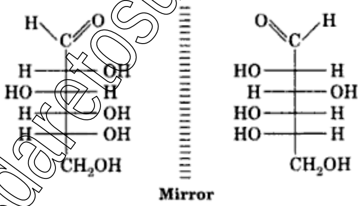
This shows the presence of five hydroxyl groups in glucose molecule. Since two —OH groups, if present on the same carbon atom, lose a molecule of water, knowing glucose to be stable indicates that each of the five non-aldehydic carbon atom contains one hydroxyl group.

From the above information, the following structure can be formulates for glucose.



$$\underset{OH}{H_2C}-\underset{OH}{\overset{*}{C}H}-\underset{OH}{\overset{*}{C}H}-\underset{OH}{\overset{*}{C}H}-\underset{OH}{\overset{*}{C}H}-\overset{O}{\overset{\|}{C}}-H$$

This structure was proposed by the great German chemist E. Fischer. The above molecule is chiral, it contains four asymmetric carbon atoms, therefore, it has $2^4 = 16$ stereoisomers. These can be divided into two enantiomeric sets of eight diastereoisomers. The two enantiomers of glucose have the following structures.



Cyclic Structure of Glucose. Though the open-chain structure accounts for many properties of glucose, it fails to accommodate the following observations:

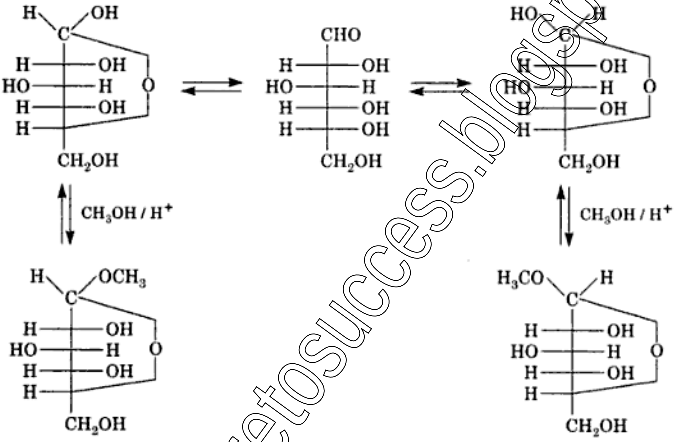
(*a*) Glucose contains a - CHO group but it does not react with $NaHSO_3$ as aldehydes do.

(*b*) Two isomeric glucosides (α and β) can be obtained by heating D-glucose with methanol and a mineral acid, which no longer form osazones or reduce Fehling solution.

(*c*) D-Glucose displays mutarotation, *i.e.*, when dissolved in water, its specific rotation changes from + 113° to an equilibrium value of + 52.5°. For L-Glucose, the value rises from 19° to 52.7°.

Tollens (1863) concluded that the simple sugars do not exist in the form of straight chain aldehydes and ketones but as ring structures. There are two lines of evidence to support a cyclic structure.

First. As discussed earlier, on treatment of glucose with methanol and HCl a molecule of water was eliminated but only one methyl group was introduced. But two isomeric products are formed. These two compounds no longer reduce Fehling's solution or form osazones. Moreover, they behaved like acetals in that they were readily hydrolyzed in acid solution, but were stable to alkali. This behavior is explainable if it is assumed that the aldehyde group of sugar first reacts with a –OH group in the chain to given an internal cyclic hemiacetal. The hemiacetal subsequently reacts with methanol to form the acetal. Since a new chiral carbon atom is produced in this process, two diastereoisomers are formed and in unequal amounts (the α- and β-forms of glucose are optical isomers but they are not enantiomers).



Methyl-α-D-glucose **Methyl-β-D-glucose**

These cyclic acetals and ketals of carbohydrates are called glycosides.

These glycosides are designated α and β. The –OH in the α-form is written to the right while in the β-form it is to the left. Isomers of these type are called *anomers,* and the carbon atom responsible for the existence of anomers is known as *anomeric carbon atom.*

Diastereoisomeric sugars that differ in configuration only at the C—1 chiral carbon (as a result of cyclization to a hemiacetal) are called *anomers.*

Anomeric sugars give the same osazone.

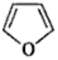
Second. Another indication of the cyclic nature of glucose comes from the observation of another phenomenon known as mutarotation.

According to this the two forms of glucose D- and L-attain an equilibrium value of optical rotation when dissolved separately in water even though they have different initial values. The explanation of mutarotation is that the sugar exists in solution as a mixture of two ring forms in equilibrium with a comparatively small proportion of glucose in the open-chair or aldehydic form. The cyclic structure thus can be represented as above.

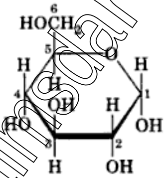
Although the Fischer projection formulas are accurate they are somewhat cumbersome to draw. The English chemist W.H. Haworth proposed that the cyclic form of carbohydrates be represented in another manner that emphasizes their structural relationship to furan and pyran.

If the aldehyde group and the hydroxyl group are part of the same molecule a cyclic hemiacetal results. These cyclic hemiacetals are particularly stable if they lead to the formation of a five-or-six-membered ring, for instance:

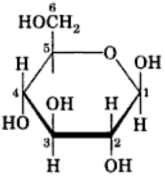
Aldoses and ketoses contain both a carbonyl group and several hydroxyl groups, therefore, both five- and six-membered ring hemiacetals and hemiketals are formed. The names of these cyclic forms of sugars are based on the unsaturated heterocyclic ethers furan and pyran. A five membered ring hemiacetal is a *furanose* (after furan), and the six-membered-ring analog is a *pyranose* (after pyran).



In aqueous solution simple sugars exist almost entirely in the cyclic form. Haworth described the structure by putting the substituents on a simple planar hexagon. In this structure, the oxygen atom is always placed at the right rear position with C-1 located at the extreme right of the structure. The thicker lines at the bottom of the Haworth formula represent those atoms of the hexagon which are nearer to the reader. The substituents on the carbon atoms extend below and above the plane of the six-membered ring. These are called the *Haworth projection formulas* and are known as pyranose because of the presence of a pyran ring. α-D-glucose is thus called α-D-glucopyranose and β-D glucose is called β-D-glucopyranose.



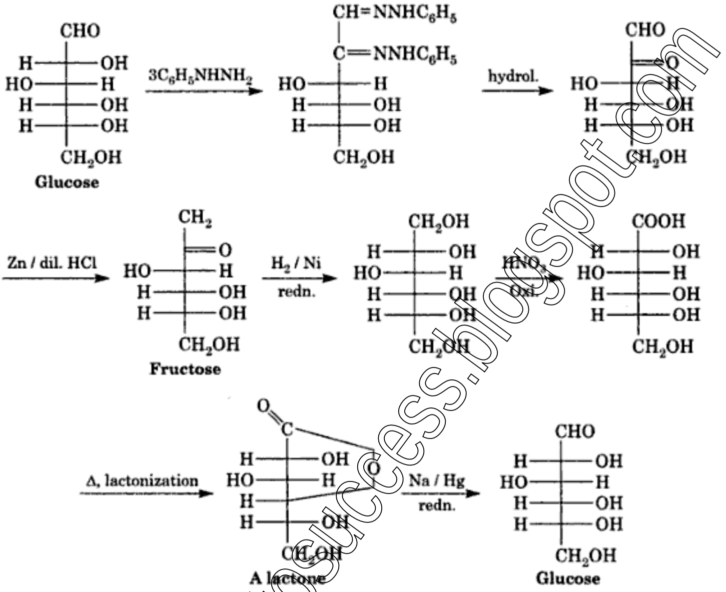
α-D-Glucopyranose



β-D-Glucopyranose

The assignment of the cyclic structure also explains the formation of two different glucosides on reaction with methanol.

Conversion of Glucose into Fructose and vice versa. These conversions can be brought about by the following sequence of reactions:



Problem 24.19:

Describe the evidence which indicates a cyclic structure for fructose.

Solution: The following three process of evidence support a cyclic structure for fructose.

(*i*) Fructose does not add $NaHSO_3$ as ketones do. (*ii*) Fructose shows mutarotation. (*iii*) Fructose forms anomeic fructoside.

Problem 24.20:

Why is mutarotation catalyzed by hydroxypyridine but not by pyridine alone.

Solution: Because the hydroxypyridine molecule behaves both as an acid and a base.

Problem 24.21:

How do the R, S- and D, L-systems of nomenclature differ?

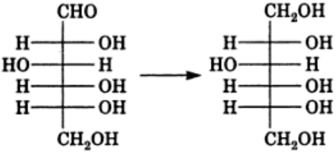
Solution: The D, L-system specifies the configuration of only the highest-numbered chiral carbon atom. According to the RS-system, the configuration of the individual carbon atoms is specified. There is no necessary simple relationship between the two systems.

Problem 24.22:

Name all hexoses which would be expected to give the same osazone.

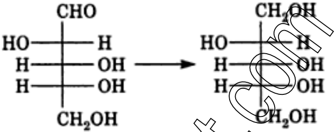
Solution: D-glucose, D-fructose and D-mannose.

(*b*)



D-Glucose

(*c*)

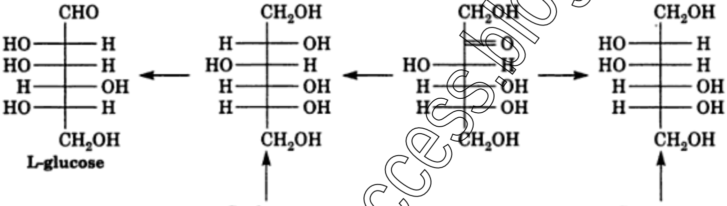


D-Arabinose

Problem 24.26:

Reduction of D-fructose would yield two epimeric alditols. Which aldose would yield these two ?

Solution:



Problem 24.27:

The anomers of α- and β-glucopyranose are formed in equal amounts. True or False. Explain.

Solution: False. They are formed in unequal amounts because the two diastereoisomers differ in their stabilities.

Problem 24.28:

Reduction of D-ribose with $NaBH_4$ gives a product without optical activity. Why ?

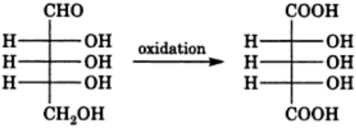
Solution: The reduction product is ribitol which is a *meso* compound.

Problem 24.29:

How will you convert ?

(*i*) **D (+) Glucose into D (–) Fructose** (*ii*) **D (+) Mannose into D (–) Arabinose.**

Solution: (*i*) D (+) Glucose into D (–) Fructose



D-(+) Glucose

(B)

Problem 24.36:

Would you expect

(*a*) Lactose to mutarotate (*b*) Sucrose to mutarotate

Solution: (*a*) Yes, because there is a hemiacetal present in its structure. (*b*) No, because there is no hemiacetal rather an acetal is present in its structure.

Problem 24.37:

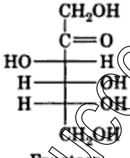
Suggest a reason that glucose reacts with only one mole of methanol in HCl.

Solution: Glucose exists as an hemiacetal.

Problem 24.38:

(*a*) State the number of chiral centers present in (–) fructose. (*b*) How many stereoisomers of two ketohexoses are possible ? (*c*) Draw Fisher projection formula of one enantiomer of each pair, placing C=O near the top, and —OH on the right on the lowest chiral center (C-5).

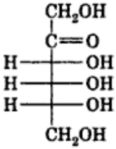
Solution: (*a*) Three chiral centers:



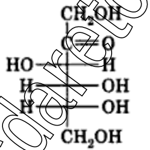
Fructose

(*b*) There should be eight 2-ketohexoses ($2^3 = 8$) possible : four pairs of enantiomers.

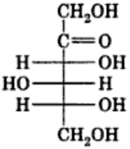
(*c*)



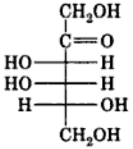
Psicose



Fructose



Sorbose

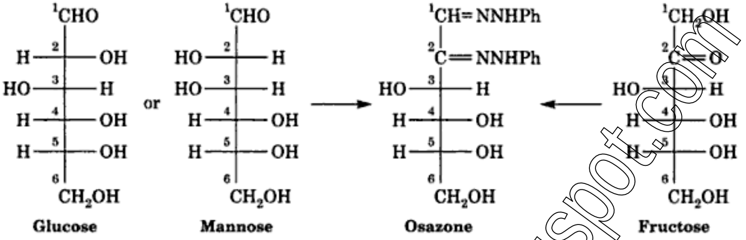


Tagatose

Problem 24.39:

When ketohexose, (–)-fructose is treated with phenyl-hydrazine, it yields an osazone that is identical with the one prepared from either (+)-glucose or (+)-mannose. How is the configuration of (–)-fructose related to those of (+) glucose and (+)-mannose ?

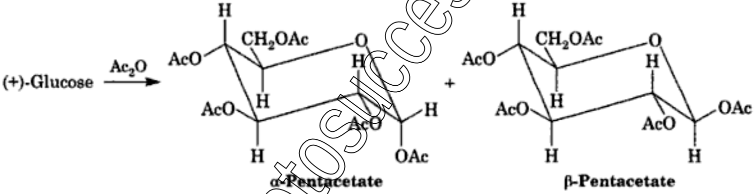
Solution: All three sugars have identical configuration at C-3, C-4 and C-5.



Problem 24.40:

(+)-Glucose on treatment with acetic anhydrides leads to two isomeric pentaacetyl derivatives neither of which reduces Tollens' or Fehling's reagent. Account for these observations.

Solution: Acetylation of D-glucose does not lead to an open-chain aldehyde derivative with acetate groups present at C-2 through C-6. The products, instead are cyclic. Furthermore acetylation occurs at C-1 but not at C-5 to give α- and β-forms.



Problem 24.41:

What is starch ? Describe its uses ?

Solution: The most important and the best known food storage polysaccharide is starch. Starch is a polymer of glucose and occurs in two forms—amylose and amylopectin. The relative amounts of the two forms vary considerably. Amylose is a linear polymer of glucose joined together by α, 1-4-glycosidic linkages. Amylopectin is a branched polymer. The chain has the same α-1, 4-linkages as amylose. Amylopectin is larger in size.

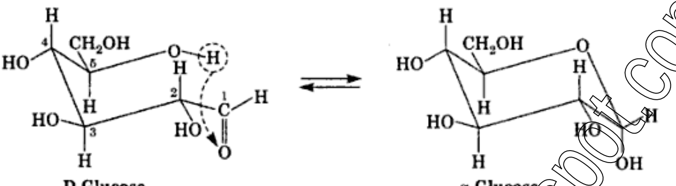
The starches are found in many plant with each plant having its characteristic starch. They are present usually in the seeds and fleshy root plants. They are obtained commercially from corn (75%), potatoes (20%), wheat (65%), rice (75%) and arrow-root in large quantities.

The starches are used in confectionary, chewing gum, baking powder, laundry, textiles, explosives, cosmetics, paper sizing, brewing and adhesives. Starch is also used in the preparation of glucose by hydrolysis.

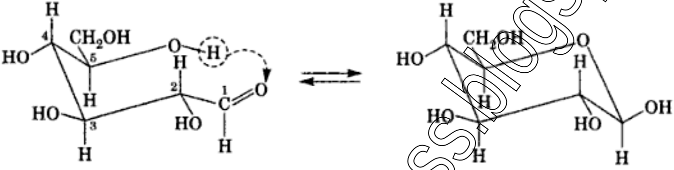
Problem 24.42:

By drawing pertinent structures, show how the cyclic structures of glucose is formed ? Express these structures into Haworth and pyranose forms.

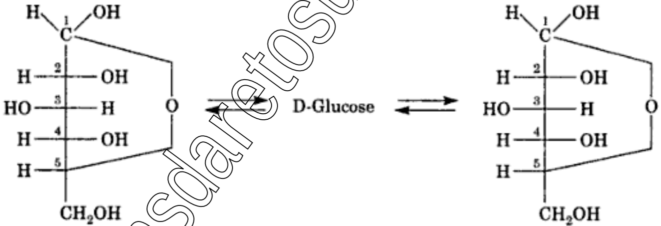
Solution: Mutarotation is explained on the basis of two ring forms in equilibrium with a comparatively small proportion of glucose in the open-chain or the aldehydic form. Ring closure can result easily through intramolecular acetal formation with the hydroxyl group at C-5 is brought into close proximity to the carbonyl group. It should be noted that two different modes of addition are possible. The C-1 in each of the cyclic hemiacetal structures shown represents a new asymmetric center and two diastereomisoners are thus possible.



D-Glucose α-Glucose

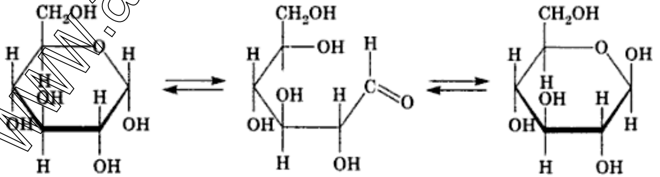


D-Glucose β-Glucose



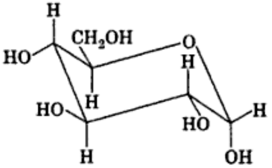
α-D-Glucopyranose β-D-Glucopyranose

The Haworth formula of the two cyclic forms of glucose are drawn as a planar hexagonal slabs with darkened edge towards the viewer

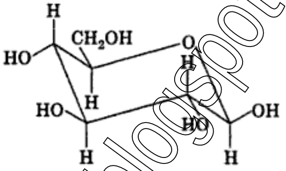


Hydroxyl groups and hydrogens are shown either above or below the plane of the hexagone.

The pyranose representation of the cyclic forms of glucose indicates a structure similar to the six-membered heterocyclic pyran. A furanose designation for a sugar indicates a five-membered ring with a structural relationship to the heterocycle furan. When drawn in the chair conformation, they have the most stable conformation because all substituents are equatorial.



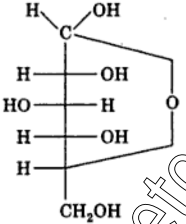
α-D-Glucose



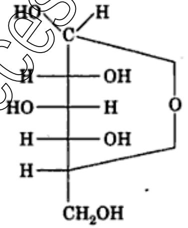
β-D-Glucose

Problem 24.43:

Are the following two forms of D-glucopyranose, epimer or anomer ?



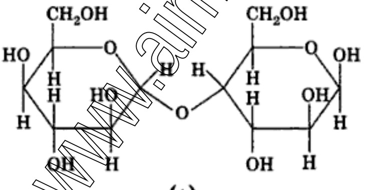
and



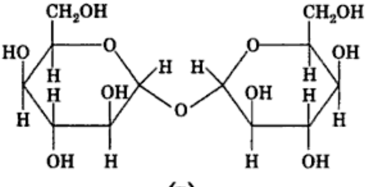
Solution: These structures are anomers because they differ in the stereochemistry at C—1.

Problem 24.44:

Define a hemiacetal and an acetal. Give one example of each. Show how a cyclic hemiacetal is formed. Will the sugar be reducing or non reducing if one of the rings in a disaccharide is in a hemiacetal form ? Classify the following sugars into reducing and non reducing.

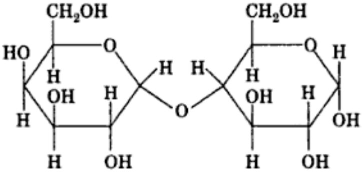


(A)



(B)

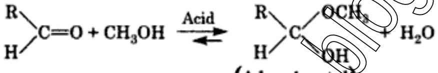
and



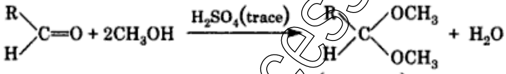
(c)

Solution: A *hemiacetal* is a compound in which an -OH and -OR groups are attached to the same carbon atom.

An *acetal* is a compound in which two ether oxygens are linked to the same carbon atom.



(A hemiacetal)



(An acetal)

A cyclic hemiacetal is formed by an intramolecular reaction of a hydroxyaldehyde. For instance, 5-hydroxypentanal exists predominantly in the hemiactal form.

Hemiacetals can be hydrolyzed to aldehydes and ketones by acids as well as bases. The sugar will be reducing (gives positive test with Fehling's solution and Tollens' reagent) because it is part of a hemiacetal group of monosaccharides and can be hydrolyzed to an aldehyde.

For the above reasons A and C are reducing and B is non-reducing, because both A and C have a free hemiacetal group.

CHAPTER

25

Amino Acids, Peptides and Proteins

Problem 25.1:

Define the following terms :

A prosthetic group, a conjugated protein, a dipeptide, enzyme. Edman degradation, terminal residue analysis, isoelectric point, α-helix, primary, secondary and tertiary structures of a protein and electrophoresis.

Solution: A Prosthetic Group. A *prosthetic group* is the non-protein part of a conjugated protein such as nucleic acids, sugars.

Conjugated Protein. A *conjugated protein* is one which yields α-amino acids and one or more groups of nonprotein nature.

A Dipeptide. A peptide which yields two α-amino acids on hydrolysis is a *dipeptide*.

Enzyme. *An enzyme* is a protein that is synthesized in a living cell and catalyzes or speeds up a thermodynamically possible reaction so that the rate of the reaction is compatible with the biochemical process essential for the maintenance of a cell. Reaction of an enzyme is specific and stereoselective. The products obtained are enantioselective. An enzyme reaction is affected by heat, concentration and pH.

Edman Degradation. A method for removing one amino acid residue at a time from the end of the peptide (N-terminal) and identifying the residue without destroying the rest of the chain is called *Edman degradation*. In this method the peptide is treated with phenyl isothiocyanate followed by a mild acid hydrolysis to convert the N-terminal amino acid into its phenyl hydantoin derivative.

Terminal Residue Analysis. Sequencing of α-amino acids in a peptide by removing and identifying the residue at the N-terminal or at the C-terminal is termed as the *terminal residue analysis*.

Isoelectric Point. The pH at which the concentration of the dipolar ion form of an amino acid is maximum is called the isoelectric point.

α-Helix. It is a coiled secondary structure of a protein. In this structure the protein has a chain of repeating amino acid units wound into a spiral chain which is held together by hydrogen bonds between each carbonyl group and N—H hydrogen.

Primary Structure of a Protein. The covalently bonded sequencing of amino acids in a protein is referred to as the *primary structure*.

Secondary Structure. The hydrogen bonded arrangement of a protein is the *secondary structure*. It constitutes α-helix, pleated sheet or random coil.

Tertiary Structure. A structure resulting from the interaction of secondary structures to form larger aggregates.

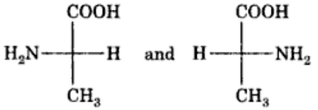
Electrophoresis. It is an important technique for separating amino acids and proteins by observing their migration under the influence of an electric field.

Problem 25.2:

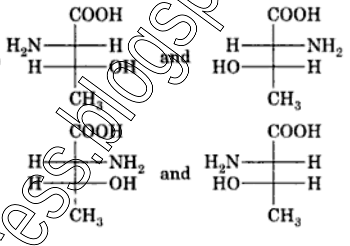
Write configuration formulas for all the stereoisomers corresponding to (*a*) alanine and (*b*) threonine.

Solution: For alanine only two stereoisomers *d* and *l* are possible. In threonine since there are two chiral carbons, four stereoisomers are possible.

(*a*)



(*b*)

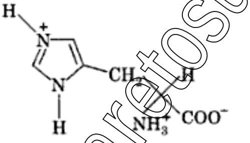


Problem 25.3:

Draw the structures of two amino acids that are:

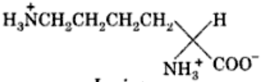
(*a*) Positively charged at neutral pH. (*b*) Negatively charged at neutral pH.

Solution: (*a*) (*i*)



Histidine

(*ii*)

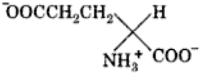


Lysine

(*b*) (*i*)

Aspartic acid

(*ii*)



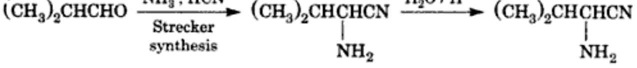
Glutamic acid

Problem 25.4:

Write the necessary chemical reactions to show how each of the following transformations can be carried out:

(*a*) Isobutyraldehyde to valine (*b*) Toluene to phenylalanine

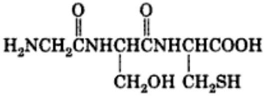
Solution: (*a*)



$$(CH_3)_2CHCHO \xrightarrow[\text{Strecker synthesis}]{NH_3\text{ , }HCN} (CH_3)_2CH\underset{\displaystyle NH_2}{\underset{|}{C}}HCN \xrightarrow{H_2O\,/\,H^+} (CH_3)_2CH\underset{\displaystyle NH_2}{\underset{|}{C}}HCN$$

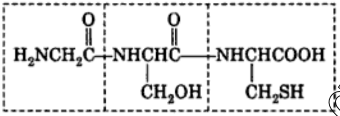
Problem 25.6:

Name the following tripeptide:



$$\mathrm{H_2NCH_2\overset{O}{\overset{\|}{C}}NH\underset{CH_2OH}{\underset{|}{C}H}\overset{O}{\overset{\|}{C}}NH\underset{CH_2SH}{\underset{|}{C}H}COOH}$$

Solution:



$$\mathrm{H_2NCH_2\overset{O}{\overset{\|}{C}}\!-\!NH\underset{CH_2OH}{\underset{|}{C}H}\overset{O}{\overset{\|}{C}}\!-\!NH\underset{CH_2SH}{\underset{|}{C}H}COOH}$$

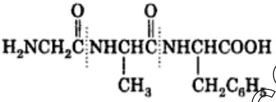
Name : Glycylserylcysteine

Problem 25.7:

Write the structure of the following tripeptides:

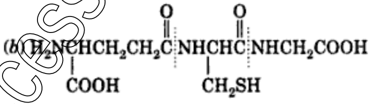
(*a*) Gly. Ala. Phe. (*b*) Glu. Cys. Gly.

Solution: (*a*)



$$\mathrm{H_2NCH_2\overset{O}{\overset{\|}{C}}NH\underset{CH_3}{\underset{|}{C}H}\overset{O}{\overset{\|}{C}}NH\underset{CH_2C_6H_5}{\underset{|}{C}H}COOH}$$

(*b*)

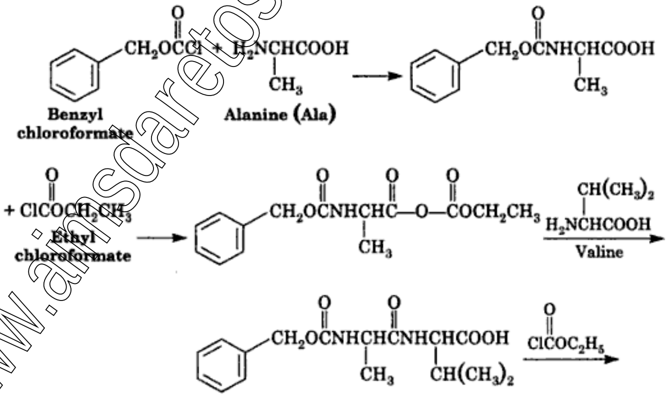


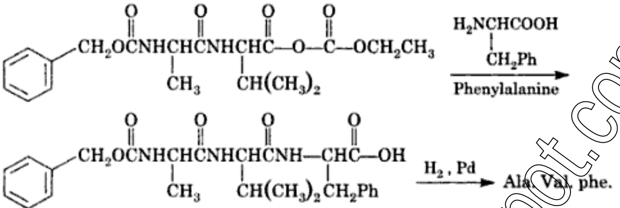
$$\mathrm{H_2N\underset{COOH}{\underset{|}{C}H}CH_2CH_2\overset{O}{\overset{\|}{C}}NH\underset{CH_2SH}{\underset{|}{C}H}\overset{O}{\overset{\|}{C}}NHCH_2COOH}$$

Problem 25.8:

Show all the steps for the synthesis of tripeptide Ala. Val. Phe.

Solution:



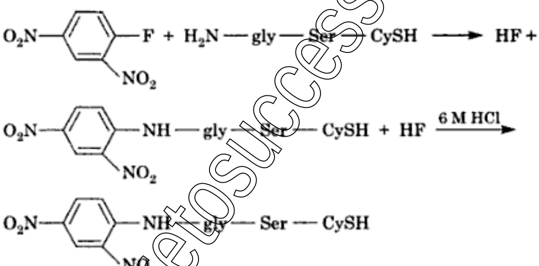


Problem 25.9:

Establish the structure of the tripeptide gly. Ser. CyS by terminal residue analysis.

Solution: Tripeptide—Gly. Ser. CyS

A complete hydrolysis of the peptide will tell that I mol each of glycine, serine and cysteine is present. The tripeptide is treated with DNFB, and then hydrolyzed with 6M HCl. The N-terminal amino acid is recovered and identified.



This will establish that the N-terminal amino acid is glycine. The remaining chain is now treated with the enzyme *carboxypeptidase*. This cleaves the C-terminal peptide bond. The products are the free C-terminal amino acid and the third amino acid. In this manner the structure of the tripeptide is established. The structure of peptide must thus be gly. ser. CySH

Problem 25.10:

Write names of (*a*) any two naturally occurring neutral α-amino acids (*b*) any two naturally occurring basic α-amino acids (*c*) any two naturally occurring acidic α-amino acids.

Solution: (*a*) Alanine and leucine (*b*) Aspartic acid and glutamic acid (*c*) Lysine and histidine.

Problem 25.11:

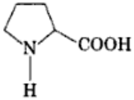
In an alkaline solution, glycine, $H_2NCH_2COO^-$ has two basic groups. What products would form on the addition of 1 equivalent of acid ? 2 equiv ? and 3 equiv ?

Solution: (*a*) $H_3\overset{+}{N}CH_2COO^-$ (*b*) H_2NCH_2COOH (*c*) $H_3\overset{+}{N}CH_2COOH$

Problem 25.12:

A naturally occurring amino acid forms a monoacetyl derivative with excess acetic anhydride, but treatment with nitrous acid yields no nitrogen. Suggest a structure for this compound.

Solution: Since the amino acid forms a monoacetyl derivative, therefore, it contains an amino group. The acid does not react with nitrous acid, therefore, it is a secondary amino group. The acid is proline. It is a secondary amine and the amino nitrogen is part of a five-membered ring.



Problem 25.13:

How will you distinguish between the following pairs chemically ?

(*a*) Serine and threonine (*b*) Glycine ethyl ester and valine (*c*) Phenylalanine and acetylphenylalanine (*d*) Aspartic acid and malic acid

Solution: (*a*) Threonine gives iodoform test (*b*) Glycine ethyl ester is alkaline towards litmus (*c*) Acetyl phenylalanine is insoluble in dil. HCl. (*d*) Aspartic acid evolves CO_2 on reaction with sod. bicarbonate.

Problem 25.14:

Why does proline give a yellow colour toward ninhydrin ?

Solution: Ninhydrin reacts with α-amino acids to give a purple color. According to the mechanism, a nitrogen of the amino acid is incorporated between two molecules of ninhydrin. Proline and 4-hydroxyproline are 2° amines and give different adducts that absorb hight at different wavelength and thus give yellow color.

Problem 25.15:

Why is it necessary to protect the amino group of α-amino acids in polypeptide synthesis?

Solution: The problem of making peptides is complicated by the fact that all α-amino acids are bifunctional compounds. Thus, while we may wish to carry out a reaction on only one functional group, we may inadvertently carry out a reaction on the other as well. Therefore, in order to avoid a reaction taking place at the second functional group, the amino group is protected.

Problem 25.16:

State giving equations, the chemical properties of amino acids in which :

(*a*) Only an amino group is involved. (*b*) Only a carboxyl group is involved. (*c*) Both the groups are involved.

Solution: (*a*) Acetylation reaction. (*b*) Esterification reaction. (*c*) Heating of the amino acid.

Problem 25.17:

(*a*) What are proteins. How are amino acids related to them ? Describe the important properties and reactions of proteins. (*b*) Describe the methods of preparing pure amino acids. State the behavior of α, β-and γ-amino acids on heating.

Solution: *Proteins* are complex organic molecules containing nitrogen as well as carbon, hydrogen, oxygen and sulfur. They are present in cytoplasm as well as in the cell membrane of all cells without exception. Proteins occur in every part of plant and animal organisms and are major constituent of skin, hair, muscle, blood, nails, horns, etc. In plants they are principally found in seeds. The hydrolysis of proteins gives rise to amino acids hence proving that the amino acids are the constituents of proteins.

Proteins exhibit the following properties:

(1) **Molecular weights of proteins.** The molecular weight of proteins vary from few thousands to several millions.

(2) **Amphoteric nature of proteins.** The protein molecules like amino acid exist as zwitterion in solution.

(3) **Viscosity of protein solutions.** Solutions of fibrous proteins are highly viscous compared to globular proteins like albumin.

(4) **Hydration of proteins.** Protein molecules swell up when brought in contact with water.

(5) **Precipitation of proteins.** Precipitation of proteins can be brought about by salting out or by addition of alcohol or acetone.

(6) **Heat coagulation of proteins.** Most proteins when heated in solution become insoluble and get precipitated in the form of coagulum.

(7) Strong acids and alkalies, alcohols, acetone, concentrated solutions of urea and salicylates, exposure to *u.v.* rays or X-rays and even vigorous mechanical shaking can bring about denaturation of proteins.

Chemical properties of properties are as follows:

(1) Proteins form salts with bases : Casein, for instance, is present in milk as its calcium salt.

(2) On acid or enzymatic hydrolysis of proteins, amino acids are formed. Digestive enzyme hydrolyze proteins to peptides and amino acids which are absorbed and transported by blood to various body tissues.

(3) Proteins respond to several color tests:

(*a*) With ninhydrin, a purple color is produced

(*b*) Million's reaction yields a pink color.

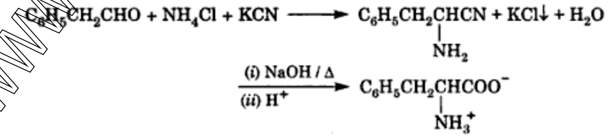
(*c*) A yellow color is obtained with iodine

(*d*) Red color in Sakaguchi reaction

(*e*) Red color with sodium nitroprsside and Tollens' reagent.

The methods of preparation of amino acids are

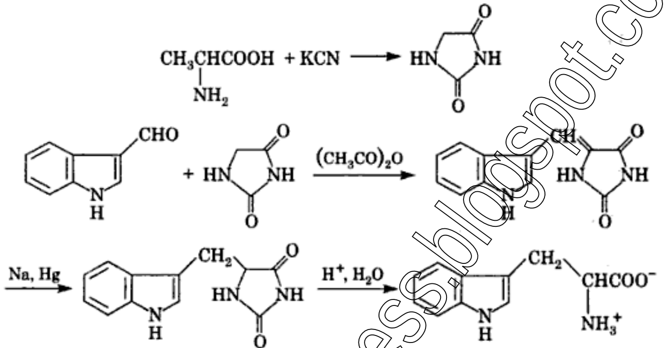
(*i*) The Strecker synthesis : An aldehyde is treated with ammonium chloride and potassium cyanide to yield an amino nitrile which on subsequent hydrolysis forms an amino acid.



$$C_6H_5CH_2CHO + NH_4Cl + KCN \longrightarrow C_6H_5CH_2\underset{NH_2}{CH}CN + KCl\downarrow + H_2O$$

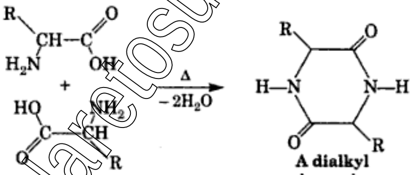
$$\xrightarrow[(ii)\ H^+]{(i)\ NaOH/\Delta} C_6H_5CH_2\underset{NH_3^+}{CH}COO^-$$

(*ii*) **Hydantoin synthesis.** Hydantoin itself is prepared by treatment of glycine with KCN ; the active methylene group can then be condensed with aldehydes and the desired product is obtained by reduction and subsequent hydrolysis. This synthesis is illustrated for the preparation of tryptophan.



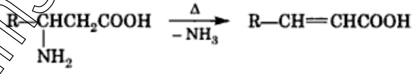
The effect of heat on the behavior of α, β, γ-amino acids is illustrated below.

(*i*) α-Amino acids : A cyclic diamide is obtained on heating two molecules of an α-amino acid.



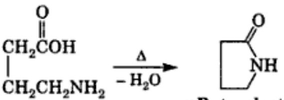
A dialkyl piperazine

(*ii*) β-Amino acids : β-amino acids lose ammonia to form α, β-unsaturated acids



$$\underset{\displaystyle NH_2}{R\text{—}\overset{|}{C}HCH_2COOH} \xrightarrow[-NH_3]{\Delta} R\text{—}CH{=}CHCOOH$$

(*iii*) γ-Amino acids : A γ-amino acid is easily converted to a lactam by loss of water intramolecularly on heating.



γ-Butyrolactam

Problem 25.18:

What are peptides, proteins and enzymes ? What is their importance in biological processes ?

Solution: Peptides are polyamides that contain between 2 to 100 units of amino acids. A peptide contains a free -COO$^-$ group (called C-terminal end) and a free –NH$_3^+$ group (called N-terminal end) at the terminal positions.

Proteins are complex organic molecules containing nitrogen as well as carbon, hydrogen, oxygen and sulfur. Amino acids are their constituent units.

Enzymes are biological catalysts which accelerate the rate of physiological reactions by factors of 10^6-10^{12} and allow the rapid attainment of equilibrium without side reactions, in dilute solution at low temperature and under neutral conditions.

Proteins are vital for the living organism in which they constitute their important structural and functional units *e.g.*, haemoglobin acts as a oxygen carrier from lungs to the tissues, nucleoproteins form the important constituents of the cells that supply and transmit genetic message in cells. The blood proteins thrombin and fibrinogen participate in blood clotting and thus prevent the loss of blood. Hormones such as insulin and thyroxin are proteins which regulate various metabolic processes in the body.

Glutathione is a tripeptide which helps in maintaining optimal redox potential in the cell and in keeping the enzymes in an active state. Bradykinin and kallidin contain 9 and 10 amino acids respectively and are powerful vaso-depressors and inhibitors of the heart.

Enzymes catalyze physiological reactions. For instance, urease, catalyzes the conversion of urea to ammonia and CO_2. phosphatases catalyze the hydrolysis of phosphate esters.

Problem 25.19:

(*a*) What are essential amino acids ? Name two of them and write their structures.

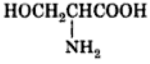
(*b*) How will you prepare glycine by the Gabriel method ?

Solution: (*a*) Amino acids which are not synthesized inside the body and therefore must be supplied from outside through food are called *essential amino acids.* Valine and serine are two examples of essential amino acids

$CH_3\underset{CH_3}{\underset{|}{C}H}-\underset{NH_2}{\underset{|}{C}H}COOH$

Valine

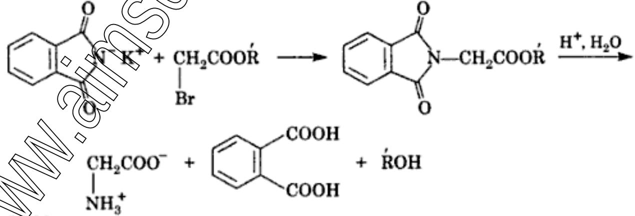
and



$HOCH_2\underset{NH_2}{\underset{|}{C}H}COOH$

Serine

(*b*)



Problem 25.20:

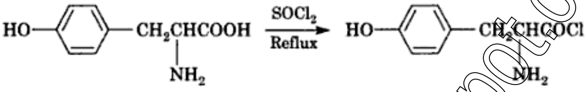
Would you expect an α-amino acid to be more or less soluble in water at its isoelectric point ?

Problem 25.25:

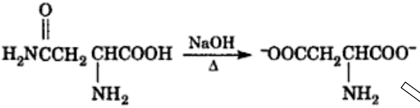
Write the reaction of :

(*a*) Tyrosine with thionyl chloride (*b*) Asparagine with aq. NaOH and heat (*c*) Serine with acetic anhydride (excess) and heat (*d*) Glutamic acid with one mole of HNO_2 (*e*) Proline with methyl iodide (*f*) Glutamic acid with ethyl alcohol, sulfuric acid and heat.

Solution: (*a*)

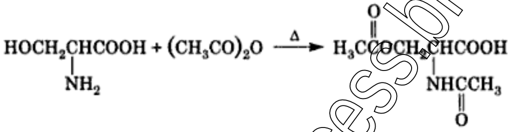


(*b*)



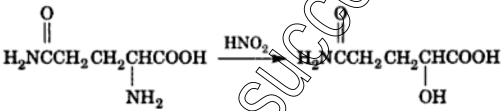
$$\mathrm{H_2N\overset{O}{\overset{\|}{C}}CH_2\underset{NH_2}{\underset{|}{C}}HCOOH \xrightarrow[\Delta]{NaOH} {}^{-}OOCCH_2\underset{NH_2}{\underset{|}{C}}HCOO^{-}}$$

(*c*)



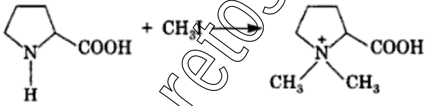
$$\mathrm{HOCH_2\underset{NH_2}{\underset{|}{C}}HCOOH + (CH_3CO)_2O \xrightarrow{\Delta} H_3C\overset{O}{\overset{\|}{C}}OCH_2\underset{NH\overset{}{\underset{\underset{O}{\|}}{C}}CH_3}{\underset{|}{C}}HCOOH}$$

(*d*)

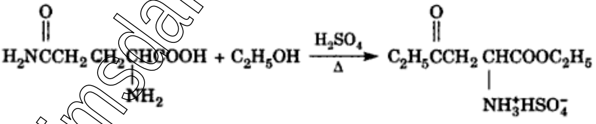


$$\mathrm{H_2N\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{NH_2}{\underset{|}{C}}HCOOH \xrightarrow{HNO_2} H_2N\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{OH}{\underset{|}{C}}HCOOH}$$

(*e*)



(*f*)



$$\mathrm{H_2N\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{NH_2}{\underset{|}{C}}HCOOH + C_2H_5OH \xrightarrow[\Delta]{H_2SO_4} C_2H_5\overset{O}{\overset{\|}{C}}CH_2\underset{NH_3^{+}HSO_4^{-}}{\underset{|}{C}}HCOOC_2H_5}$$

Problem 25.26:

Explain the difference in dipole moments of the following molecules :

$\mathrm{H_3\overset{+}{N}{-}CH_2{-}COO^-}$ $\mu = 14$ D

$\mathrm{CH_3{-}CH_2{-}COOH}$ $\mu = 1.7$ D

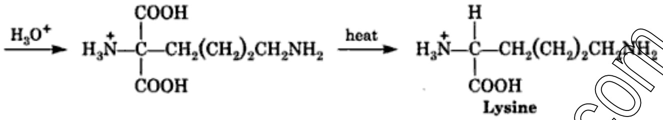
$\mathrm{CH_3{-}CH_2{-}CH_2{-}COOH}$ $\mu = 1.4$ D

Solution: A large value in case of glycine is due to a great deal of charge separation (it exists as a zwitterion). The values for the other two acids is almost normal.

Problem 25.27:

Indicate what structure will be present at a pH 6.05 for leucine, aspartic acid and lysine.

(*a*) Zwitterionic (*b*) Cationic (*c*) Anionic



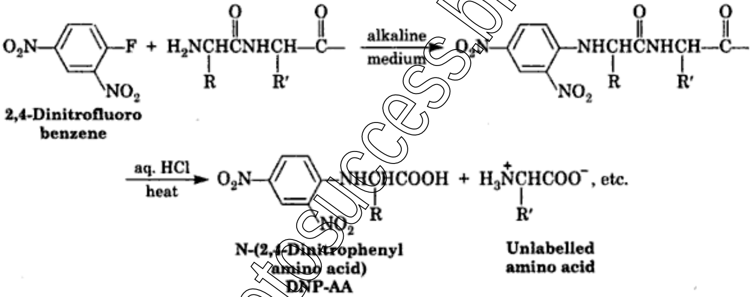
$$\xrightarrow{H_3O^+} H_3\overset{+}{N}-\underset{COOH}{\overset{COOH}{C}}-CH_2(CH_2)_2CH_2NH_2 \xrightarrow{heat} H_3\overset{+}{N}-\underset{COOH}{\overset{H}{C}}-CH_2(CH_2)_2CH_2NH_2$$

Lysine

Problem 25.35:

Describe the DNFB method of Sanger pointing out the purpose for which this is applied to proteins.

Solution: Sanger's method is used to identify the N-terminal residue of a peptide chain. This method makes use of 2, 4-dinitrofluorobenzene (DNFB) which undergoes nucleophilic substitution by the free amino group to give an N-dinitrophenyl (DNP) derivative. The substituted peptide is hydrolyzed to the component amino acids and the N-terminal residue, labelled by the 2, 4-dinitrophenyl group is separated and identified.



2,4-Dinitrofluoro benzene

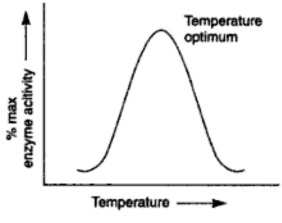
N-(2,4-Dinitrophenyl amino acid) DNP-AA

Unlabelled amino acid

Problem 25.36:

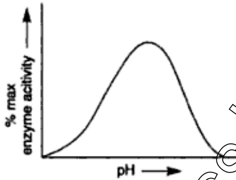
Describe the effect of temperature and pH on enzyme activity.

Solution: Effect of Temperature. Raising the temperature increases the rate of an enzyme-catalyzed reaction. However, this holds only over a strictly limited range of temperature. The reaction rate initially increases as temperature rises owing to increased kinetic energy of the reacting molecules. Eventually however, the kinetic energy of enzyme exceeds the energy barrier



for breaking the weak hydrogen- and hydrophobic- bonds that maintain its secondary and tertiary structures. At this temperature denaturation, with an accompanying precipitated loss of catalytic activity predominates. Enzymes, therefore, exhibit an optical temperature for catalyzing a reaction.

Effect of pH. pH can effect the activity of an enzyme by changing its structure or by changing the charge on a residue, functional in substrate binding or catalysis. Enzymes may also undergo changes in conformation when pH is varied. A charged group distal to the region where the substrate is bound may be necessary to maintain an active tertiary or quarternary structure. As the charge on this group is changed, the proteins may unravel, becoming more compact, or dissociate into protomers-all with the resulting loss of activity.



Problem 25.37:

Differentiate between a co-factor and a co-enzyme.

Solution: *Co-factor* is any non-protein component in enzyme. Co-factors may be roughly categorized into (*a*) prosthetic groups (*b*) coenzymes (*c*) metal ions. Biotin group of acetyl CoA carboxylase is an example of prosthetic group. Zn^{2+} (metal ion) is required in carbonic anhydrase and carboxypeptidase. Coenzymes are heat stable, low molecular weight organic compounds required for the activity of enzymes. Most coenzymes are linked to enzymes by non-covalent forces. NAD (Nicotinamide adenine dinucleotide) is a coenzyme which transfers hydrogen atoms.

Problem 25.38:

Explain the term 'isoelectric point' and its application in the separation of amino acids.

Solution: An amino acid bears a negative charge in basic solution (high pH) and a positive charge in acidic solution (low pH). There must be an intermediate pH where the amino acid is evenly balanced between two forms, as the dipolar zwitterion with a net charge of zero. This pH is called the *isoelectric pH or the isoelectric point*. An amino acid usually shows its lowest solubility in a solution at the isoelectric point because there is the highest concentration of the dipolar ion. At this point, an amino acid does not migrate under the influence of an electric field. Differences in isoelectric points can be used to separate mixture of amino acids by electrophoresis. A streak of amino acid mixture is placed in the center of a layer of acrylamide gel or a piece of filter paper wet with a buffer solution. Two electrodes are placed in contact with the edges of the gel or paper and a potential of several thousand volts is applied acorss the electrodes. Positively charged (cationic) amino acids are attracted to the negative electrode (the cathode), and negatively charged (anionic) amino acids are attracted to the positive electrode (the anode). An amino acid at its isoelectric point has no net charge and it does not move towards either electrode.

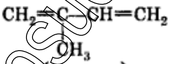
CHAPTER
26
Terpenes

Problem 26.1:

Define the following:

(*a*) Essential oils (*b*) Isoprene rule

Solution: (*a*) An essential oil may be described as a substance that possesses a characteristic odor. Terpenes are the most important constituents of essential oils. These compounds have a variety of uses particularly in perfumes and medicines. (*b*) Terpenes generally have a common structural feature. They consist of repeating units that have the same carbon skeleton as the five-carbon diene, isoprene. This generalization is usually known as the *isoprene rule*.



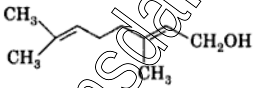
$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2$$

(Isoprene)

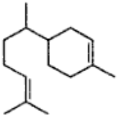
Problem 26.2:

Mark the Head-Tail combination in the following terpenes:

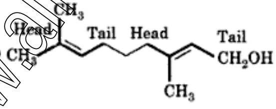
(*a*)



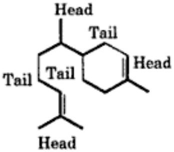
(*b*)



Solution: (*a*)

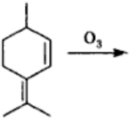


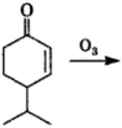
(*b*)

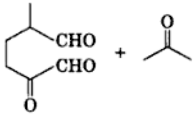


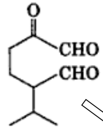
Problem 26.3:

Give the structural formulas for the products that you would expect from the following reactions:

(*a*)


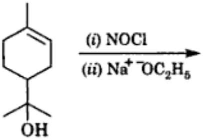
(*b*)


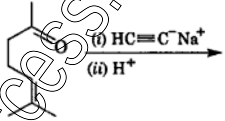
Solution: (*a*)


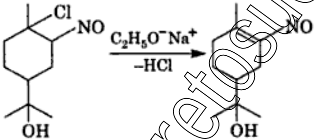
(*b*)


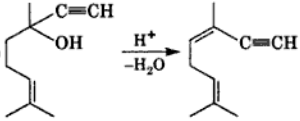
Problem 26.4:

Predict the major product of the following reactions:

(*a*)


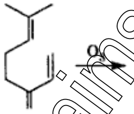
(*b*)


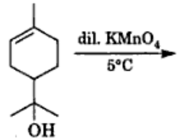
Solution: (*a*)


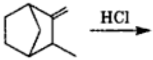
(*b*)


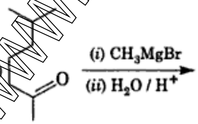
Problem 26.5:

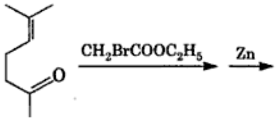
Predict the products of the following reactions:

(*a*)


(*b*)


(*c*)


(*d*)


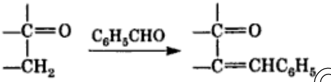
(*e*)


Problem 26.7:

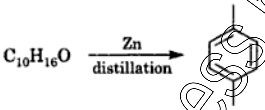
How will you prove that camphor is a saturated cyclic ketone containing —CO—CH_2 group ? Discuss its synthesis.

Solution: (1) Camphor forms addition compounds with hydroxylamine, semicarbazide and sodium bisulfite and on oxidation with nitric acid leads to a dicarboxylic acid. Therefore, the oxygen atom in camphor is present as a keto group.

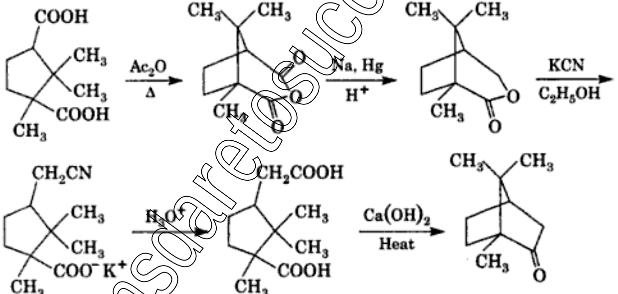
(2) Camphor condenses with benzaldehyde to form a monobenzilidene derivative. This suggests the presence of a —CO—CH_2—grouping. This is further confirmed by the formation of *o*-nitrosocamphor on treatment of camphor with nitrous acid.



(3) On distilling camphor with zinc dust, *p*-cymene is obtained. It indicates that camphor contains one six-membered ring.



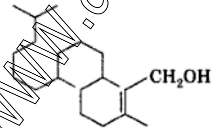
Synthesis of Camphor :



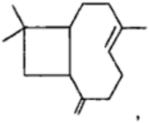
Camphor

Problem 26.8:

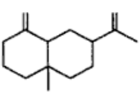
Mark the isoprene units and label as Head (H) to Tail (T) in the following terpenes.



Phytol

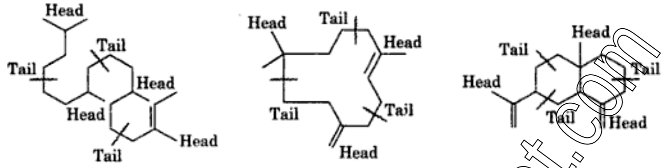


Caryophyllene



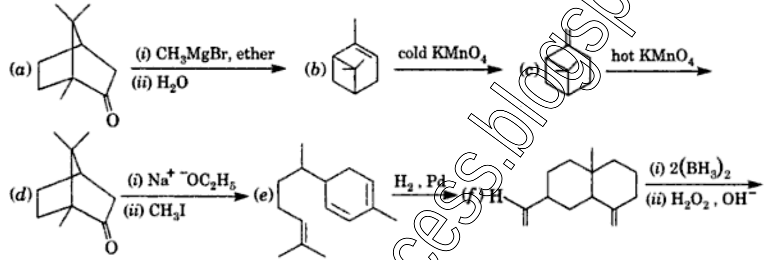
β-Selinene

Solution:

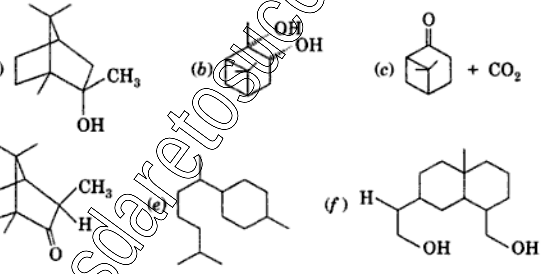


Problem 26.9:

Write the structural formulas of the products expected from the following reactions:

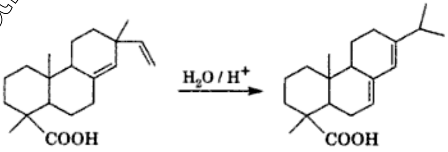


Solution: (a)



Problem 26.10:

Suggest a suitable mechanism for the acid catalyzed conversion of dextropimaric acid (a diterpene) into abietic acid.



CHAPTER

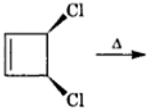
27

Pericyclic Reactions

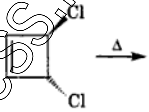
Problem 27.1:

Write the product of the following thermal reactions. Indicate stereochemistry.

(*a*)

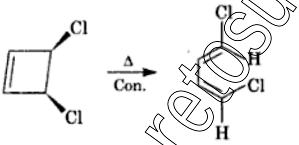


(*b*)



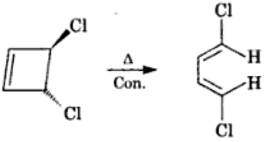
Solution: Conrotatory movement must convert a *cis*-3, 4-disubstituted cyclobutene into *cis, trans*-diene and *trans* into a *trans, trans*-diene.

(*a*)



***cis, trans*-Diene**

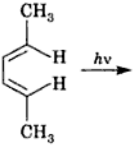
(*b*)



***trans, trans*-Diene**

Problem 27.2:

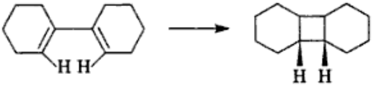
Would the photochemical cyclization of the following diene give *cis* or *trans* product ? Explain.



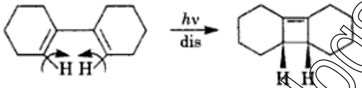
Solution: The photochemical cyclization of this diene does not yield *trans*-3, 4-dimethylcyclobutene. It being a polyene containing $4n\pi$ electrons can cyclize by a disrotatory movement only to give *cis*- cyclobutene.

Problem 27.3:

For the following reaction indicate whether a *con* or *dis* movement of groups is involved and whether the reaction is favored by heat or light.

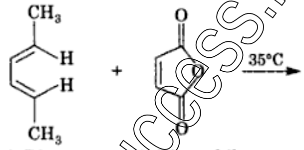


Solution: This reaction takes place by a disrotatory transformation. It is a $4n\pi$ electron system and thus should occur under the influence of light.



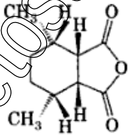
Problem 27.4:

Write product of the following cycloaddition reaction and show the stereochemistry.



***cis*-Diene** **cis-Dienophile**

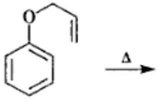
Solution:



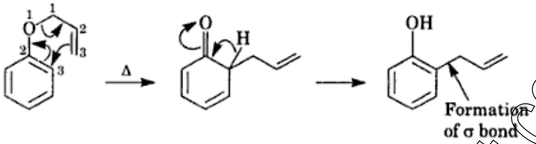
The Diels-Ader reaction is a pericyclic reaction and takes place in a single step. The reaction is a *syn*-addition and the configuration of the dienophile is retained in the products.

Problem 27.5:

Show the product of the thermal [3, 3] sigmatropic rearrangement of the following Claisen rearrangement.



Solution: In the Claisen rearrangement, an allylic ether undergoes a [3, 3] sigmatropic rearrangement.



Problem 27.6:

Describe the following:

A pericyclic reaction, molecular orbitals, HOMO, LUMO, conservation of orbital symmetry, conrotatory and disrotatory modes of rotations, symmetry allowed and symmetry forbidden processes and antibonding molecular orbitals.

Solution: A Pericyclic reaction. A reaction that involves a concerted cyclic shift of electrons is called a *pericyclic reaction*. A pericyclic reaction is insensitive to the presence of polar solvents and catalyst. No intermediate is involved and the reaction takes place in a highly stereospecific manner.

Molecular Orbitals. *Molecular orbitals* are those orbitals which include more than one atom in a molecule. They are formed by the overlap of two atomic orbitals.

HOMO. It is an abbreviation for *highest occupied molecular orbitals.*

LUMO. It is an abbreviation for *lowest unoccupied molecular orbitals.*

Conservation of orbital symmetry. It is the principle of pericyclic reactions that the MOs of the reactants must flow smoothly into the MOs of the products which have the same symmetry. This should cause bonding interactions in order to result in a stable transition state.

Conrotatory and disrotatory modes of rotations. For a σ bond to be formed between the end carbon atoms of the conjugated π-electron chain (a polyene), these atoms must rotate. The rotations of the end groups can be in the same direction termed *conrotatory* or the groups can rotate in opposite direction, termed *disrotatory*.

Symmetry allowed and symmetry forbidden. In the frontier orbital method for cycloadditions, we make the assumption that in order to form bonds between the reactants, the electrons will flow smoothly from atoms of one reactants into LUMO of the other. If such a reaction proceeds through a bonding transition state, the reaction is termed symmetry allowed.

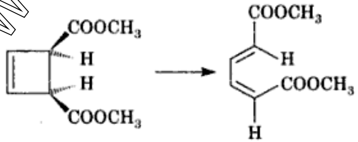
If such a phase overlap (+ phase with +, and – phase with –) of HOMO and LUMO does not take place, then the reaction is termed *symmetry forbidden*.

Antibonding Molecular Orbitals. Molecular orbitals that are higher in energy than the isolated atomic orbitals from which they are made.

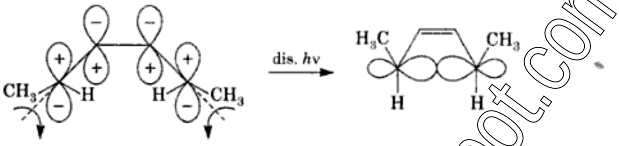
Problem 27.7:

State whether conrotatory or disrotatory mode of rotation is involved in each of the following reactions. Also state whether you would expect the reaction to occur under the influence of heat or light.

(*a*)



Solution: Since it is a photochemical reaction, therefore, we use the HOMO of butadiene which is ψ_3.

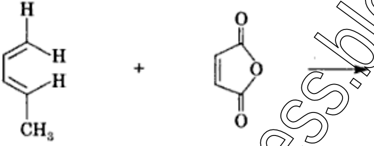


Since it is a $4n\pi$ system, a disrotatory motion will close the ring.

Problem 27.12:

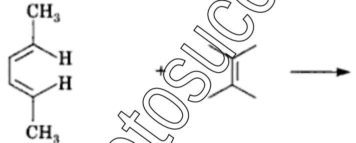
Write the structure of the product expected from each of the following reactions:

(a)



trans-1,3-Pentadiene Maleic anhydride

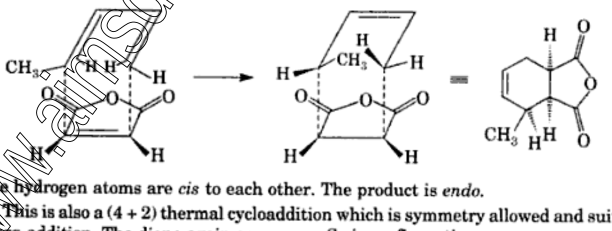
(b)



trans, trans-2,4-hexadiene Ethylene

Solution: (a) It is (4 + 2) thermal cycloaddition which is favored-*supra-supra*. The diene is in the S-*cis*-configuration, the dienophile adds in a *syn* manner.

(a)



The hydrogen atoms are *cis* to each other. The product is *endo*.

(b) This is also a (4 + 2) thermal cycloaddition which is symmetry allowed and suitable for *supra-supra* addition. The diene again assumes a *S-cis* configuration.

Index

Solution: (*a*) **Since a *trans*** product is obtained, it is a conrotatory movement and also this is a **4*n*π electron** system it should occur under the influence of heat. (*b*) It is a photochemical reaction, called the *Paterno-Büchi reaction*. (*c*) The reaction does not take place (conrotatory, thermal) because a strained ring system will be obtained. (*d*) It is a disrotatory motion and since it has (4*n* + 2) π electrons, heat is required. (*e*) This is a thermal oxy-Cope rearrangement. (*f*) It is a 1, 5 sigmatropic rearrangement. (*g*) This is a (4*n* + 2) π electron system undergoing conrotatory **movement.** It occurs under the influence of light.

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ISBN 81-224-1797-3
9788122417975

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