ORGANIC CHEMISTRY

VOLUME – II

(ENGLISH)

CONTENTS

ALCOHOL

1. INTRODUCTION

Their general formula is $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$.

These are of following types, depending upon the no. of OH groups.

(i) Monohydric alcohol:-
Contains one –OH group only, eg.C_2H_5OH

(ii) Dihydric alcohol :-
Contains two –OH groups. eg. glycol

(iii) Trihydric alcohol:-
Contains three –OH groups eg. glycerol

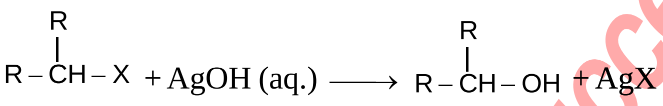
(iv) Polyhydric alcohol :-
Contains more than three - OH groups. eg, sorbitol, manitol.

2. METHODS OF PREPARATION

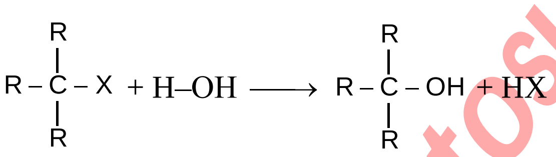
2.1 From Alkyl halides:-

Alkyl halides reacts with aq. KOH/aq. AgOH or H_2O and forms alcohol.

$$R–CH_2–X + K–OH\ (aq.) \longrightarrow R–CH_2OH + KX$$



$$R-\overset{R}{\overset{|}{C}}H-X + AgOH\ (aq.) \longrightarrow R-\overset{R}{\overset{|}{C}}H-OH + AgX$$

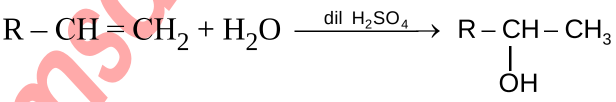


$$R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}-X + H–OH \longrightarrow R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}-OH + HX$$

2.2 From Alkenes :

2.2.1 Hydration – Alkenes are catalytically hydrated by dilute mineral acid solution.

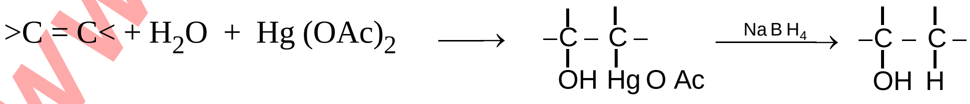
$$CH_2 = CH_2 + H_2O \xrightarrow{\text{dil } H_2SO_4} CH_3CH_2OH$$



$$R - CH = CH_2 + H_2O \xrightarrow{\text{dil } H_2SO_4} R-\underset{OH}{\underset{|}{C}H}-CH_3$$

2.2.2 Oxymercuration – demercuration :

Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds, which on reduction yield alcohols. (Markovnikov addition)

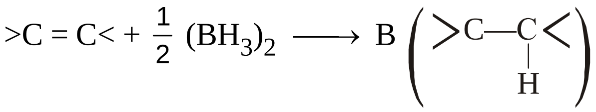


$$>C = C< + H_2O + Hg\,(OAc)_2 \longrightarrow -\underset{OH}{\underset{|}{\overset{|}{C}}}-\underset{Hg\,O\,Ac}{\underset{|}{\overset{|}{C}}}- \xrightarrow{NaBH_4} -\underset{OH}{\underset{|}{\overset{|}{C}}}-\underset{H}{\underset{|}{\overset{|}{C}}}-$$

Mercuric acetate Alcohol

2.2.3 Hydroboration – Oxidation :

(Anti–Markownikov orientation)



$$>C=C< + \frac{1}{2}(BH_3)_2 \longrightarrow B\left(>C-\underset{H}{\underset{|}{C}}<\right)_3$$

Alkene Diborane Tri alkyl borane

$$\xrightarrow[OH^-]{H_2O_2} -\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{OH}{\underset{|}{\overset{|}{C}}}- + B(OH)_3$$

2.3 By Reduction of Carbonyl compounds :-

$$R-\underset{O}{\underset{\|}{C}}-H + 2H \xrightarrow{LiAlH_4/Na+C_2H_5OH} R-CH_2OH$$

1° alcohol

$$R-\underset{O}{\underset{\|}{C}}-R + 2H \xrightarrow{LiAlH_4/Na+C_2H_5OH} R-\underset{OH}{\underset{|}{CH}}-R$$

2° alcohol

Note :

(i) We cannot obtain 3° alcohol from this method

(ii) If we use NaH as reductant then the process is called as '**Darzen's process**'.

2.4 By Reduction of Acid & its derivatives :

$$R-\underset{O}{\underset{\|}{C}}-OH + 4H \xrightarrow{LiAlH_4} RCH_2OH$$

$$R-\underset{O}{\underset{\|}{C}}-X + 4H \xrightarrow{LiAlH_4} R\,CH_2OH + HX$$

$$R-\underset{O}{\underset{\|}{C}}-OR' + 4H \xrightarrow{LiAlH_4} RCH_2OH + R'OH$$

$$RCOOCOR + 8H \xrightarrow{LiAlH_4} 2\,RCH_2OH + H_2O$$

Important Note :- Acid amide does not form alcohol on reduction. It forms primary amine.

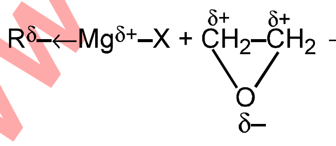
2.5 From Grignard reagent :

2.5.1 With oxygen : –

Grignard reagent forms alcohol of same no. of carbon atoms as in Grignard reagent.

$$2R-Mg-X + O_2 \xrightarrow[Al_2O_3]{\Delta} 2R-O-Mg-X \xrightarrow{2HOH} 2ROH + 2\,Mg(X)OH$$

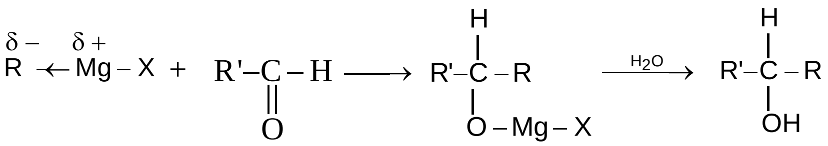
2.5.2 With ethylene oxide :



$$R^{\delta-}\leftarrow Mg^{\delta+}-X + \overset{\delta+}{CH_2}-\overset{\delta+}{CH_2}\ (\underset{\delta-}{O}) \longrightarrow R-CH_2-CH_2-O-Mg-X \xrightarrow{H_2O} R-CH_2-CH_2OH + Mg(X)OH$$

[Alcohol with two carbon more than Grignard reagent]

2.5.3 With carbonyl compounds :



$$\overset{\delta-}{R} \leftarrow \overset{\delta+}{Mg}-X + R'-\underset{\underset{O}{||}}{C}-H \longrightarrow R'-\overset{\overset{H}{|}}{\underset{\underset{O-Mg-X}{|}}{C}}-R \xrightarrow{H_2O} R'-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-R$$

Note :

(i) If R' = H , Product will be 1° alcohol.

(ii) If R' = R, Product will be 2° alcohol.

(iii) If carbonyl compound is ketone, product will be 3° alcohol.

(iv) It is the best method for preparation of alcohol because we can prepare every type of alcohols.

2.6 From Primary amines :-

$R–NH_2 + HNO_2 \xrightarrow{HCl} R–OH + N_2 + H_2O.$

But it is not a good method for preparation of alcohol because a number of byproducts are formed in this reaction like alkyl chloride, alkyl nitrite, alkene and ether.

Note : In this reaction if we take ethyl amine then main product will be ethanol while if we take methyl amine, then main product will be dimethyl ether.

3. PHYSICAL PROPERTIES

(a) Alcohols are colourless with specific smell liquid. They are soluble is water due to H-bonding. These are partially soluble in organic solvents.

(b) They are liquid in nature up to 12-carbon.

(c) Melting point and Boiling point α molecular mass $\alpha \ \dfrac{1}{\text{No. of branches}}$

(d) Boiling point of alcohols are higher than equivalent ethers. It is due to H-bonding.

(e) Alcohols are poisonous in nature also. Poisonous character increase with increment in molecular weight or branching. Ethanol is exception, which is non-poisonous in nature. It is most useful organic solvent.

(f) Methanol causes blindness.

(g) Isopropyl alcohol is called as rubbing alcohol.

(h) Cholestrol is also an example of complex alcohol which is called notorious alcohol because it causes heart attack.

(i) Viscous nature of alcohol is directly proportional to H-bonding or number of -OH groups. That is why we can say alcohol is less viscous than glycerol & manitol is more viscous than glycerol.

(j) Ethanol is liquid while glucose is solid. It is due to more H-bonding in glucose.

4. CHEMICAL PROPERTIES

Chemical reactions of alcohols are classified in the following three types :-

(i) Reaction of H atom of –OH group of Alcohols

(ii) Reaction of OH group of Alcohols

(iii) General reaction of Alcohols.

4.1 Reaction of H atom of –OH group of Alcohols :

These are the reactions in which alcohol shows acidic character.

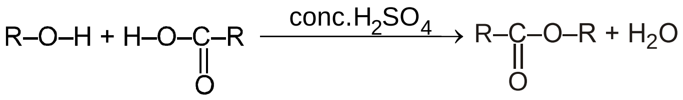
4.1.1 Reaction with Na :

$2R\text{–}O\text{–}H + Na \longrightarrow 2R - O - Na + H_2\uparrow$

The acidic order of alcohols is

MeOH > 1º > 2º > 3º

4.1.2 Esterification / Reaction with carboxylic acid:-

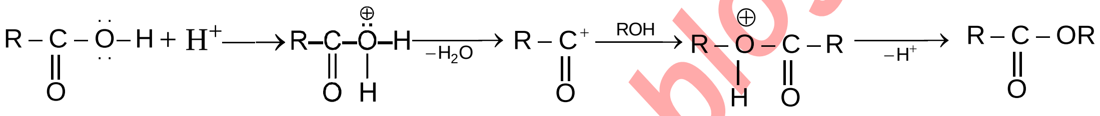


$$R\text{–}O\text{–}H + H\text{–}O\text{–}\underset{\underset{O}{\|}}{C}\text{–}R \xrightarrow{\text{conc.}H_2SO_4} R\text{–}\underset{\underset{O}{\|}}{C}\text{–}O\text{–}R + H_2O$$

ester

Mechanism :

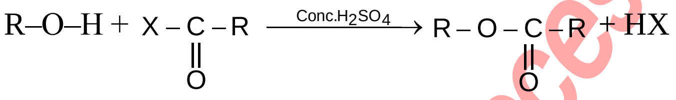
$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$



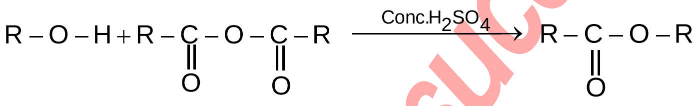
$$R-\underset{\underset{O}{\|}}{C}-\ddot{\underset{..}{O}}-H + H^+ \longrightarrow R\text{–}\underset{\underset{O}{\|}}{C}\text{–}\underset{\underset{H}{|}}{\overset{\oplus}{\ddot{O}}}\text{–}H \xrightarrow[-H_2O]{} R-\underset{\underset{O}{\|}}{C^+} \xrightarrow{ROH} R-\underset{\underset{H}{|}}{\overset{\oplus}{O}}-\underset{\underset{O}{\|}}{C}-R \xrightarrow[-H^+]{} R-\underset{\underset{O}{\|}}{C}-OR$$

Note : The above reaction is laboratory method of ester preparation.

4.1.3 Reaction with Acid derivatives :

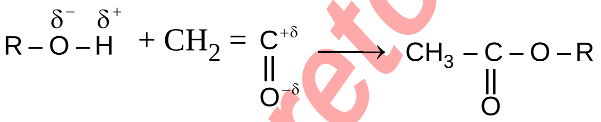


$$R\text{–}O\text{–}H + X-\underset{\underset{O}{\|}}{C}-R \xrightarrow{\text{Conc.}H_2SO_4} R-O-\underset{\underset{O}{\|}}{C}-R + HX$$



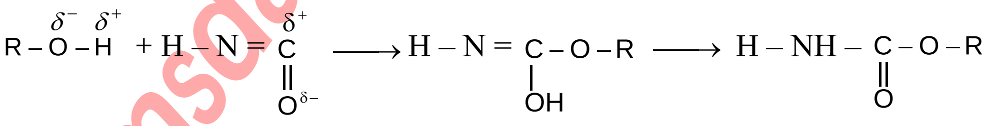
$$R-O-H+R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R \xrightarrow{\text{Conc.}H_2SO_4} R-\underset{\underset{O}{\|}}{C}-O-R$$

4.1.4 Reaction with Ketene :-



$$R-\overset{\delta^-}{O}-\overset{\delta^+}{H} + CH_2 = \underset{\underset{O^{-\delta}}{\|}}{C^{+\delta}} \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-O-R$$

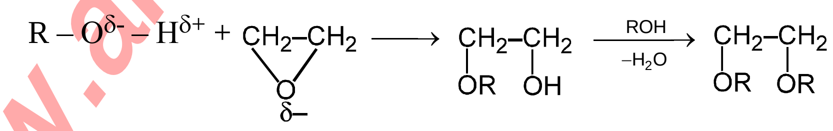
4.1.5 Reaction with Isocyanic Acid :-



$$R-\overset{\delta^-}{O}-\overset{\delta^+}{H} + H-N=\underset{\underset{O^{\delta-}}{\|}}{\overset{\delta^+}{C}} \longrightarrow H-N=\underset{\underset{OH}{|}}{C}-O-R \longrightarrow H-NH-\underset{\underset{O}{\|}}{C}-O-R$$

amino ester (urethane)

4.1.6 Reaction with ethylene oxide :



$$R-O^{\delta-}-H^{\delta+} + \underset{\underset{\delta-}{O}}{CH_2\text{–}CH_2} \longrightarrow \underset{OR}{\underset{|}{CH_2}}\text{–}\underset{OH}{\underset{|}{CH_2}} \xrightarrow[-H_2O]{ROH} \underset{OR}{\underset{|}{CH_2}}\text{–}\underset{OR}{\underset{|}{CH_2}}$$

1,2-dialkoxy ethane

4.1.7 Reaction with Diazomethane :-

$R\text{–}O\text{–}H + CH_2\,N_2 \longrightarrow R\text{–}O\text{–}CH_3$

(ether)

4.2 Reaction of – OH group of Alcohols :-

4.2.1 Reaction with dry HX (Grove's Process) :

$$R\text{–}OH + HX \longrightarrow R - X + H_2O$$

4.2.2 Reaction with PCl_5 :

$$R\text{–}OH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$$

4.2.3 Reaction with PCl_3 :

$$3R\text{–}OH + PCl_3 \longrightarrow 3R\text{–}Cl + H_3PO_3$$

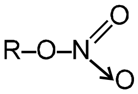
4.2.4 Reaction with $SOCl_2$ (Darzen reaction): –

$$R\text{–}OH + SOCl_2 \xrightarrow{\text{Pyridine}} R\text{–}Cl + SO_2 + HCl$$

4.2.5 Reaction with ammonia :

$$R - OH + NH_3 \xrightarrow[300°C]{\text{anhy.}ZnCl_2} RNH_2 + H_2O$$

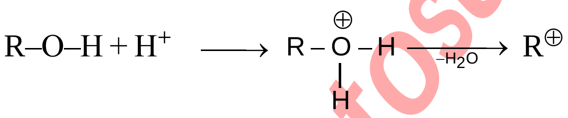
4.2.6 Reaction with HNO_3 :

$R\text{–}OH + HNO_3 \longrightarrow$  $+ H_2O$

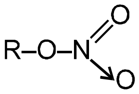
(conc.) alkyl nitrate
(soluble ester)

Mechanism :-

$$HNO_3 \longrightarrow H^+ + NO_3^-$$

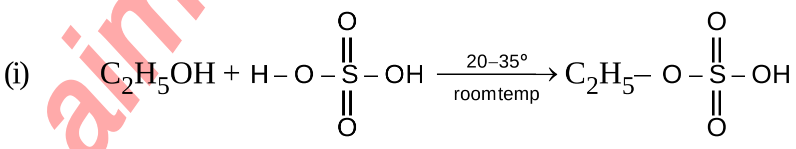


$$R\text{–}O\text{–}H + H^+ \longrightarrow R - \overset{\oplus}{\underset{\substack{| \\ H}}{O}} - H \xrightarrow{-H_2O} R^{\oplus}$$

$R^{\oplus} + NO_3^{\ominus} \longrightarrow$ 

alkyl nitrate

4.2.7 Reaction with H_2SO_4 :-



$$\text{(i)} \quad C_2H_5OH + H - O - \overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}} - OH \xrightarrow[\text{roomtemp}]{20\text{–}35°} C_2H_5 - O - \overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}} - OH$$

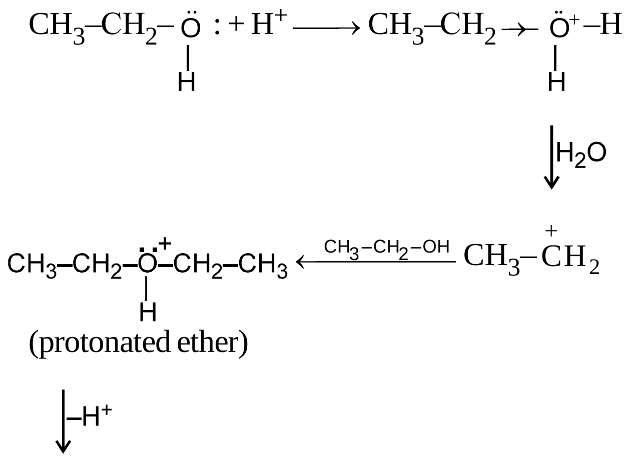
stable upto (80-100ºC)

$$\text{(ii)} \quad CH_3 - CH_2 - OH + H_2SO_4 \xrightarrow{140°C} CH_3\text{–}CH_2\text{–}\overset{..}{\underset{..}{O}}\text{–}CH_2\text{–}CH_3$$

(excess)

Mechanism :-

$H_2SO_4 \longrightarrow H^+ + HSO_4^-$



$$CH_3{-}CH_2{-}\underset{H}{\underset{|}{\ddot{O}}}: + H^+ \longrightarrow CH_3{-}CH_2 \rightarrow \underset{H}{\underset{|}{\ddot{O}^+}}{-}H$$

$$\downarrow H_2O$$

$$\underset{\text{(protonated ether)}}{CH_3{-}CH_2{-}\underset{H}{\underset{|}{\dot{\overset{+}{O}}}}{-}CH_2{-}CH_3} \xleftarrow{CH_3-CH_2-OH} CH_3{-}\overset{+}{C}H_2$$

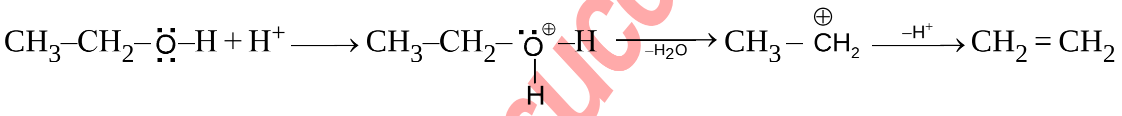
$$\downarrow -H^+$$

$CH_3 - CH_2 - \ddot{O} - CH_2 - CH_3$

(iv) $CH_3{-}CH_2{-}OH + \underset{\text{(excess)}}{H_2SO_4} \xrightarrow{160°C} CH_2 = CH_2$

Mechanism :-

$H_2SO_4 \longrightarrow H^+ + HSO_4^-$



$$CH_3{-}CH_2{-}\ddot{O}{-}H + H^+ \longrightarrow CH_3{-}CH_2{-}\underset{H}{\underset{|}{\ddot{O}^{\oplus}}}{-}H \xrightarrow[-H_2O]{} CH_3{-}\overset{\oplus}{C}H_2 \xrightarrow{-H^+} CH_2 = CH_2$$

Note :-

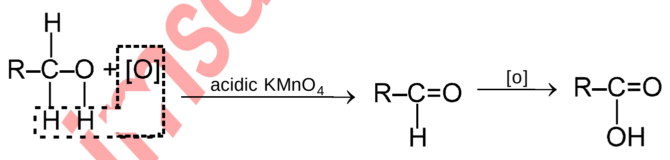
In the above reaction excess of ethanol is present so, intermediate carbocation satisfies itself by elimination.

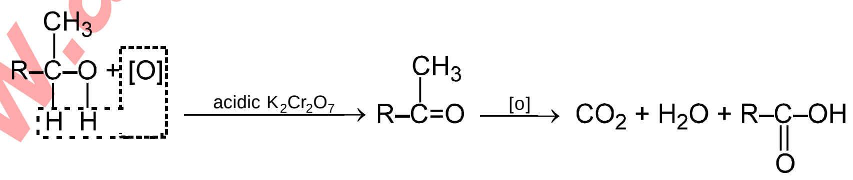
4.3 General reaction of Alcohols :-

4.3.1 Reduction :-

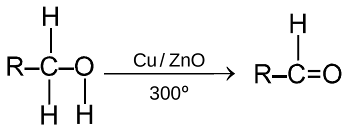
$R{-}O{-}H + 2\,HI \xrightarrow[150°C]{RedP} R - H$

Reacting species of solution is $HCrO_4^-$.



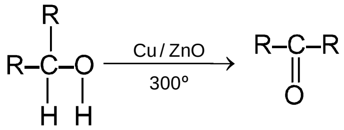


4.3.2 Catalytic Oxidation / Dehydrogenation :



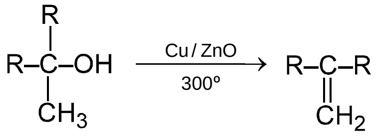
$$R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\underset{\underset{H}{|}}{O} \xrightarrow[300^\circ]{Cu/ZnO} R-\overset{\overset{H}{|}}{C}=O$$

1° alcohol aldehyde



$$R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-\underset{\underset{H}{|}}{O} \xrightarrow[300^\circ]{Cu/ZnO} R-\underset{\underset{O}{||}}{C}-R$$

secondary alcohol ketone



$$R-\overset{\overset{R}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[300^\circ]{Cu/ZnO} R-\underset{\underset{CH_2}{||}}{C}-R$$

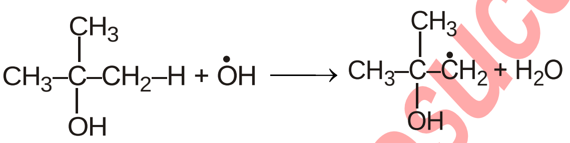
tert. alcohol alkene

(**Note :** – This is dehydration process.)

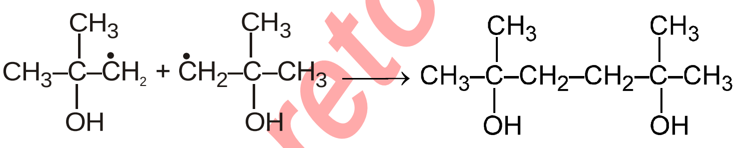
4.3.3 Oxidation through Fenton's Reagent :

Higher and branched alcohols are converted into diols through Fentons reagent. ($FeSO_4 + H_2O_2$) is Fenton's reagent.

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + \overline{O}H + \dot{O}H$$



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-H + \dot{O}H \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-\dot{C}H_2 + H_2O$$

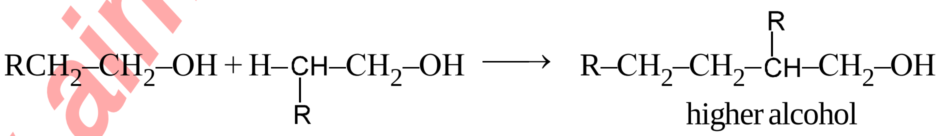


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-\dot{C}H_2 + \dot{C}H_2-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

2,5-dimethyl hexandiol-2,5

4.3.4 Self Condensation :

When alcohol is heated with sodium ethoxide then by self condensation they convert into higher alcohol.



$$RCH_2-CH_2-OH + H-\underset{\underset{R}{|}}{CH}-CH_2-OH \longrightarrow R-CH_2-CH_2-\overset{\overset{R}{|}}{CH}-CH_2-OH$$

higher alcohol

Note : The above reaction is called as '**Guerbet's Reaction**'.

5.1 Preparation of methanol :

Methanol is also called as carbinol or wood spirit.

5.1.1 From Water Gas :

$$[CO + H_2] + H_2 \xrightarrow[\substack{ZnO/CrO_3 \\ 200-300^\circ}]{Al_2O_3} CH_3OH\ (90\ \%)$$

5.1.2 From Methane : -

CH_4 gives methanol on partial oxidation in Cu tube.

$$CH_4 + \frac{1}{2}O_2 \xrightarrow[200°C]{\text{Cu tube}} CH_3OH\ (90\%)$$

5.1.3 By Pyroligneous Acid : -

anhy. $CaCl_2 + CH_3OH \longrightarrow CaCl_2 \bullet 4CH_3OH$

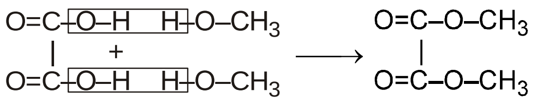
anhy. $MgCl_2 + CH_3OH \longrightarrow MgCl_2 \bullet 6CH_3OH$

anhy. $CuSO_4 + CH_3OH \longrightarrow CuSO_4 \bullet 2CH_3OH$

we get pure methanol on steam distillation

or

we can use oxalic acid to separate water impurities.

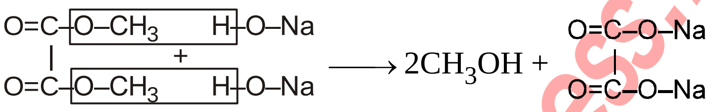


$$\begin{array}{l} O{=}C\boxed{-O-H\quad H-}O-CH_3 \\ \quad | \qquad + \\ O{=}C\boxed{-O-H\quad H-}O-CH_3 \end{array} \longrightarrow \begin{array}{l} O{=}C-O-CH_3 \\ \quad | \\ O{=}C-O-CH_3 \end{array}$$

oxalic acid methyl

methanol oxalate(solid)

we get pure methanol on alkaline hydrolysis



$$\begin{array}{l} O{=}C\boxed{-O-CH_3\quad H-}O-Na \\ \quad | \qquad\qquad + \\ O{=}C\boxed{-O-CH_3\quad H-}O-Na \end{array} \longrightarrow 2CH_3OH + \begin{array}{l} O{=}C-O-Na \\ \quad | \\ O{=}C-O-Na \end{array}$$

5.2 Preparation of Ethanol :

5.2.1 From Ethene :

By hydration with dil. H_2SO_4

$$CH_2{=}CH_2 + H-OH \xrightarrow{\text{dil. } H_2SO_4} CH_3-CH_2-OH$$

5.2.1 Preparation of ethanol from sugar : -

(i) **Molasses : -** Waste product in sugar industry is called molasses. It is a mixture of sugar (30%) and invert sugar (32-40%).

(ii) **Invert sugar : -** Combine form of glucose and fructose is called as invert sugar.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{invertase enzyme}]{\text{yeast cell}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{zymase enzyme}]{\text{yeast cell}} C_2H_5OH + CO_2 + H_2O$$

Note: Glucose and fructose are functional isomers.

5.2.3 Preparation of ethanol from starch :

(i) Starch solution is technically called 'Mesh'

(ii) Crushed germinated barley solution is called 'Malt'.

$$\underset{\text{starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{diastase}} \underset{\text{maltose (wort)}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{maltase}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{maltase}} \underset{\substack{\text{glucose} \\ \text{(monosaccharide)}}}{2C_6H_{12}O_6}$$

$$2C_6H_{12}O_6 \xrightarrow{\text{zymase}} C_2H_5OH + CO_2 + H_2O + \text{energy}$$

(iii) From both of the methods conc. of ethanol achieved is 10-12% which is called 'Wash'.

(iv) Distillation of wash is done in special apparatus 'Coffee's still', which is based on counter current method. From this distillation yield of alcohol is 90%, which is called Raw spirit.

$$\text{Raw spirit} \xrightarrow{\text{Fractional distillation}} 95.5\%\ C_2H_5OH + 4.5\%\ H_2O$$

(rectified spirit)

(v) Further purification is done in the following ways : -

$$95.5\%\ C_2H_5OH + 4.5\%\ H_2O \xrightarrow{\text{Fractional distillation}} \underset{(64^\circ C)}{C_6H_6 + H_2O} + \underset{\underset{(99.7\%)}{(78.5\ ^\circ C)}}{C_2H_5OH} + \text{Remaining } \underset{\underset{(68^\circ C)}{+\ CH_3CHO}}{C_6H_6}$$

$$\underset{(99.7\%)}{C_2H_5OH} + \text{Ca metal} \xrightarrow{2-3\text{ days}} \underset{(100\%)}{C_2H_5OH} + Ca(OH)_2$$

$$\underset{(99.7\%)}{C_2H_5OH} + \underset{\text{white}}{\text{anhy. } CuSO_4} \longrightarrow \underset{(100\%)}{C_2H_5OH} + CuSO_4 \cdot 5H_2O$$

6. DIFFERENCE BETWEEN PRIMARY, SECONDARY & TERTIARY ALCOHOLS

6.1 By Oxidation Reaction :-

Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary alcohols are resistant to oxidation.

6.2 By Catalytical Oxidation / Dehydrogenation :

Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary alcohol gives alkene (dehydration takes place in this condition to tertiary alcohols.)

6.3 Lucas Test :-

A mixture of (anhydrous $ZnCl_2$ + Conc. H_2SO_4) is called as **Lucas Reagent.**

(i) 3° alcohol gives white ppt. with lucas reagent in 2-3 seconds only.

(ii) 2° alcohol takes 9 - 10 minutes.

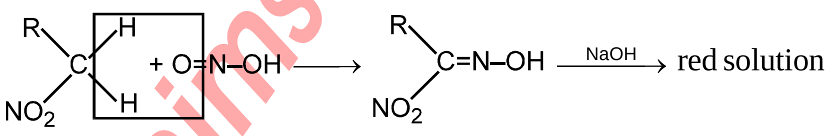
(iii) 1° alcohol does not gives white ppt. at room temperature.

6.4 Victor Meyer Test : -

This test is also known as RBW (Red, Blue, White) test.

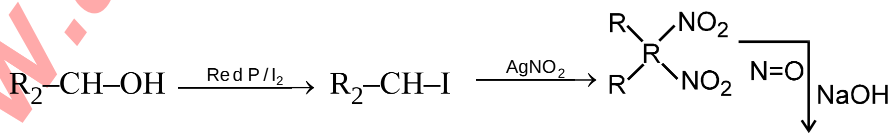
(a) $R–CH_2–OH \xrightarrow{\text{Red P}/I_2} R–CH_2–I \xrightarrow[-\text{AgI}]{\text{AgNO}_2} R–CH_2–NO_2 + HNO_2$

nitrate



nitrolic acid

(b)



nitrosoderivative NaOH (blue ppt.)
Pseudonitrile

(c) $R_3–C–OH \xrightarrow{\text{Red P}/I_2} R_3–C–I \xrightarrow{\text{AgNO}_2} R_3–C–NO_2 \xrightarrow{\text{HNO}_2} \text{no. reaction.}$

6.5 Difference between Methanol and Ethanol :

Methanol	Ethanol
1. When CH_3OH is heated on Cu coil it gives formalin like smell.	1. Ethanol does not give formalin like smell.
2. When CH_3OH is heated with salicylic acid in H_2SO_4 (conc.) then methyl salicylate is formed which has odour like winter green oil	2. No such odour is given by ethanol
3. It does not give haloform or Iodoform test.	3. It gives haloform test.

ALCOHOL

GMP

(1) Alkene $\xrightarrow{H_2O}$

(2) RX $\xrightarrow[\text{or aq. } K_2CO_3 \text{ or moist } Ag_2O]{\text{aq. NaOH or aq. KOH}}$

(3) R - O - R $\xrightarrow{\text{dil. } H_2SO_4}$

(4) RCOOR $\xrightarrow[-RCOOH]{\text{dil. } H_2SO_4}$

(5) 1° amine $\xrightarrow{HNO_2}$

Exception - (Methyl amine gives CH_3-O-CH_3 or ether)

(6) Aldehyde or ketone $\xrightarrow[\text{Darzon reduction}]{NaH}$

(1° alc.) (2° alc.)

(7) Acid or $\xrightarrow[\text{Bouveault–Blanc reduction}]{Na/EtOH}$

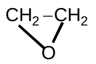
Acid derivative

(8) HCHO or Ald.or ketone $\xrightarrow[H_2O]{R-MgX}$

(1° alc) (2°alc) (3° alc.)

(9) RMgX $\xrightarrow[H_2O]{O_2}$

(10) CH_3MgBr



$\xrightarrow[H_3O^+]{}$

(11) Sugar $\xrightarrow{\text{Fermentation}}$

$\boxed{R\text{-}OH}$

GR

(1) $\xrightarrow[\text{or KI } +H_3PO_4 \text{ or } SOCl_2 \text{ or } SO_2Cl_2]{HX \text{ or } PX_3 \text{ or } PX_5}$ RX

(2) $\xrightarrow{\text{Red P/HI}}$ RH

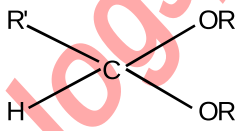
(3) $\xrightarrow{NH_3}$ 1° , 2° , 3° amines

(4) $\xrightarrow[ThO_2]{H_2S}$ R - SH Thiol

(5) $\xrightarrow{Na}$ RONa

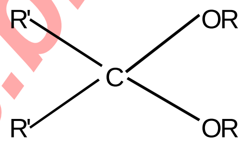
(6) $\xrightarrow{CH_3MgX}$ CH_4

(7) $\xrightarrow[\text{dry HCl}]{\text{ald.R'–CHO}}$



Acetal

(8) $\xrightarrow[\text{dry HCl}]{\text{Ketone R'COR'}}$



Ketal

(9) $\xrightarrow{R'COZ}$ R'COOR ester (Z = OH,Cl, $OCOCH_3$)

(10) $\xrightarrow{H_2SO_4}$ $ROSO_2OH$ (Alkyl hydrogen sulphate)

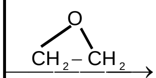
(11) $\xrightarrow{HNO_3}$ $RONO_2$ (Alkyl nitrate)

(12) $\xrightarrow{PhSO_2Cl}$ RSO_2Ph (Alkyl benzene sulphonate)

(13) $\xrightarrow{CH\equiv CH}$ H_3C - CH $(OR)_2$ Acetal

(14) $\xrightarrow{CH_2N_2}$ R - O - CH_3 Ether

(15)



$\longrightarrow$ RO - CH_2 - CH_2 - OH

Alkoxyalkanol

(16) $\xrightarrow{CH_2=C=O}$ $ROCOCH_3$ Ester

(17) $\xrightarrow{\text{Dehydration}}$ Alkene

(18) $\xrightarrow[1^0 \text{ or } 2^0 \text{ alcohol , Cu or ZnO , } 300^0 C]{\text{Catalytic dehydrogenation}}$ Aldehyde or ketone

Exception - 3° alc → Alkene

(19) 1°alc. $\xrightarrow{[O]}$ Aldehyde $\xrightarrow{[O]}$ Acid (same no. of C-atom)

(20) 1° or 2°alc. $\xrightarrow[\text{(orange)}]{O\ HCrO_4^-}$ Aldehyde or ketone + Cr^{+3} (green)

(21) 3° alc $\xrightarrow[\text{(orange)}]{O,\ HCrO_4^-}$ No reaction (No. green colour)

Formation of EtOH by fermention -

(1) Cane sugar $\xrightarrow[\text{Sucrose}]{\text{Crystallization}}$ Molasses

$\xrightarrow[\text{hydrolysis}]{\text{Invertase}}$ Invert sugar $\xrightarrow[\text{Fermentation}]{\text{zymase}}$ EtOH

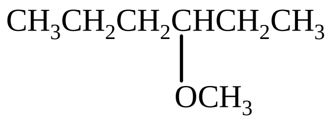
(2) Grain → Starch $\xrightarrow[HOH]{\text{Diastase}}$ Maltose

$\xrightarrow[\text{hydrolysis}]{\text{Maltase}}$ Glucose $\xrightarrow[\text{Fermentation}]{\text{Zymase}}$

EtOH

ETHERS

Ethers are compounds of the general formula R — O — R, Ar — O — R or Ar — O — Ar, where Ar is an aromatic group. An ether is symmetrical if the two groups attached to the oxygen atom are the same, and it is unsymmetrical if the groups are different.



$$CH_3CH_2CH_2\underset{\displaystyle OCH_3}{\underset{|}{C}}HCH_2CH_3$$

3-Methoxyhexane

$CH_3CH_2OCH_2CH_2CH_3$

1-Ethoxypropane

PREPARATION :

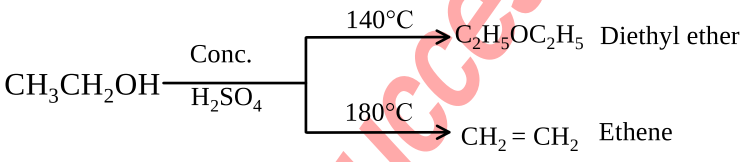
1. Dehydration of alchols

$$2R - O - H \xrightarrow[\Delta]{H_2SO_4} R - O - R + H_2O$$

A water molecule is lost for every pair of alcohol molecules. Dehydration is limited to the preparation of symmetrical ethers, because a combination of two different alcohols yields a mixture of three ethers.

Alcohols can also dehydrate to alkenes, but dehydration to ethers is controlled by the choice of reaction conditions.

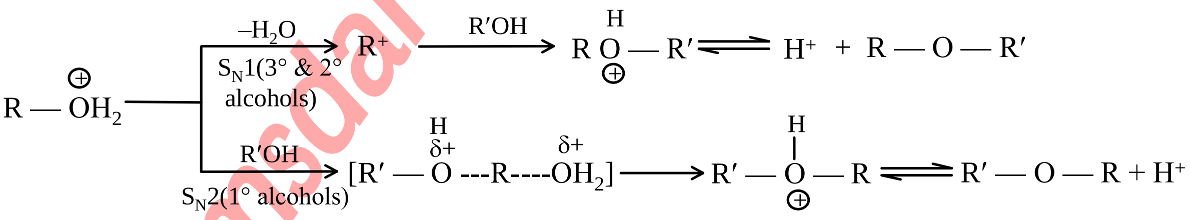
Example:



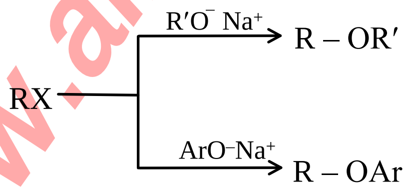
Ether formation by dehydration is an example of nucleophilic substitution: protonated alcohol is the substrate and the second molecule of alcohol is the nucleophile.

The reaction is $S_N{}^1$ for 2° and 3° alcohols and $S_N{}^2$ for 1° alcohol.

$$R - OH + \overset{\oplus}{H} \rightleftharpoons R - \overset{\oplus}{O}H_2 \text{ (Protonated alcohol)}$$



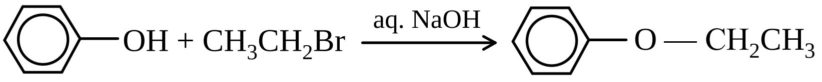
2. Williamson synthesis



Yield from RX: $CH_3 > 1° > 2° > 3°$

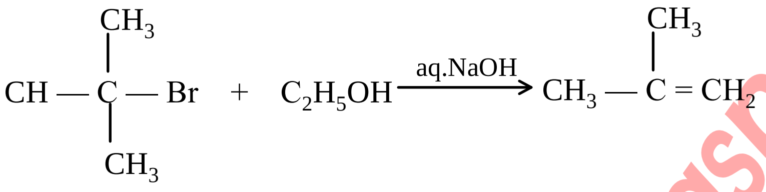
The reaction involves the nucleophic substitution of an alkoxide (or phenoxide) ion for a halide ion. This method can be used for preparing symmetrical as well as asymmetrical ethers.

$$(CH_3)_2\ CH(OH) \xrightarrow{Na} (CH_3)_2CHO^-Na^+ + CH_3CH_2CH_2Br \longrightarrow CH_3(CH_2)_2O\ CH(CH_3)_2$$



Ethoxybenzene

The reaction gives the best yield with 1° alkyl halides. With tertiary alkyl halides, elimination becomes an important reaction and no ether is obtained.



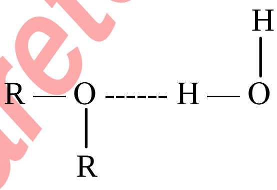
$$CH-\underset{CH_3}{\overset{CH_3}{C}}-Br + C_2H_5OH \xrightarrow{aq.NaOH} CH_3-\overset{CH_3}{C}=CH_2$$

Physical Properties

1. The C — O — C bond angle in ethers is not 180° and the dipole moments of the two C — O bonds do not cancel each other. Hence, ethers possess a small net dipole moment.

2. The boiling point of ethers are the same as those of alkanes of comparable molecular weights. The boiling points of alcohols are much higher than those of ethers, as ethers are incapable of intermolecular hydrogen bonding.

3. The solubility of ethers in water is comparable to that of alcohols, because ethers can form hydrogen bonds with water molecules.



Chemical Properties

Ethers are unreactive compounds. The ether linkage is quite stable towards bases, oxidising, and reducing agents.

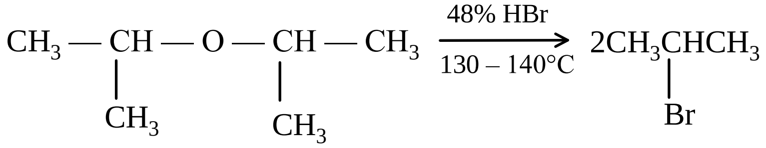
1. **Cleavage by acids**

$$\begin{tikzcd} R-O-R' + HX \arrow[r] & R-X + R'OH \arrow[d, "HX"'] \\ & R'-X \end{tikzcd}$$

Reactivity of HX **:** HI > HBr > HCl.

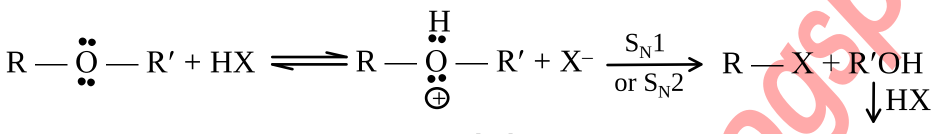
Cleavage takes place under vigorous conditions using concentrated acids and high temperature.

A dialkyl ether initially yields an alkyl halide and an alcohol; the alcohol may further react to form second mole of alkyl halide.



$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{CH}}-O-\underset{\displaystyle CH_3}{\underset{|}{CH}-CH_3} \xrightarrow[130-140^{\circ}C]{48\%\ HBr} 2CH_3\underset{\displaystyle Br}{\underset{|}{CH}}CH_3$$

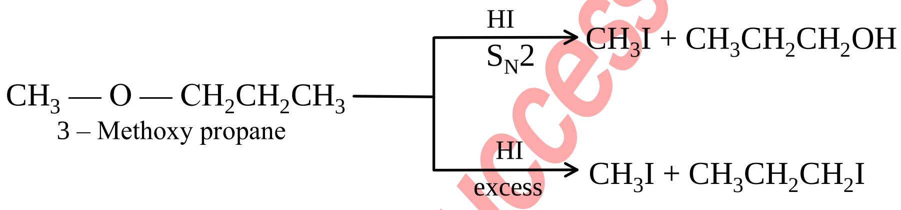
The initial reaction between an ether and an acid results in the formation of a protonated ether. The cleavage then involves a nucleophilic attack by a halide ion on this protonated ether with the displacement of the weakly basic alcohol molecule.



$$R-\ddot{\underset{\cdot\cdot}{O}}-R' + HX \rightleftharpoons R-\overset{H}{\underset{\oplus}{\ddot{O}}}-R' + X^- \xrightarrow[\text{or } S_N2]{S_N1} R-X + R'OH \xrightarrow{HX} R'X$$

Protonated ether

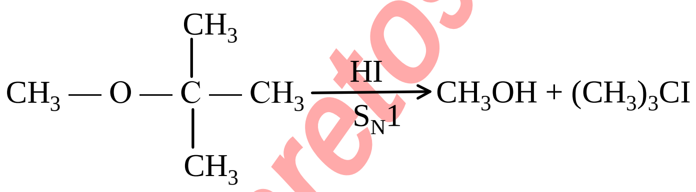
A primary alkyl group tends to undergo S_N2 displacement and a tertiary alkyl group tends to undergo S_N1 displacement.



$CH_3-O-CH_2CH_2CH_3$
3 – Methoxy propane

$\xrightarrow[S_N2]{HI} CH_3I + CH_3CH_2CH_2OH$

$\xrightarrow[\text{excess}]{HI} CH_3I + CH_3CH_2CH_2I$

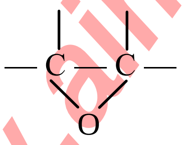


$$CH_3-O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \xrightarrow[S_N1]{HI} CH_3OH + (CH_3)_3CI$$

2 – Methoxy–2–methyl propane

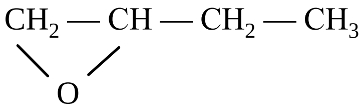
Epoxides

Epoxides are compounds containing the three-membered ring.

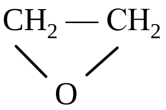


(Epoxide or oxirane ring)

Epoxides belong to a class of compounds called cyclic ethers. The three-membered ring makes epoxides an exceedingly important class of compounds.



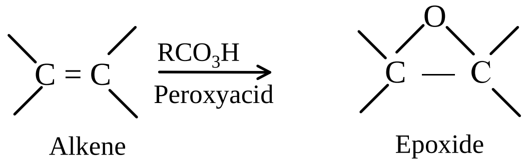
1, 2 – Epoxybutane



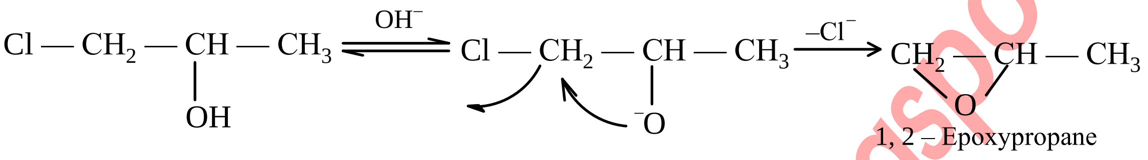
Epoxyethane

PREPARATION

Epoxides are commonly obtained by oxidation of alkenes by peroxy acids.



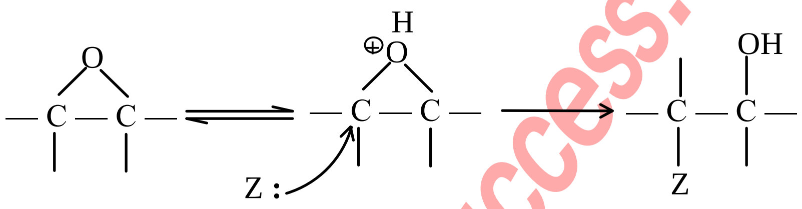
Silver oxide can also oxidise alkenes to epoxides. An internal S_N2 reaction in a chlorohydrin can be used to prepare three membered cyclic ethers.



Reactions :

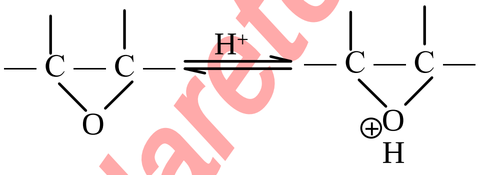
Epoxides have highly strained three-membered rings that can undergo acid- or base-catalysed ring cleavage.

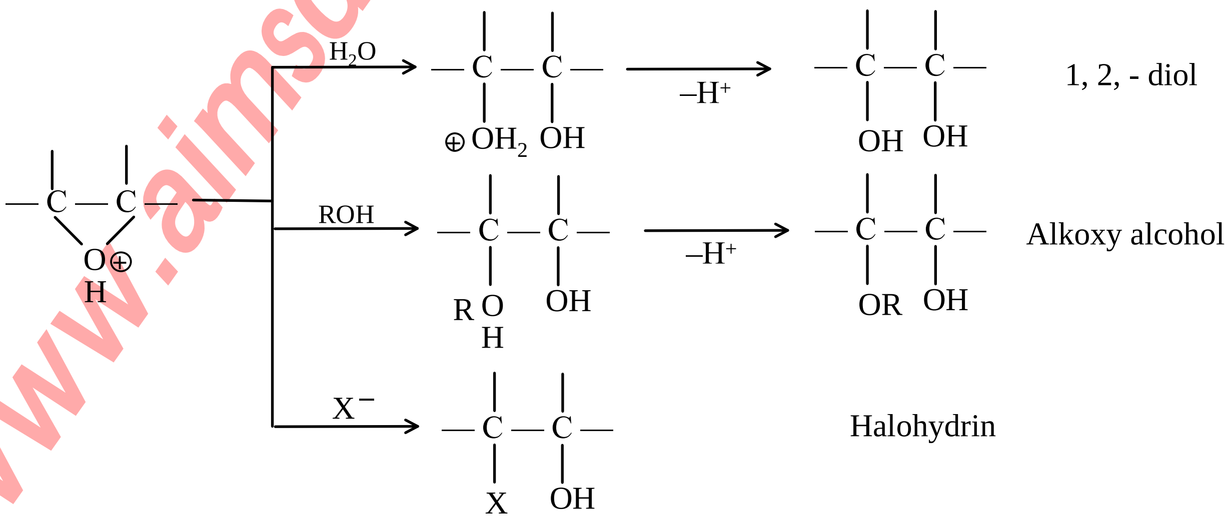
1. **Acid-catalysed cleavage**



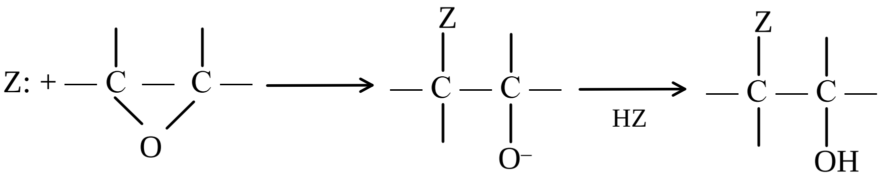
z: = nucleophile

At first, the epoxide is protonated by an acid and the protonated epoxide can then undergo an attack by nucleophilic reagents.

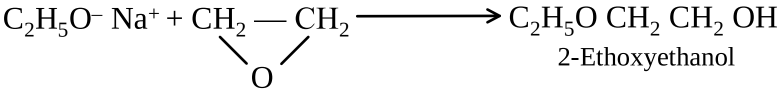




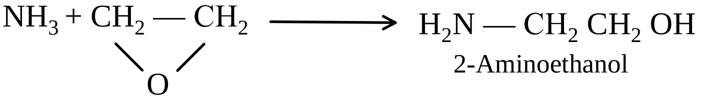
2. Base-catalysed cleavage



Under alkaline conditions, an epoxide itself undergoes nucleophilic attack.

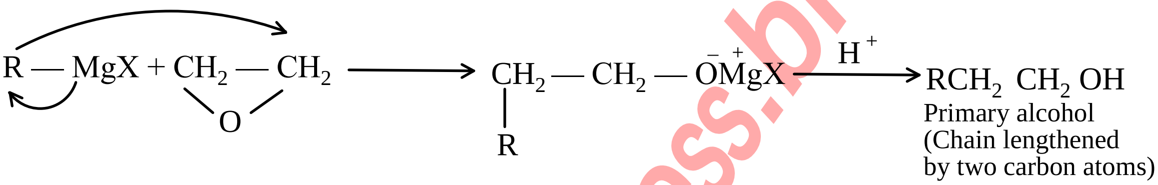


2-Ethoxyethanol

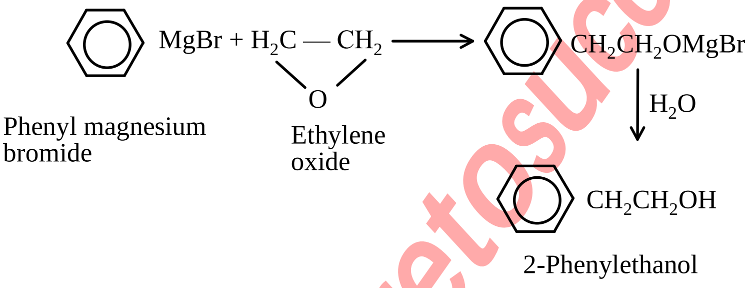


2-Aminoethanol

3. Reaction with Grignard reagent



Primary alcohol
(Chain lengthened
by two carbon atoms)



Phenyl magnesium bromide

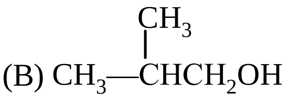
Ethylene oxide

2-Phenylethanol

EXERCISE–I

Q.1 Which of the following is produced when an aqueous solution of butan-2-ol is refluxed with dilute acidic $KMnO_4$?
(A) butanol (B) butanoic acid
(C) potassium butanoate (D) butanone

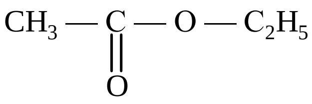
Q.2 Which of the following has the lowest solubility in water?
(A) $CH_3CH_2CH_2CH_2OH$

(B) 
$CH_3—\underset{}{\overset{CH_3}{|}}\!\!CHCH_2OH$

(C) $HOH_2C — CH_2OH$ (D) $C_6H_5CH_2CH_2OH$

Q.3 Chlorine reacts with ethanol to give
(A) ethylchloride (B) chloroform (C) chloral (D) acetaldehyde

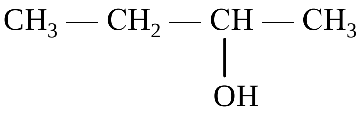
Q.4 Ethanol is heated with concentrated H_2SO_4. The product formed is

(A) 
$CH_3 — \underset{\underset{O}{\|}}{C} — O — C_2H_5$

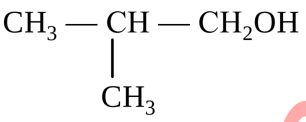
(B) C_2H_6

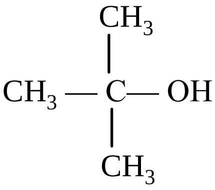
(C) C_2H_4 (D) C_2H_2

Q.5 Which of the following has the highest boiling point?

(A) 
$CH_3 — CH_2 — \underset{\underset{OH}{|}}{CH} — CH_3$

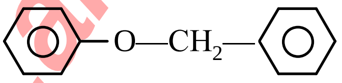
(B) $CH_3 — CH_2 — CH_2 — CH_2OH$

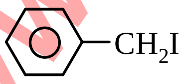
(C) 
$CH_3 — \underset{\underset{CH_3}{|}}{CH} — CH_2OH$

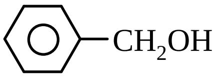
(D) 
$CH_3 — \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} — OH$

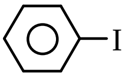
Q.6 Lucas test is used to determine the type of
(A) amines (B) alcohols (C) acids (D) phenols

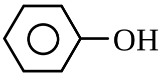
Q.7 Separation of a higher phenol and an aromatic carboxylic acid can be easily carried out by
(A) NaOH (B) Na_2CO_3 (C) lime (D) $NaHCO_3$

Q.8 The ether  when treated with HI produces

(A) 

(B) 

(C) 

(D) 

Q.9 The reaction between sodium ethoxide and bromoethane yields

(A) methyl ethyl ether (B) dimethyl ether

(C) diethyl ether (D) propane

Q.10 The hydroboration oxidation of 2-methyl propene yields-

(A) 1° alcohol (B) 2° alcohol (C) 3° alcohol (D) None

Q.11 Action of HNO_2 on CH_3NH_2 gives-

(A) CH_3OH (B) $CH_3—O—CH_3$ (C) $CH_3—O—N=O$ (D) B and C both

Q.12 The alkaline hydrolysis of esters is known as:

(A) Hydration (B) Esterification

(C) Dehydration (D) Saponification

Q.13 Which of the following reactions of an alcohol does not involve O – H bond breaking :

(A) Reaction with alkali metals (B) Reaction with an acyl chloride

(C) Reaction with sulphonyl chloride (D) Reaction with conc. sulphuric acid.

Q.14 Replacement of -OH group in alcohol by -Cl cannot be carried out with-

(A) PCl_5 (B) SO_2Cl_2 (C) PCl_3 (D) $SOCl_2$

Q.15 A on treatment with Na gives B and with PCl_5 gives C. B and C react together to give diethyl ether. A, B and C are in the order-

(A) $C_2H_5OH, C_2H_5Cl, C_2H_5ONa$ (B) $C_2H_5OH, C_2H_6, C_2H_5Cl$

(C) $C_2H_5OH, C_2H_5ONa, C_2H_5Cl$ (D) $C_2H_5Cl, C_2H_6, C_2H_5OH$

Q.16 A compound is soluble in concentrated H_2SO_4. It does not decolourise bromine in carbon tetrachloride but oxidised by chromic anhydride in aq. sulphuric acid within two seconds, turning orange solution to blue green then opaque. The original compound is-

(A) A primary alcohol (B) A tertiary alcohol

(C) An alkene (D) An ether

Q.17 Which of the following alcohols does not give a red colour in Victor Meyer test-

(A) Isobutyl alcohol (B) Isoamyl alcohol

(C) Diethyl carbinol (D) Phenylcarbinol

Q.18 Water gas is mixture of-

(A) $CO + H_2$ in the ratio 1 : 2 (B) $CO_2 + H_2$ in the ratio 1 : 1

(C) Steam + CO in the ratio 1 : 1 (D) $CO + CO_2$ + Steam

Q.19 Absolute alcohol contains-

(A) 40% H_2O (B) 10% H_2O (C) 5% H_2O (D) 100% C_2H_5OH

Q.20 Proof spirit contains about-

(A) 40% alcohol by weight (B) 50% alcohol by weight

(C) 25% alcohol by weight (D) 10% alcohol by weight

Q.21 Reaction of alcohol does not show cleavage of R-O linkage-

(A) ROH + PCl_5 (B) ROH + $SOCl_2$ (C) ROH + HCl (D) ROH + Na

Q.22 An organic compound dissolved in dry benzene, evolved hydrogen on treatment with sodium. It is-

(A) A ketone (B) An aldehyde (C) A tertiary amine (D) An alcohol

Q.23 Alkyl chloride is formed when alcohol is treated with HCl in presence of anhydrous $ZnCl_2$. The order of reactivity with respect to alcohol is :

(A) $3^\circ > 2^\circ > 1^\circ$ (B) $1^\circ > 2^\circ > 3^\circ$ (C) $2^\circ > 1^\circ > 3^\circ$ (D) $1^\circ > 3^\circ > 2^\circ$

Q.24 The increasing order of boiling points of 1°, 2°, 3° alcohol is -

(A) $1^\circ > 2^\circ > 3^\circ$ (B) $3^\circ > 2^\circ > 1^\circ$

(C) $2^\circ > 1^\circ > 3^\circ$ (D) None

Q.25 Hydrogen bonding is possible in-

(A) Ethers (B) Hydrocarbons (C) Alkanes (D) Alcohols

Q.26 Consider the reaction: $CH_3CH_2CH_2OH \xrightarrow{PCl_5} A \xrightarrow[KOH]{alc.} B$. The compound 'B' is

(A) propane (B) propene (C) propyne (D) propanal

Q.27 The solubility of lower alcohols in water is due to -

(A) Formation of hydrogen bond between alcohol and water molecules

(B) Hydrophobic nature of alcohol

(C) Increases in boiling points

(D) None of these

Q.28 A compound 'A' reacts with sodium metal and also undergoes iodoform reaction. 'A' is

(A) phenol (B) methanol (C) n-propanol (D) iso-propanol

Q.29 Which of the following ethers is cleaved even by HCl at room temperature?

(A) $C_6H_5OCH_2CH_3$ (B) $CH_3CH_2OCH_2CH_3$

(C) $(CH_3)_3COCH_2CH_3$ (D) $(CH_3)_3COC(CH_3)_3$

Q.30 Anhydride of alcohol is-

(A) Ether (B) Aldehyde

(C) Alkanoic anhydride (D) Alkoxides

EXERCISE–II

Q.1 When CH_2=CH–COOH is reduced with $LiAlH_4$, the compound obtained will be – **[AIEEE-2003]**

(A) CH_3–CH_2–CH_2OH (C) CH_3–CH_2–CHO

(C) CH_3–CH_2–COOH (D) CH_2=CH–CH_2OH

Q.2 Among the following compounds which can be dehydrated very easily is - **[AIEEE-2004]**

(A) $CH_3CH_2CH_2CH_2CH_2OH$ (B) CH_3 CH_2 CH_2 CH_3

(C) CH_3CH_2 CH_3 (D) CH_3 CH_2 CH_2 CH_2OH

Q.3 For which of the following parameters the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values ? (Assume ideal behaviour) **[AIEEE-2004]**

(A) Heat of vaporization

(B) Vapour pressure at the same temperature

(C) Boiling points

(D) Gaseous densities at the same temperature and pressure

Q.4 A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was **[AIEEE 2009]**

(A) HCHO (B) CH_3COCH_3 (C) CH_3COOH (D) CH_3OH

Q.5 When phenol is treated with bromine water in excess, it gives

(A) m-bromophenol (B) o-and p-bromophenol

(C) 2, 4–dibromophenol (D) 2, 4, 6–tribromophenol

Q.6 The compound that does not change the orange colour of chromic acid to blue green is

(A) 2° alcohol (B) 1° alcohol (C) 3° alcohol (D) none of the above

Q.7 HBr reacts the fastest with

(A) 2-methyl propan-2-ol (B) propan-1-ol

(C) propan-2-ol (D) 2-methyl propan-1-ol

Q.8 A compound 'X' on oxidation gave 'B' and then again on oxidation gave an acid. After the first oxidation, it reacted with ammoniacal silver nitrate to produce a black precipitate. 'X' is

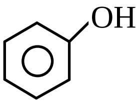
(A) a primary alcohol (B) a tertiary alcohol (C) acetaldehyde (D) acetone

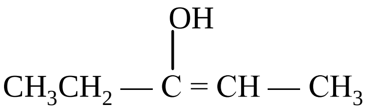
Q.9 R—CH_2—CH_2 OH can be converted into RCH_2CH_2COOH. The correct sequence of reagent is

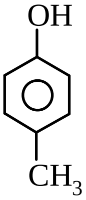
(A) P Br_3, KCN, H^+ (B) P Br_3, KCN, H_2

(C) KCN, H^+ (D) HCN, PBr_3, H^+

Q.10 The characteristic dark colour with neutral $FeCl_3$ is given by

(A) 

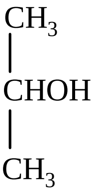
(B) 
$CH_3CH_2-\overset{\overset{\Large OH}{|}}{C}=CH-CH_3$

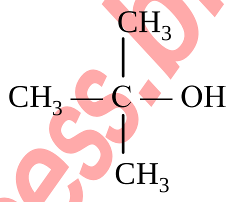
(C) 

(D) $CH_3CH_2CH_2OH$

Q.11 Which of the following has a higher pH?
(A) phenol (B) o-cresol (C) p-nitrophenol (D) glycerol

Q.12 Which of the following alcohols is a stronger acid?
(A) CH_3OH (B) CH_3-CH_2-OH

(C) 
$\begin{array}{c} CH_3 \\ | \\ CHOH \\ | \\ CH_3 \end{array}$

(D) 
$CH_3-\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-OH$

Q.13 The reaction of anisole with HI leads to the formation of
(A) phenol and methanol (B) phenol and methyl iodide
(C) iodobenzene and methanol (D) iodobenzene and methyl iodide

Q.14 Methyl-tert-butyl ether on heating with HI gives
(A) $CH_3I + (CH_3)_3COH$ (B) $CH_3OH + (CH_3)_3CCI$
(C) $CH_3I + (CH_3)_3CI$ (D) $(CH_3)_3CCI + CH_3OH$

Q.15 Which of the following compounds is resistant to nucleophilic attack by hydroxyl ions?
(A) methyl acetate (B) acetonitrile (C) dimethyl ether (D) acetamide

Q.16 Diethyl ether absorbs oxygen to form
(A) a red-coloured sweet-smelling compound (B) acetic acid
(C) ether suboxide (D) ether peroxide

Q.17 On boiling with concentrated HBr, phenyl ethyl ether will yield
(A) phenol and ethyl bromide (B) bromobenzene and ethanol
(C) phenol and ethane (D) bromobenzene

Q.18 Which of the following alcohols is least soluble in water ?
(A) n-Butyl alcohol (B) iso-Butyl alcohol (C) tert-Butyl alcohol (D) sec-Butyl alcohol

Q.19 2-Bromopentane is heated with potassium ethoxide in ethanol.The major product obtained is-
(A) 2-ethoxypentane (B) pentene-1 (C) cis-pentene-2 (D) trans-pentene-2

Q.20 Which of the following reactions of alkanols does not involve C – O bond breaking :

(A) $CH_3CH_2OH + SOCl_2$ (B) $CH_3CH(OH)CH_3 + PBr_3$
(C) $CH_3CH_2OH + CH_3COOH$ (D) $ROH + HX$

Q.21 Reactivity of alcohols with HCl is in the order of :

(A) Tert butyl alcohol > sec. butyl alcohol > primary butyl alcohol
(B) Primary butyl alcohol > sec. butyl alcohol > tert butyl alcohol
(C) Sec. butyl alcohol > tert butyl alcohol >primary butyl alcohol
(D) Sec. butyl alcohol > primary butyl alcohol > tert butyl alcohol

Q.22 Given :

Four Alcohols	Number of α–hydrogen	Number of β–hydrogen
A	3	0
B	2	3
C	1	6
D	0	9

Which alcohol will give blue colour with Victor Meyer reagent :

(A) C (B) B (C) D (D) A

Q.23 Non–occurence of the following reaction

$Br^- + CH_3OH \rightarrow BrCH_3 + OH^-$, is due to:

(A) Attacking nucleophile is stronger one (B) Leaving group is a strong base
(C) Alcohols are not good substrate (D) Hydroxide ions are weak bases

Q.24 Ethyl alcohol is less acidic than phenol because :

(A) The phenoxide ion is more resonance stabilized than phenol
(B) There is more hydrogen bonding in phenol than in ethyl alcohol
(C) The ethoxide ion is less resonance stabilized than ethyl alcohol
(D) Phenol has a higher b.p. than ethyl alcohol

Q.25 The compound obtained by the acidolysis of ether [dil. H_2SO_4] gives the following test :

(A) Yellow precipitate with NaOH and I_2
(B) Smell of formaline with hot copper wire
(C) Smell of oil of winter-green with salicylic acid and H_2SO_4
(D) Acid obtained by oxidation decolourises $KMnO_4$

Q.26 2-Bromoethanol reacts with magnesium to from :

(A) $HOCH_2CH_2MgBr$ (B) $CH_3 - CH_2OH$
(C) CH_3CH_2MgBr (D) $BrCH_2–CH_2MgBr$

Q.27 Methylethylketone can be obtained by the oxidation of :

(A) 2-Butanol (B) 2-Propanol (C) 1-Butanol (D) Tert.butyl alcohol

Q.28 An alcohol (ROH) reacts with an acid to form initially :

(A) $RCH_2–H_2$ (B) R^+ (C) $R–H_2$ (D) An alkene

Q.29 will have the minimum value of pK_a when X is :

(A) F (B) Cl (C) Br (D) NO_2

Q.30 The oxidation of a secondary alkanol with Cr (VI) leads to the formation of :

(A) An alkanone and Cr (II) (B) An aldehyde and Cr (III)
(C) An alkanone and Cr (III) (D) An aldehyde and Cr (II)

ANSWER KEY

EXERCISE–I

Q.1	D	Q.2	D	Q.3	C	Q.4	C	Q.5	B	Q.6	B	Q.7	D
Q.8	A	Q.9	C	Q.10	A	Q.11	D	Q.12	D	Q.13	D	Q.14	B
Q.15	A	Q.16	A	Q.17	C	Q.18	A	Q.19	D	Q.20	B	Q.21	D
Q.22	D	Q.23	A	Q.24	A	Q.25	D	Q.26	B	Q.27	A	Q.28	D
Q.29	D	Q.30	A										

EXERCISE–II

Q.1	D	Q.2	D	Q.3	D	Q.4	C	Q.5	D	Q.6	C	Q.7	A
Q.8	A	Q.9	A	Q.10	A	Q.11	D	Q.12	A	Q.13	B	Q.14	C
Q.15	C	Q.16	D	Q.17	A	Q.18	A	Q.19	D	Q.20	D	Q.21	A
Q.22	A	Q.23	B	Q.24	A	Q.25	A	Q.26	B	Q.27	A	Q.28	D
Q.29	D	Q.30	C										

CARBONYL COMPOUND

1. INTRODUCTION :

(a) Organic compounds in which $-\underset{\underset{\displaystyle O}{||}}{C}-$ group is present are called '**Aldehyde & Ketone**'.

(b) The group $-\underset{\underset{\displaystyle O}{||}}{C}-$ is called as carbonyl group so, compound are also called carbonyl compounds. If H atom is attached with this carbonyl group then compound is called **aldehyde** and if alkyl group is present on both sides then compound is called **Ketone**.

(c) In ketone if both alkyl group are same then they are called simple ketone, if different then called mixed ketone.

(d) Their general formula is $C_nH_{2n}O$. Hybridisation state of carbon is sp^2 and C = O bond length is 1.23 A°.

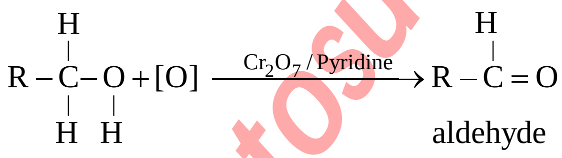
(e) The ratio of C, H & O in formaldehyde is 1 : 2 : 1 (CH_2O). It is called simplest sugar.

(f) Aldehyde shows chain, position and functional isomerism.

(g) Ketone shows chain, position, functional and metamerism also. Aldehyde and ketone both are functional isomers with each other.

2. GENERAL METHODS OF PREPARATION

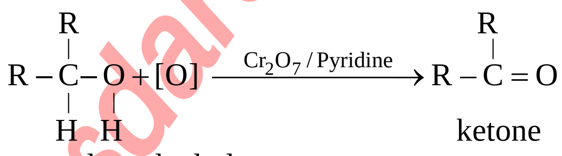
2.1 From Alcohol (By Oxidation) :–



$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{O}+[O]\xrightarrow{Cr_2O_7\,/\,Pyridine}R-\overset{\overset{\displaystyle H}{|}}{C}=O$$

aldehyde

primary alcohol



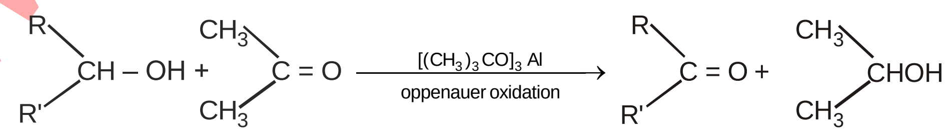
$$R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{O}+[O]\xrightarrow{Cr_2O_7\,/\,Pyridine}R-\overset{\overset{\displaystyle R}{|}}{C}=O$$

ketone

secondary alcohol

NOTE :–

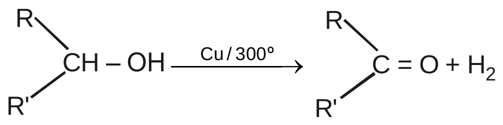
In this reaction if we take acidic $KMnO_4$ or $K_2Cr_2O_7$ then reaction will not stop on aldehyde or ketone because they are strong oxidising agent. They further oxidise aldehyde, ketone into acid. So, to stop the reaction on aldehyde & ketone, we use mild oxidant Cr_2O_7 in pyridine solution. For better yield, we can use CrO_3 in 3° butyl alcohol. For 2° alcohol we can use aluminium tertiary butoxide $[(CH_3)_3\,CO]_3\,Al$



2.2 From Alcohol (By Catalytical Oxidation) :–

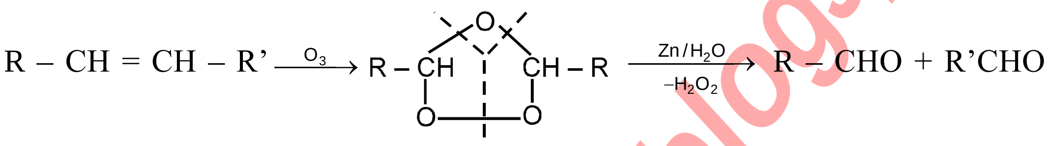
When vapours of a primary alkanol (or secondary alkanol) are passed over heated copper (or zinc oxide) at 300º then alkanals (or alkanones) are formed.

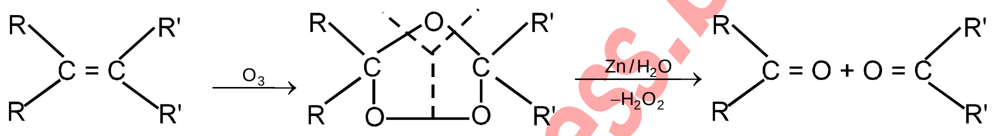
$$R-CH_2OH \xrightarrow{Cu/300^\circ} R-CHO + H_2$$



2.3 From Alkene (Ozonolysis) :–

Desired alkanals and alkanones can be obtained by ozonolysis of appropriate alkenes.





2.4 From Alkyne : –

Acetaldehyde is formed on passing acetylene in 40% aqueous solution of H_2SO_4 at 60º in the presence of 1% $HgSO_4$. It is called Kucherov's reaction.

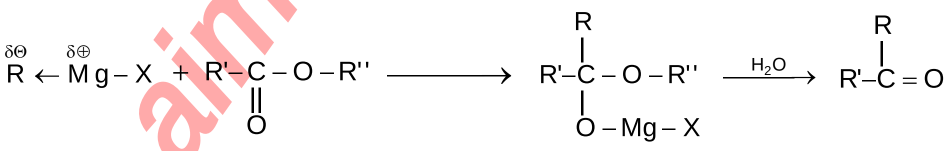
$$CH \equiv CH + HOH \xrightarrow{HgSO_4/dil.H_2SO_4} CH_2=CH-OH \xrightarrow{rearrangement} CH_3-CHO$$

$$R-C\equiv C-H + HOH \xrightarrow{HgSO_4/dil.H_2SO_4} R'-\underset{OH}{\underset{|}{C}}=CH_2 \xrightarrow{rearrangement} R-\underset{O}{\underset{||}{C}}-CH_3$$

NOTE : Methanal cannot be formed from the above reaction.

2.5 From Grignard's Reagent : –

Alkanal is formed by reaction of formic ester and an alkylmagnesium halide.



Ketones are obtained from acetic and higher esters. Acid chlorides and amides can be taken in place of esters. However HCOCl cannot be taken because it is unstable.

$$R–MgX + C_2H_5O–CO–R' \rightarrow R–CO–R' + C_2H_5O–MgX$$

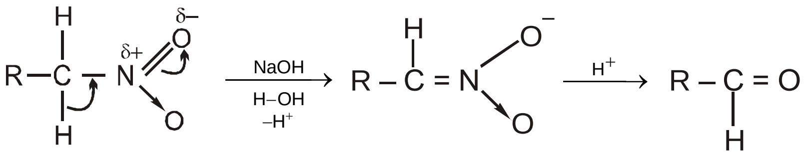
$$R–MgX + Cl–CO–R' \rightarrow R–CO–R' + MgXCl$$

$$R–MgX + H_2N–CO–R' \rightarrow R–CO–R' + Mg(NH_2)X$$

NOTE : Formaldehyde cannot be formed from the above reaction.

2.6 From Nitroalkane (Nef reaction) : –

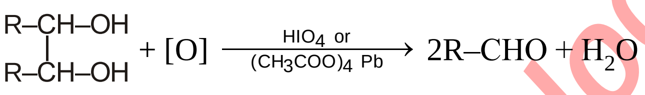
By Nef reaction, formaldehyde can be obtained from nitromethane, acetaldehyde from nitroethane and acetone from 2–nitropropane.



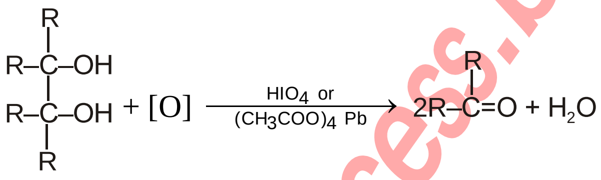
aldehyde

2.7 From Vicinal Glycol (Oxidation) :–

Carbonyl compounds are obtained on oxidation of vicinal alkanediols by periodic acid or lead tetraacetate



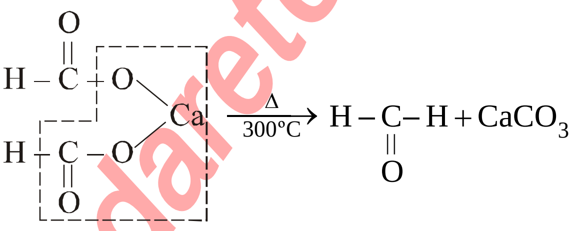
$$\begin{matrix}\text{R–CH–OH}\\ |\\ \text{R–CH–OH}\end{matrix} + [O] \xrightarrow[(CH_3COO)_4\,Pb]{HIO_4 \text{ or}} 2R\text{–}CHO + H_2O$$

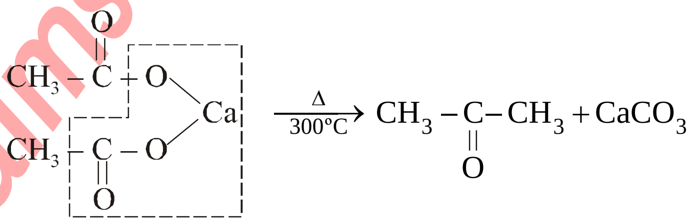


$$\begin{matrix}\text{R}\\ |\\ \text{R–C–OH}\\ |\\ \text{R–C–OH}\\ |\\ \text{R}\end{matrix} + [O] \xrightarrow[(CH_3COO)_4\,Pb]{HIO_4 \text{ or}} 2R\text{–}\overset{\overset{\displaystyle R}{|}}{C}{=}O + H_2O$$

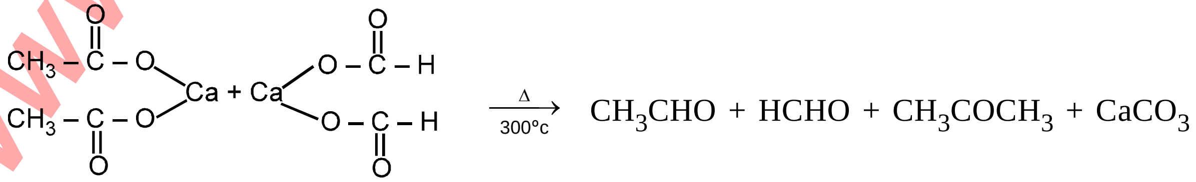
2.8 From Calcium or Barium salt of Carboxylic acid : –

When calcium salts of alkanoic acids are subjected to dry distillation, then carbonyl compounds are formed. The yield increases on taking barium, manganese and thorium salts of alkanoic acids. Formaldehyde is formed on taking calcium formate (R = H) and acetone is formed on taking calcium acetate (R = CH_3).





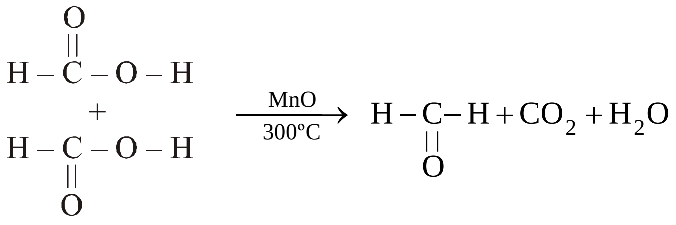
Acetaldehyde can be formed by taking a mixture of calcium formate and calcium acetate.



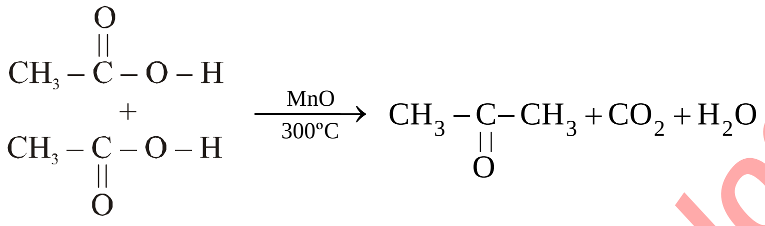
$CH_3CHO + HCHO + CH_3COCH_3 + CaCO_3$

2.9 From Carboxylic Acid : – When vapours of carboxylic acid are passed on mangnese oxide MnO at 300ºC, then carbonyl compounds are formed.

Formaldehyde is prepared from formic acid (R = R' = H), acetone from (R = R' = CH_3), and acetaldehyde from a mixture of acetic acid (R' = CH_3) and formic acid (R = H).



$$H-\underset{}{\overset{O}{\overset{\|}{C}}}-O-H + H-\underset{\underset{O}{\|}}{C}-O-H \xrightarrow[300^\circ C]{MnO} H-\underset{\underset{O}{\|}}{C}-H + CO_2 + H_2O$$



$$CH_3-\overset{O}{\overset{\|}{C}}-O-H + CH_3-\underset{\underset{O}{\|}}{C}-O-H \xrightarrow[300^\circ C]{MnO} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CO_2 + H_2O$$

2.10 From Alkyne (Hydroboration) :–

When a dialkylborane is reacted with an alkyne, then dialkylvinylbroane adduct is formed, which on reacting alkaline hydrogen peroxide solution forms a carbonyl compound. Alkanals are formed from terminal alkynes, and alkanones from nonterminal alkynes.

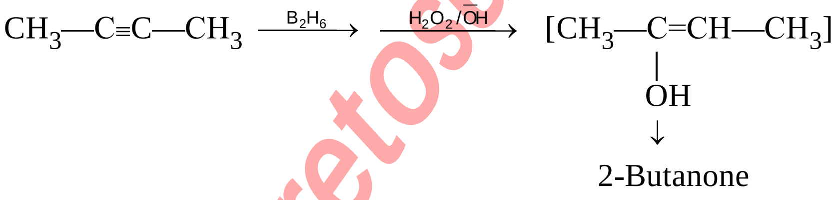
1–Alkyne ⟶ Aldehyde

Other alkynes ⟶ Ketone

(i) $CH_3—C \equiv CH \xrightarrow{B_2H_6} (CH_3—CH=CH—)_3B \xrightarrow{H_2O_2/\overline{O}H} [CH_3—CH=CHOH]$

$\hookrightarrow CH_3–CH_2–CHO$

(ii)



$$CH_3—C\equiv C—CH_3 \xrightarrow{B_2H_6} \xrightarrow{H_2O_2/\overline{O}H} [CH_3—\underset{\underset{OH}{|}}{C}=CH—CH_3] \downarrow \text{2-Butanone}$$

2.11 From Hydrolysis of oximes and acetals :-

Carbonyl compounds are formed from hydrolysis of oximes and acetals.

$CH_3CH=NOH \xrightarrow{H_2O} CH_3CHO + NH_2OH$

Acetaldoxime

$(CH_3)_2C=NOH \xrightarrow{H_2O} (CH_3)_2C=O + NH_2OH$

Acetone-oxime

$CH_3CH(OC_2H_5)_2 \xrightarrow{H_2O} CH_3CHO + 2C_2H_5OH$

Acetal

2.12 From Hydrolysis of gemdihalide :-

Carbonyl compounds are formed on heating alkylidene dihalides with aqueous caustic alkali solution.

$>CCl_2 \xrightarrow{NaOH} > C(OH)_2 \xrightarrow{-H_2O} >C=O$

$CH_3CHCl_2 \xrightarrow{NaOH} \xrightarrow{-H_2O} CH_3–CHO$

$CH_3CCl_2CH_3 \xrightarrow{NaOH} \xrightarrow{-H_2O} (CH_3)_2C=O$

3. METHODS OF PREPARATION ONLY FOR ALEDHYDES

3.1 Stephen's Method : –

By dissolving an alkyl cyanide in ether and reacting it with stannous chloride and conc. hydrochloride, aldimine chlorostannate salt is obtained. Alkanal is formed on hydrolysis of this salt.

$$\underset{\text{Acid nitrile}}{R{-}C{\equiv}N} \xrightarrow{HCl} R{-}C{\equiv}N^{+}HCl^{-} \xrightarrow[HCl]{SnCl_2} \underset{\text{Aldimine chlorostannate}}{[R-CH=\overset{\oplus}{N}H_2]_2SnCl_6^{2-}}$$

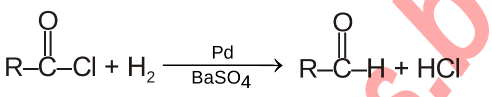
$$[R{-}CH{=}NH]_2SnCl_6 + 2H_2O \rightarrow 2\underset{\text{Alkanal}}{R-CH=O} + (NH_4)_2SnCl_6$$

Taking the example of acetonitirle (methyl cyanide) Stephen reaction can be shown expressed as follows.

$$\underset{\text{Acetonitrile}}{CH_3-C\equiv N} + 2H \xrightarrow[HCl]{SnCl_2} \underset{\text{Acetaldimine}}{CH_3-CH=NH} \xrightarrow{HOH} \underset{\text{Acetaldehyde}}{CH_3-CH=O}$$

3.2 Rosenmund Reaction :

Aldehydes are formed on reduction of a carboxylic acid chloride in boiling xylene medium by hydrogen and palladised barium sulphate.

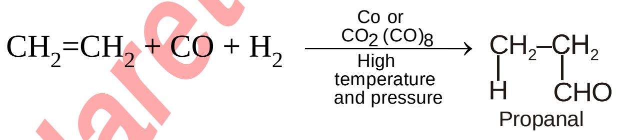


$$R-\overset{\overset{\Large O}{\|}}{C}-Cl + H_2 \xrightarrow[BaSO_4]{Pd} R-\overset{\overset{\Large O}{\|}}{C}-H + HCl$$

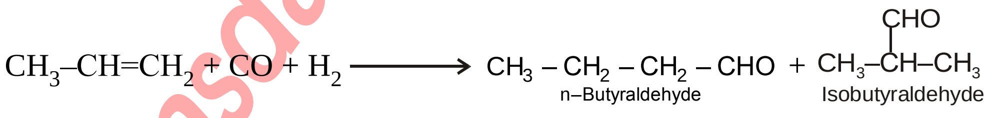
Acetaldehyde is formed on taking acetyl chloride ($R = CH_3$). Formaldehyde cannot be prepared by Rosenmund reaction, because HCOCl is not a stable compound, $BaSO_4$ acts as a catalyst poison and decreases the catalytic efficiency of Pd catalyst, due to which further reduction of acetaldehyde formed to primary alcohol cannot take place.

3.3 Oxo-reaction :-

When a mixture of an alkene, carbon monoxide and hydrgen is passed over cobalt catalyst at high temperature and pressure, then alkanals are formed. Dicobalt octacarbonyl $[Co_2(CO)_8]$ can be used as a catalyst in place of cobalt. Due to addition of hydrogen and formyl group on unsaturated carbon atoms of alkene, this reaction is called hydroformylation.



$$CH_2{=}CH_2 + CO + H_2 \xrightarrow[\text{High temperature and pressure}]{\text{Co or } CO_2(CO)_8} \underset{\text{Propanal}}{\underset{H\quad\;\; CHO}{CH_2{-}CH_2}}$$

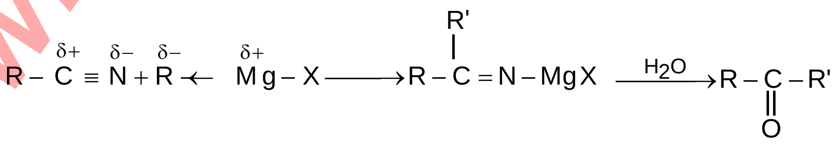


$$CH_3{-}CH{=}CH_2 + CO + H_2 \longrightarrow \underset{\text{n–Butyraldehyde}}{CH_3-CH_2-CH_2-CHO} + \underset{\text{Isobutyraldehyde}}{CH_3{-}\overset{\overset{CHO}{|}}{C}H{-}CH_3}$$

4 METHODS OF PREPARATION ONLY FOR KETONES

4.1 From Alkyl Cyanide : –

Alkanones are formed on hydrolysis after reaction of an alkylmagnesium halide with ethyl cyanide or its higher homologue.



$$\overset{\delta+}{R}-\overset{\delta-}{C}\equiv\overset{\delta-}{N}+R\leftarrow\overset{\delta+}{Mg}-X \longrightarrow R-\overset{\overset{R'}{|}}{C}=N-MgX \xrightarrow{H_2O} R-\underset{\underset{O}{\|}}{C}-R'$$

In this reaction if we take HCN with G.R., product will be aldehyde but major product will be alkane because HCN is an example of active H compound and with active hydrogen compound GR forms alkane.

4.2 Dialkyl cadmium with acid chlorides :–

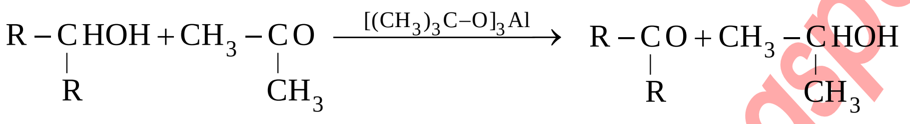
A ketone and an alkylcadmium chloride are formed on reacting a dialkylcadmium with an acid chloride.

$$R–Cd–R + Cl–CO–R' \longrightarrow R–CO–R' + R–Cd\ Cl$$

Dialkylcadmium are obtained by the reaction of cadmium chloride with a Grignard's reagent.

$$2R–Mg\ Cl + CdCl_2 \longrightarrow R–Cd–R + 2MgCl_2$$

4.3 **Oppenaur Oxidation :** In order to prepare alkanone easily, Oppenauer oxidation of secondary alkanols is done. In this process, a secondary alkanols is refluxed with aluminum tert–butoxide in excess amount in acetone. Acetone is reduced to isopropyl alcohol.



$$\underset{\displaystyle R}{\underset{|}{R-CHOH}} + \underset{\displaystyle CH_3}{\underset{|}{CH_3-CO}} \xrightarrow{[(CH_3)_3C-O]_3Al} \underset{\displaystyle R}{\underset{|}{R-CO}} + \underset{\displaystyle CH_3}{\underset{|}{CH_3-CHOH}}$$

METHODS OF PREPARATION :

Ex.1 Choose the compound whose oxime on hydrolysis yields ethanal –

(A) HCHO (B) CH_3CHO

(C) CH_3CH_2OH (D) CH_3COCH_3 **(Ans.B)**

Sol. Oxime of ethanal on hydrolysis gives ethanal

$$CH_3CH = NOH \xrightarrow{H_2O} CH_3CHO + NH_2OH$$

Ex.2 On dipping red hot coper wire in isobutyl alcohol, we get –

(A) An alkene (B) A ketone

(C) An aldehyde (D) None of the above **(Ans.C)**

Sol. Isobutyl alcohol contains primary alcoholic group $–CH_2OH$ which on oxidation converts to–CHO group

Ex.3 $CH_3COCl \xrightarrow[{[H_2]}]{Pd/BaSO_4} A$

The isomers of CH_3COCl and A will be respectively –

(A) CH_2ClCHO, oxirane (B) Chloral, vinyl alcohol

(C) α-chloroethyl alcohol, epoxyethane (D) None of the above **(Ans. A)**

Sol. α-chloroacetaldehyde and oxirane ethane are the isomers of CH_3COCl and CH_3CHO respectively.

5. PHYSICAL PROPERTIES

(a) Aldehydes are colourless with pungent smell liquid while ketones are pleasant smell liquids but formaldehyde is gaseous in nature.

(b) Lower carbonyl compounds are soluble in water. It is due to polarity in carbonyl group.

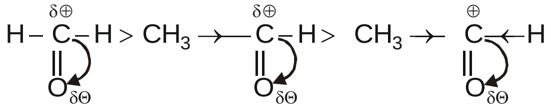
(c) Higher carbonyl compounds are insoluble in water due to more covalent character.

(d) Melting point & Boiling point $\propto$ Molecular mass

$$\propto \frac{1}{\text{No. of branches}}$$

(e) Melting point and boiling point of carbonyl compounds are more than to corresponding alkanes due to dipole-dipole attraction present between molecules in carbonyl compounds.

(f) Reactivity of carbonyl compound is dependent on alkyl group which is linked with carbonyl group.



(g) 40% solution of formaldehyde is known as '**FORMALIN**' (40% HCHO, 54-56% H_2O, 4-6% methanol)

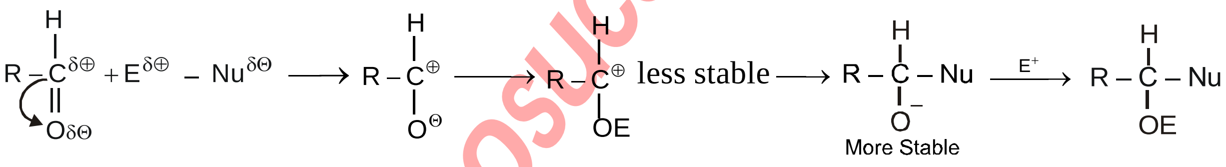
(h) Mixture of formaldehyde and lactose sugar is called '**FORMAMINT**' which is used in medicine of throat infection.

(i) Boiling point of carbonyl compounds are as under -

	Compound	Boiling Point
1.	Formaldehyde	– 21°C
2.	Acetaldehyde	+ 21°C
3.	Acetone	56°C

6. CHEMICAL PROPERTIES :

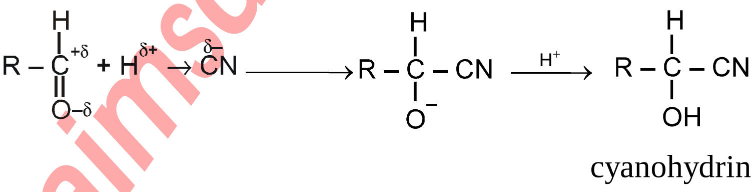
Main reaction of carbonyl compounds are nucleophilic addition reaction.



Rate of nucleophilic addition reaction of carbnyl compounds decreases in the following order :

$HCHO > CH_3CHO > CH_3COCH_3 > C_6H_5–CHO$

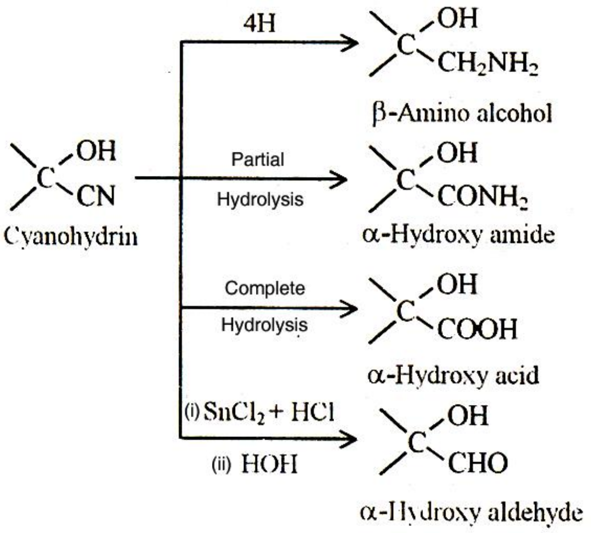
6.1 Reaction with Hydrogen Cyanide : –

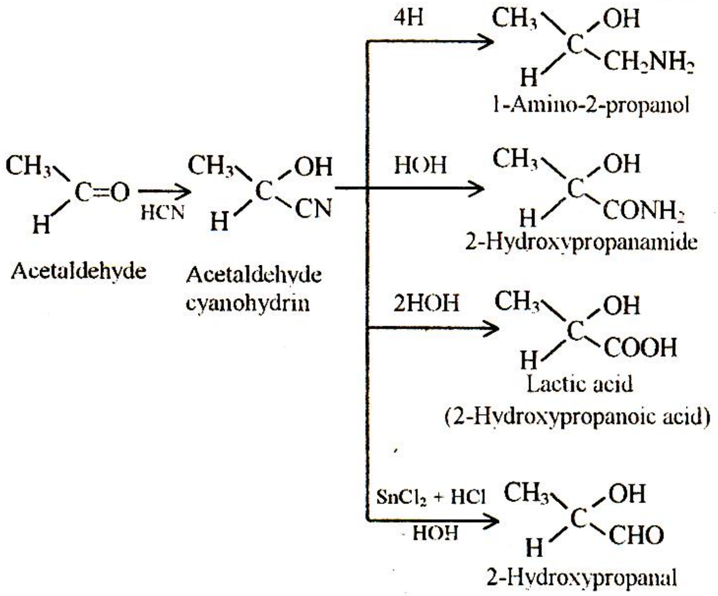


NOTE : –

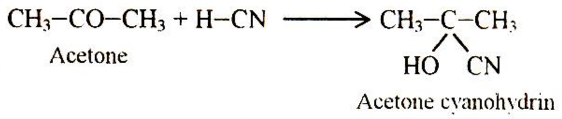
(a) If R = H then product will be formaldehyde cyanohydrin.

(b) Cyanohydrin is an important compound which gives the following product on hydrolysis and reduction.

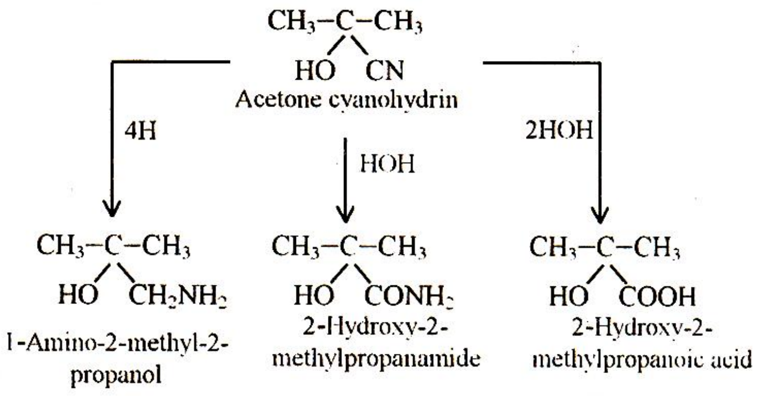




Acetone cyanohydrin is formed on reacting acetone with HCN.

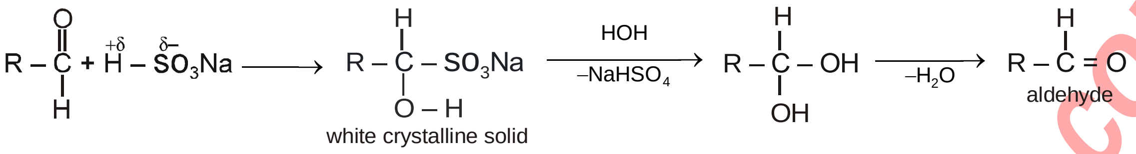


$$\underset{\text{Acetone}}{CH_3-CO-CH_3} + H-CN \longrightarrow \underset{\text{Acetone cyanohydrin}}{CH_3-\underset{HO\quad CN}{C}-CH_3}$$



6.2 Reaction with Sodium bisulphite :

Carbonyl compound form a white crystalline addition product with sodium bisulphite called **Aldehyde / Ketone** sodium bisulphite adduct.



$$R-\overset{O}{\overset{\|}{\underset{H}{C}}}+\overset{+\delta}{H}-\overset{\delta-}{SO_3Na}\longrightarrow R-\overset{H}{\underset{O-H}{C}}-SO_3Na\xrightarrow[-NaHSO_4]{HOH}R-\overset{H}{\underset{OH}{C}}-OH\xrightarrow{-H_2O}R-\overset{H}{C}=O$$

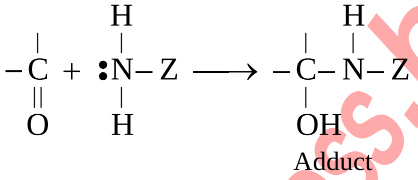
NOTE : –

(a) Bisulphite adduct is an important compound because it gives carbonyl compound on further hydrolysis.

(b) The above reaction is used in purification of carbonyl compound.

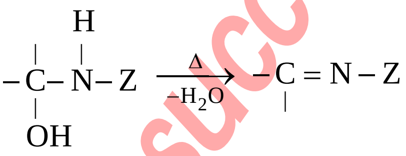
6.3 Reaction with Ammonia derivatives :

Addition of nitrogenous nucleophile on carbonyl group takes place according to the following mechanism.



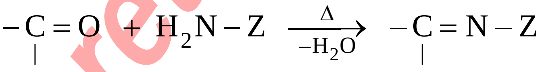
$$-\underset{O}{\overset{|}{\underset{\|}{C}}}+:\underset{H}{\overset{H}{N}}-Z\longrightarrow -\underset{OH}{\overset{|}{C}}-\overset{H}{N}-Z$$

The end product is formed by elimination of water from the adduct under appropriate energy condition.



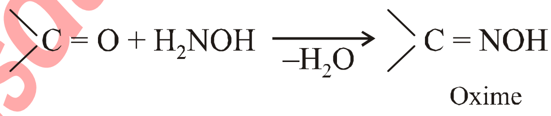
$$-\underset{OH}{\overset{|}{C}}-\overset{H}{N}-Z\xrightarrow[-H_2O]{\Delta}-\underset{|}{C}=N-Z$$

In the above two steps, it appears that an unsaturated condensation product is formed by liberation of the water molecule from carbonyl group and nitorogenous nucleohile.



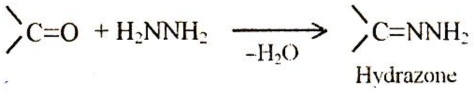
$$-\underset{|}{C}=O+H_2N-Z\xrightarrow[-H_2O]{\Delta}-\underset{|}{C}=N-Z$$

(i) With Hydroxylamine :



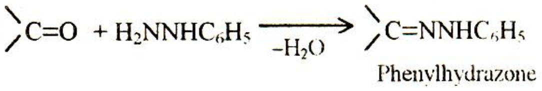
$$>C=O+H_2NOH\xrightarrow[-H_2O]{}>C=NOH$$

(ii) With Hydrzaine :



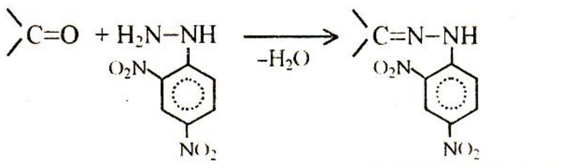
$$>C=O+H_2NNH_2\xrightarrow[-H_2O]{}>C=NNH_2$$

(iii) With Phenylhydrazine :



$$>C=O+H_2NNHC_6H_5\xrightarrow[-H_2O]{}>C=NNHC_6H_5$$

(iv) With 2,4–Dinitrophenylhydrazine :



2,4-Dinitrophenylhydrazone

(v) With Semicarbazide :

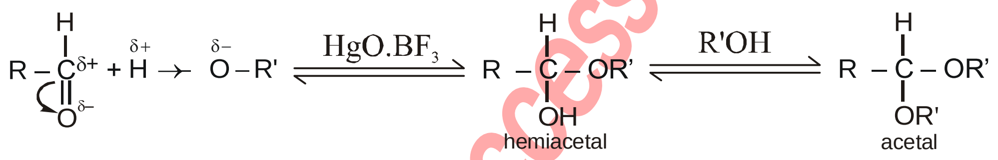
$$>C=O + H_2NNHCONH_2 \xrightarrow[-H_2O]{} >C=NNHCONH_2$$

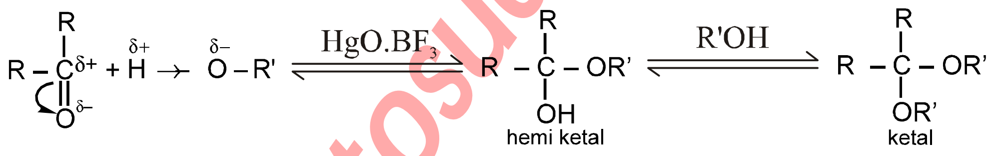
Semicarbazone

On reacting a carbonyl compound with 2,4–dinitrophenylhydrazine, a yellow precipitate of 2,4–dinitrophenylhydrazone derivative is obtained. White precipitate is obtained by the reaction with hydroxylamine, hydrazine phenylhdrazine and semicarbazide. The pure parent carbonyl compound can be obtained by hydrolysis of the above five derivatives.

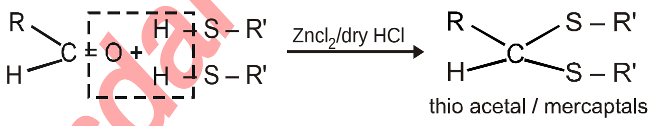
$$>C=N-Z + HOH \longrightarrow >C=O + H_2N-Z$$

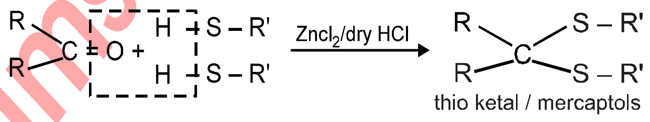
6.4 Reaction with Alcohol : In the presence of catalyst (HgO•BF$_3$) aldehyde form acetal with alcohol while ketone from ketal with alcohol.



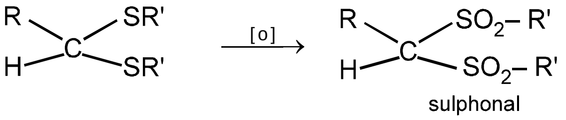


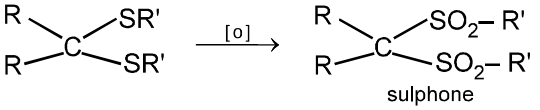
6.5 Reaction with Alkane Thiol : Aldehyde form thio acetal with alkane thiol while ketone form thio ketal with alkane thiol.





These are important compounds because they forms sulphonyl compounds on oxidation which are used as hypnotic drugs.

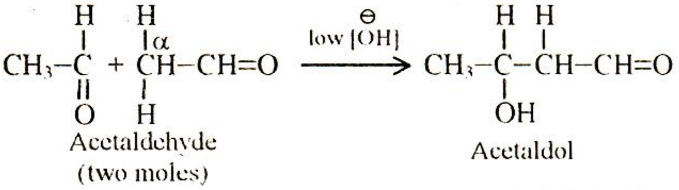




6.6 Aldol Condensation :

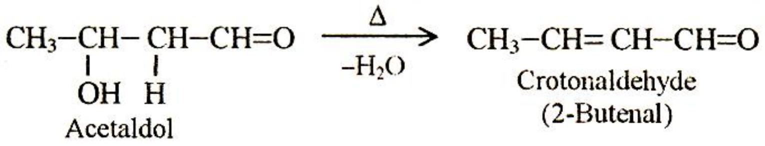
In the presence of small amounts of hydroxide ions two molecules of the carbonyl compound containing α–hydrogen atoms, give a β–hydroxy carbonyl compound. This reaction is normally called Aldol condensation. Aldol condensation of two identical carbonyl compounds is called simple aldol condenstaion.

As a source of hydroxide ions, a few drops of very dilute aqueous solution of K_2CO_3, Na_2CO_3, NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$ etc. are added.

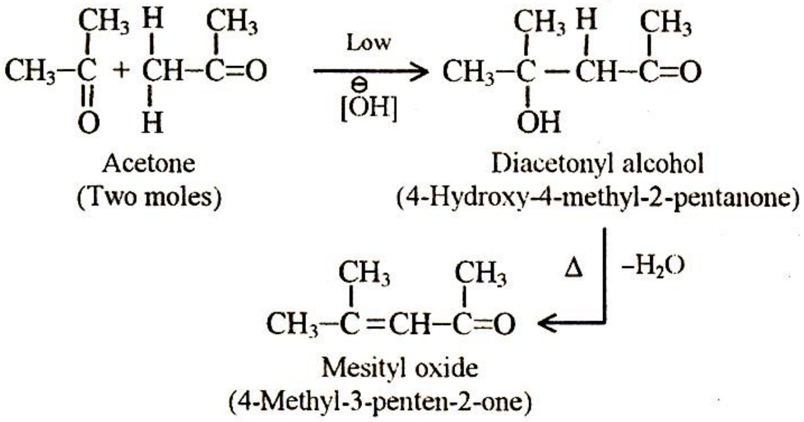


$$CH_3-\underset{O}{\overset{H}{\underset{\|}{C}}} + \overset{H}{C}H_2-CH{=}O \xrightarrow{\text{low }[\overset{\ominus}{O}H]} CH_3-\overset{H}{\underset{OH}{C}}-\overset{H}{C}H-CH{=}O$$

A α,β–unsaturated aldehyde crotonaldehyde is formed by the elimination of a water molecule on heating acetaldol (3–hydroxybutanal)

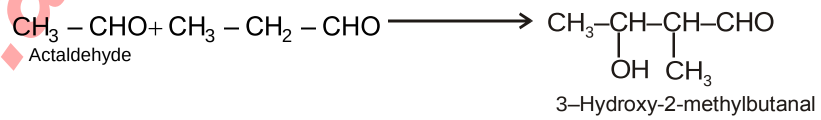


$$CH_3-\underset{OH}{C}H-\underset{H}{C}H-CH{=}O \xrightarrow[-H_2O]{\Delta} CH_3-CH{=}CH-CH{=}O$$



$$CH_3-\underset{O}{\underset{\|}{\overset{CH_3}{C}}} + \underset{H}{\overset{H}{C}}H-\overset{CH_3}{C}{=}O \xrightarrow[{[\overset{\ominus}{O}H]}]{\text{Low}} CH_3-\underset{OH}{\overset{CH_3}{C}}-\overset{H}{C}H-\overset{CH_3}{C}{=}O \xrightarrow[-H_2O]{\Delta} CH_3-\overset{CH_3}{C}{=}CH-\overset{CH_3}{C}{=}O$$

Aldol condensation of two non identical carbonyl compounds is called mixed or crossed aldol condensation. Theoretically four products can be formed from aldol condensation of the carbonyl compounds A and B.



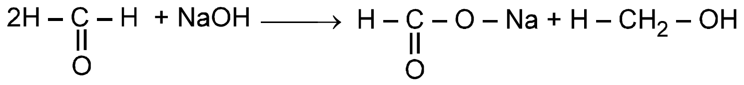
$$\underset{\text{Actaldehyde}}{CH_3-CHO} + CH_3-CH_2-CHO \longrightarrow CH_3-\underset{OH}{C}H-\underset{CH_3}{C}H-CHO$$

$$\underset{\text{Propionaldehyde}}{CH_3CH_2-CHO} + CH_3CHO \longrightarrow CH_3CH_2-\underset{OH}{C}H-CH_2CHO$$

6.7 **Cannizaro Reaction :** Carbonyl compound in which $\alpha - H$ atoms is absent, when react with strong base like NaOH or KOH then forms sodium and pottasium salt of carboxylic acid and alcohol. It is an example of the reaction in which one mole of the compounds is reduced. Such type of reaction is called disproportionation reaction, also known as cannizaro reaction. In this reaction elimination of hydride ion takes place. In this reaction oxidation number changes from 0 to +2 and 0 to –2.

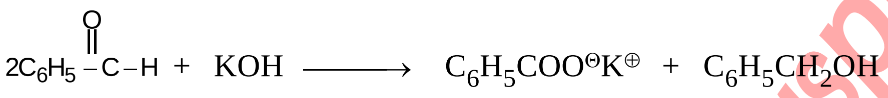
Compounds showing cannizaro reaction are -

(a)



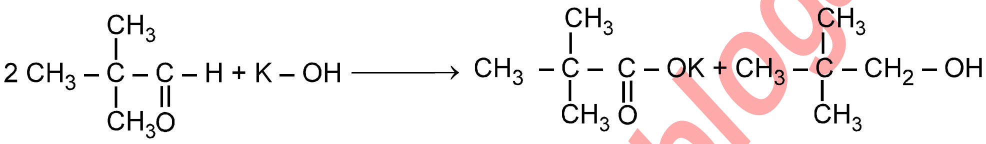
$$2H-\underset{\underset{O}{\|}}{C}-H + NaOH \longrightarrow H-\underset{\underset{O}{\|}}{C}-O-Na + H-CH_2-OH$$

(b)



$$2C_6H_5-\overset{\overset{O}{\|}}{C}-H + KOH \longrightarrow C_6H_5COO^{\ominus}K^{\oplus} + C_6H_5CH_2OH$$

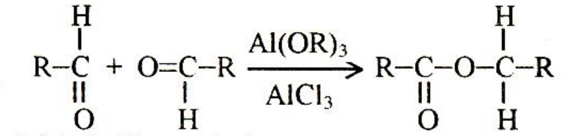
(c)



$$2\,CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{C}-H + K-OH \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{C}-OK + CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-OH$$

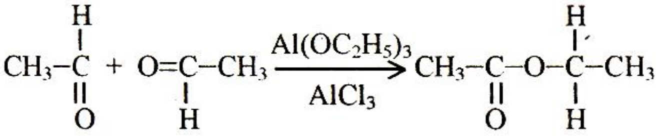
6.8 **Tischenko Reaction :**

When an aldehyde is heated with an anhydrous aluminium alkoxide in the presence of anhydrous $AlCl_3$, then a carboxylic acid ester having twice the number of carbon atoms is formed. All aldehydes give this reaction.



$$R-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}} + O=\underset{\underset{H}{|}}{C}-R \xrightarrow[AlCl_3]{Al(OR)_3} R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-R$$

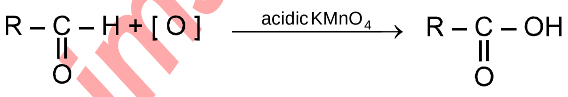
Aldehyde (Two moles) Ester (One mole)



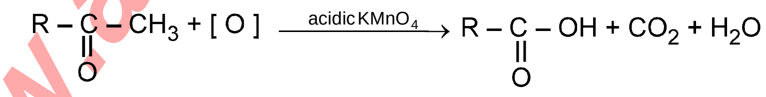
$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}} + O=\underset{\underset{H}{|}}{C}-CH_3 \xrightarrow[AlCl_3]{Al(OC_2H_5)_3} CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-CH_3$$

Acetaldehyde (Two moles) Ethyl acetate (One mole)

6.9 **Oxidation :** Aldehyde on oxidation forms respective acid while ketone forms less carbon carboxylic acid on oxidation according to popoff's rule (As discussed in Alcohol theory)



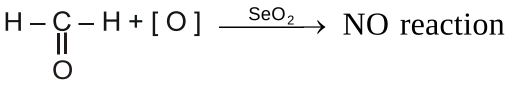
$$R-\underset{\underset{O}{\|}}{C}-H + [O] \xrightarrow{\text{acidic } KMnO_4} R-\underset{\underset{O}{\|}}{C}-OH$$



$$R-\underset{\underset{O}{\|}}{C}-CH_3 + [O] \xrightarrow{\text{acidic } KMnO_4} R-\underset{\underset{O}{\|}}{C}-OH + CO_2 + H_2O$$

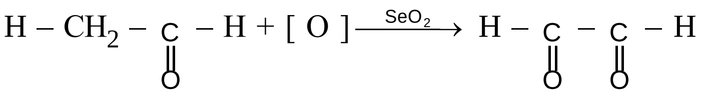
NOTE :

(a) If oxidising agent is selenium oxide SeO_2 then, α–methylene group of carbonyl compound oxidises into $-\underset{\underset{O}{\|}}{C}-$ group and resultant dicarbonyl compound will be formed.



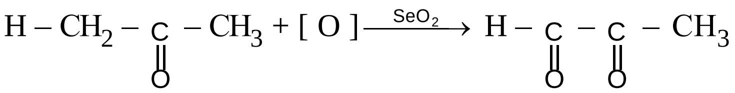
$$\mathrm{H-\underset{\underset{O}{\|}}{C}-H+[O]\xrightarrow{SeO_2}}\text{ NO reaction}$$

α - methylene group is absent.



$$\mathrm{H-CH_2-\underset{\underset{O}{\|}}{C}-H+[\,O\,]\xrightarrow{SeO_2}H-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H}$$

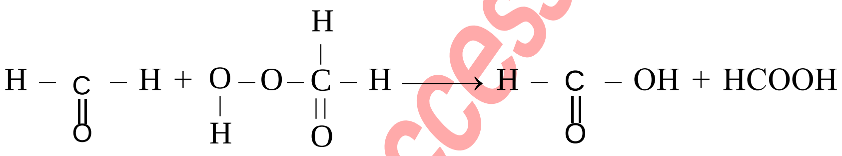
glyoxal
(dicarbonyl compound)



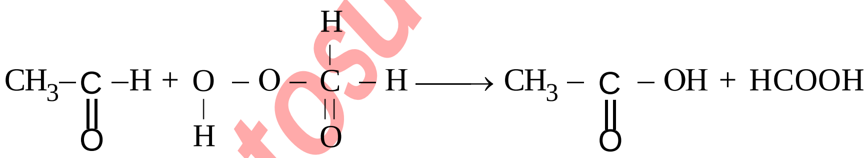
$$\mathrm{H-CH_2-\underset{\underset{O}{\|}}{C}-CH_3+[\,O\,]\xrightarrow{SeO_2}H-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3}$$

pyruvic aldehyde
(methyl glyoxal)

(b) If the oxidising agent is performic acid then aldehyde oxidises into respective acid while ketone oxidises into ester. The reaction is called '**Baeyer-villiger Oxidation**'.
Other peroxy acid also give same product.
eg. CH_3COOOH, C_6H_5COOOH, MCPBA, CF_3COOOH

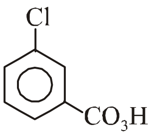


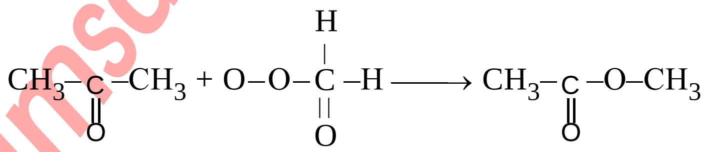
$$\mathrm{H-\underset{\underset{O}{\|}}{C}-H+\underset{\underset{H}{|}}{O}-O-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}}-H\longrightarrow H-\underset{\underset{O}{\|}}{C}-OH+HCOOH}$$



$$\mathrm{CH_3-\underset{\underset{O}{\|}}{C}-H+\underset{\underset{H}{|}}{O}-O-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}}-H\longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-OH+HCOOH}$$

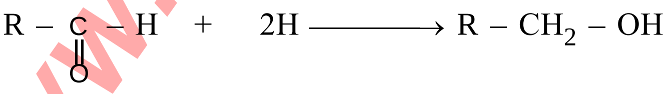
*** MCPBA → meta chloro perbenzoic acid



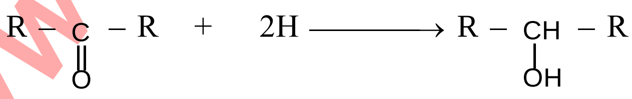


$$\mathrm{CH_3-\underset{\underset{O}{\|}}{C}-CH_3+O-O-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}}-H\longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-O-CH_3}$$

6.10 Reduction : Aldehyde on reduction form primary alcohol while ketone on reduction form secondary alcohol.



$$\mathrm{R-\underset{\underset{O}{\|}}{C}-H+2H\longrightarrow R-CH_2-OH}$$



$$\mathrm{R-\underset{\underset{O}{\|}}{C}-R+2H\longrightarrow R-\underset{\underset{OH}{|}}{CH}-R}$$

secondary alcohol

NOTE :

(a) In the above reaction if reducing agent is Na + C_2H_5OH then reaction is called '**Bouveault - Blanc Reaction**'.

(b) If reducing agent is NaH reaction is called '**Darzen's Reaction**'. We can also use $LiAlH_4$ in this reaction.

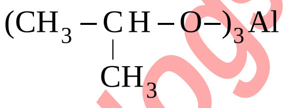
(c) If reducing agent is (red P / HI) then product will be alkane.

(d) If reducing agent is Zn-Hg/conc. HCl then product will be alkane. Reaction is called '**Clemmenson-Reduction**'.

(e) If reducing agent is alkaline solution of hydrazine, product will be alkane. Reaction is called ' **Wolf - kishner Reduction**'.

(f) The percentage yield of alkane can be increased by using diethylene glycol in wolf kishner reduction then reaction is called '**Huang-Millan Conversion**'.

(g) If reducing agent is aluminium iso propoxide



$$(CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-O-)_3Al$$

, then product will be alcohol. Reaction is called '**Meerwein-Pondorff Verley Reduction**'.

6.11 **Polymerisation Reactions :** Aldehyde shows addition as well as condensation polymerisation reactions while ketone shows only condensation polymerisation reactions.

6.11.1 Addition Polymerisation reaction of Formaldehyde : –

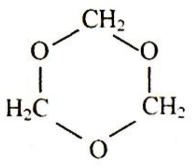
(a) When aqueous solution of formaldehyde is heated then it converts into a white crystalline solid called 'Paraformaldehyde'.

$$n\ HCHO \xrightarrow[\text{evaporation}]{\Delta} \underset{\text{paraformaldehyde}}{(HCHO)_n} \qquad n > 6,\ n < 100$$

If n ≤ 50 Linear structure polymer
If n > 50 Cyclic structure polymer

(b) If formaldehyde is kept with conc. H_2SO_4 at room temperature then it forms a cyclic trimer called meta formaldehyde or trioxane.

$$3CH_2O{=}O \longrightarrow (CH_2–O)_3$$



Metaformaldehyde
or
Trioxymethylene
or
1,3,5-Trioxan
or
sym-Trioxan

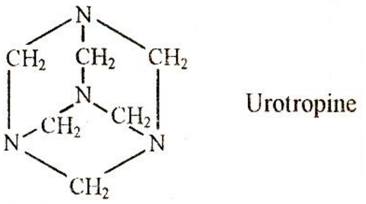
(c) If aqueous solution of formaldehyde is kept with lime water in dark room for 5-6 days then it converts into a sweet solution called 'FARMOSE
It is an example of linear polymer.

$$6HCHO \xrightarrow[\text{dark, 5–6 days}]{Ca(OH)_2\,/\,Ba(OH)_2} \underset{\text{farmose}}{C_6H_{12}O_6}$$

6.11.2 Condensation Polymerisation reaction of Formaldehyde :

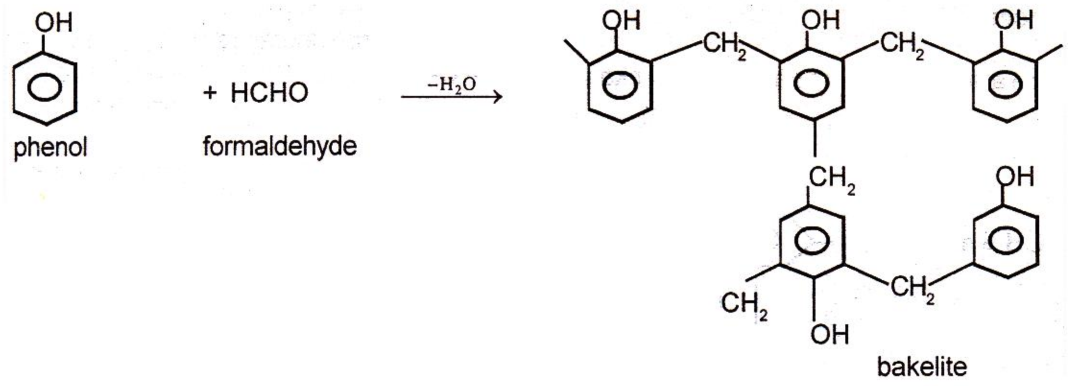
(a) **With Ammonia:–** When formaldehyde is heated with NH_3 then a white crystalline heterocyclic compound is formed called 'Hexamethylene tetramine' or urotropene' or 'Aminoform'.

$$6HCHO + 4NH_3 \xrightarrow{\Delta} (CH_2)_6N_4 + 6H_2O$$



It is used in medicine or diabities or urinary infection.

(b) **With Phenol :** – In presence of dilute alkali formaldehyde first form o- & p- hydroxy benzyl alcohol with phenol which on self condensation form a cross link polymer called '**Bakelite**'.



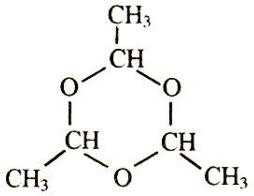
Bakelite is electric and thermal resistant. So, used in formation of electric appliances. Reaction is called '**Lederer-Manasse Reaction**'.

6.11.3 Addition Polymerisation of Acetaldehyde :

(a) When acetaldehyde is kept with conc. H_2SO_4 at room temperature then it form a cyclic trimer called paraaldehyde.

$$3CH_3CHO \xrightarrow[\text{Conc. } H_2SO_4]{\text{Room temp.}} (CH_3CHO)_3 \text{ (Paraldehyde)}$$

Paraldehyde has nonaromatic heterocyclic structure and it is called 2,4,6–trimethyl–1,3,5–trioxan.



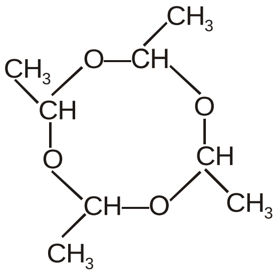
Paraldehyde or 2,4,6–trimethyl–1,3,5–trioxan

Paraldehyde is used as mild hypnotic.

(b) If acetaldehyde is kept with highly conc. HCl at low temperature then it forms a cyclic tetramer called metaaldehyde.

$$4CH_3CHO \xrightarrow[0°]{\text{Dry HCl gas}} (CH_3CHO)_4$$

Metaldehyde has the following nonaromatic eight–memebred heterocyclic structure.

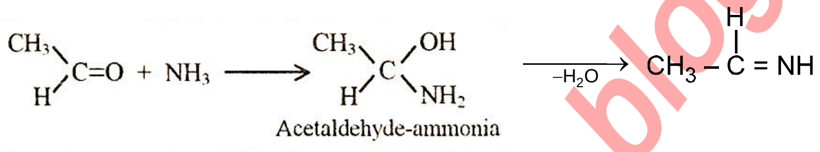


NOTE : Metaldehyde is used as smokeless powder and Para aldehyde is used as a sedative while meta aldehyde is used as a solid fuel.

6.11.4 Condensation Polymerisation of Acetaldehyde : –

(a) **Aldol condensation** – Discussed earlier.

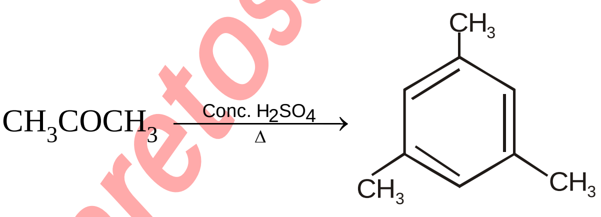
(b) **Reaction with NH_3 :**



Acetaldimine is formed by the elimination of water molecule on heating acetaldehyde–ammonia, which undergoes polymerisation to form a nonaromatic heterocylic addition trimer, namer 2,4,6–trimethylhexahydro–1,3,5–triazine trihydrate as the main product.

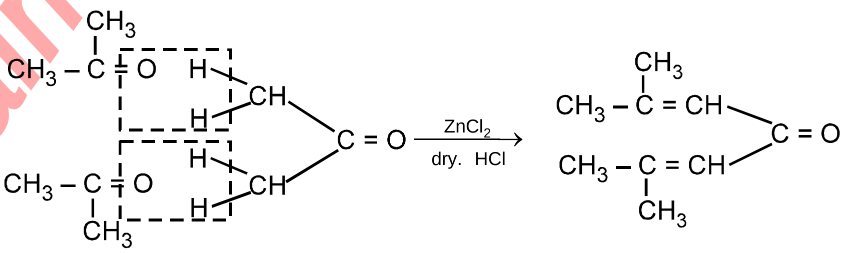
6.11.5 Condensation Polymerisation of Acetone :

(a) If acetone is heated with conc. H_2SO_4 then an aromatic compound is formed called 1,3,5-trimethyl benzene or mesitylene.



Mesitylene

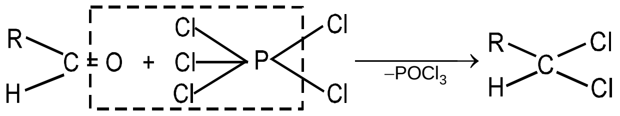
(b) If acetone would be in excess in ketal condensation or catalyst ($ZnCl_2$ / dry HCl) is used then three moles of acetone undergoes condensation polymerisation and form a compound called '**Phorone**'.



[molecular wt. of phorone = 3 mole of acetone – 2 mole of H_2O]

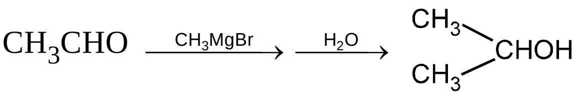
6.12 Reaction with PCl_5 :

Carbonyl compound form gemdihalide with PCl_5.

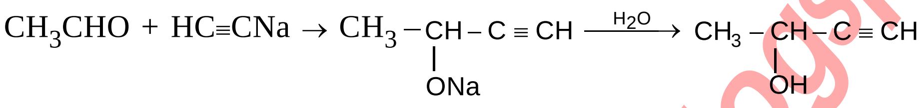


gemdihalide

6.13 With RMgX :-



6.14 With sodium acetylide :



$$CH_3CHO + HC{\equiv}CNa \rightarrow CH_3-\underset{\displaystyle ONa}{\underset{|}{CH}}-C\equiv CH \xrightarrow{H_2O} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-C\equiv CH$$

6.15 With primary amine :–

$$CH_3CH{=}O + H_2NC_6H_5 \longrightarrow CH_3{-}CH{=}NC_6H_5$$

Schiff's base

$$(CH_3)_2C{=}O + H_2NC_6H_5 \longrightarrow (CH_3)_2C{=}NC_6H_5$$

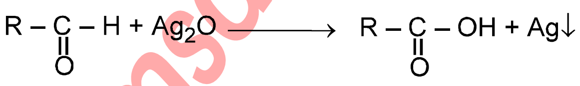
7. REACTIONS SHOWN BY ALDEHYDES ONLY

7.1 Reducing nature of Aldehyde : Aldehyde are reducing in nature, they can reduce Tollen's reagent, Fehling solution and mercuric chloride solution.

(a) Reaction with Tollen's Reagent : – Ammonical silver nitrate solution is called Tollen's reagent. Aldehyde reduce the tollen's reagent and form silver mirror. Aldehyde oxidises itself into carboxylic acid.

$$\begin{tikzcd}
AgNO_3 + NH_4OH \arrow[r] & {[Ag(NH_3)_2]\text{-}OH} \arrow[d, "NH_3^-"] \\
 & 2AgOH \arrow[r, "-H_2O"'] & Ag_2O
\end{tikzcd}$$

(simplest reacting species)



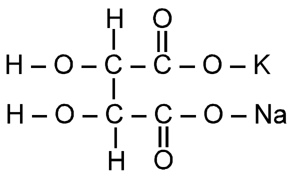
$$R-\underset{\displaystyle O}{\underset{\|}{C}}-H + Ag_2O \longrightarrow R-\underset{\displaystyle O}{\underset{\|}{C}}-OH + Ag\downarrow$$

NOTE : In the above reaction oxidation number of Ag varies from +1 to 0.

(b) Reaction with Fehling Solution : It is the mixture of two solution called Fehling solution A and Fehling solution B.

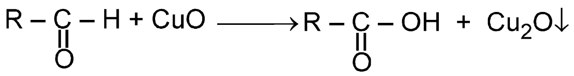
Fehling Solution A : Aqueous solution of $CuSO_4$ (blue)

Fehling Solution B : Alkaline solution of Roschelle salt (sodium potassium tartarate)



$(C_4H_4O_6NaK)$

By the mixing of both solution we get a dark blue colour solution called final fehling solution. Reacting species of this solution is cupric oxide CuO.

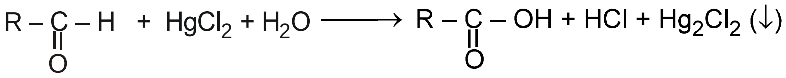


$$R-\underset{\underset{O}{\|}}{C}-H + CuO \longrightarrow R-\underset{\underset{O}{\|}}{C}-OH + Cu_2O\downarrow$$

(red ppt.)

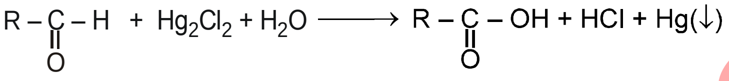
NOTE : Oxidation number of copper varies from +2 to +1

(c) **Reaction with Mercuric Chloride solution :** Aldehyde reacts with mercuric chloride solution and initially form white ppt. of mercurous chloride solution, which further react with excess of aldehyde and form black ppt. of mercury.



$$R-\underset{\underset{O}{\|}}{C}-H + HgCl_2 + H_2O \longrightarrow R-\underset{\underset{O}{\|}}{C}-OH + HCl + Hg_2Cl_2\ (\downarrow)$$

(white)



$$R-\underset{\underset{O}{\|}}{C}-H + Hg_2Cl_2 + H_2O \longrightarrow R-\underset{\underset{O}{\|}}{C}-OH + HCl + Hg(\downarrow)$$

(black)

(d) **Benedict solution :**

[A–$CuSO_4$ soln, β–NaOH, Sodium citrate]

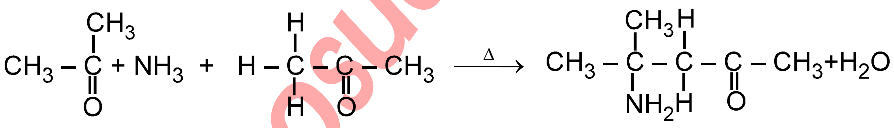
$CH_3CHO + 2CuO \longrightarrow Cu_2O + CH_3COOH$

(e) **Schiff's reagent :**

Megenta dye $\xrightarrow{SO_2}$ Colourless solution $\xrightarrow{CH_3CHO}$ Pink colour restored

8. REACTIONS SHOWN BY KETONES ONLY

(a) **Reaction with NH_3 :** If acetone is heated with ammonia then it forms diacetone amine.

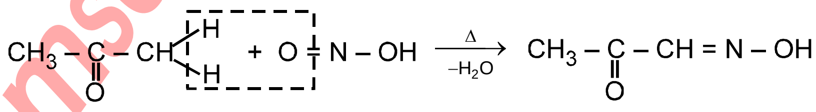


$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} + NH_3 + H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{\Delta} CH_3-\underset{\underset{NH_2}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{O}{\|}}{C}-CH_3+H_2O$$

If acetone and ammonia would be in excess then product would be tri acetone amine. If tri acetone amine is heated at high temperature then it converts into a hetrocyclic compound by the elimination of water.

(b) **Reaction with Nitrous Acid :**

Oximinoacetone is formed by liberation of a water molecule on reacting acetone with nitrous acid.

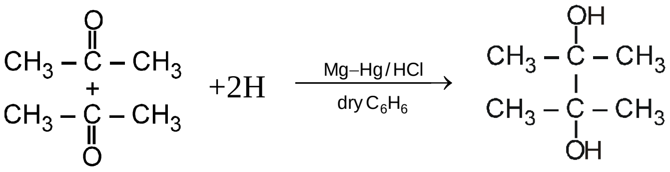


$$CH_3-\underset{\underset{O}{\|}}{C}-CH\begin{matrix}H\\H\end{matrix} + O=N-OH \xrightarrow[-H_2O]{\Delta} CH_3-\underset{\underset{O}{\|}}{C}-CH=N-OH$$

oximino acetone

(c) **Bimolecular Reduction : –**

Pinacol is formed on reduction of acetone in an inert medium (like benzene) by using magnesium amalgam and hydrogen.



$$\begin{matrix}CH_3-\overset{\overset{O}{\|}}{C}-CH_3\\+\\CH_3-\underset{\underset{O}{\|}}{C}-CH_3\end{matrix} + 2H \xrightarrow[\text{dry } C_6H_6]{Mg-Hg/HCl} \begin{matrix}CH_3-\overset{\overset{OH}{|}}{C}-CH_3\\|\\CH_3-\underset{\underset{OH}{|}}{C}-CH_3\end{matrix}$$

pinacol

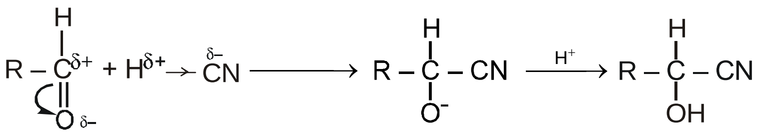
CHEMICAL REACTION :

Ex.4 What would be the product when carbonyl compound reacts with HCN -

(A) Cyanohydrin (B) Hydroxy acid

(C) Hydroxy amide (D)Amino alcohol **(Ans.A)**

Sol.



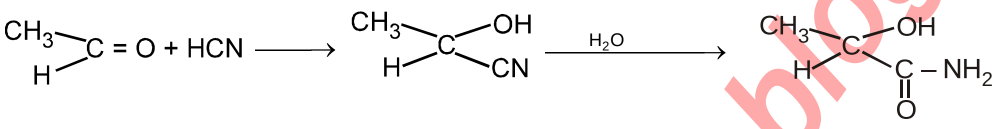
(cyanohydrin)

Ex.5 What would be the product when acetaldehyde reacts with HCN and the product is partially hydrolysed -

(A) Lactamide (B)Methyl glyconamide

(C) Both A & B (D) None **(Ans.C)**

Sol.



lactamide or methyl glyconamide

Ex.6 Which carbonyl compound will be purified with sodium bisulphite -

(A) 2-Pentanone (B) 3-Hexanone

(C) 4-Heptanone (D) All above **(Ans.A)**

Sol. The reaction is used in purification of all types of aldehydes and methyl ketones only because the ketones having bulky alkyl group form unstable adduct.

Ex.7 Reaction involving formation of trioxane from methanal is called :

(A) Aldol condensation (B) Addition polymerisation

(C) Condensation polymerisation (D) Cannizzaro's reaction **(Ans. B)**

Sol. $3CH_2O \xrightarrow{\text{dil.}H_2SO_4} [CH_2O]_3$ trioxane [addition polymer]

Ex.8 >C – CN group is called –

$\underset{\displaystyle OH}{\underset{|}{>C}} - CN$

(A) Hydroxy nitrile (B) Hdroxy cyanide (C) Cyanohydrin (D) Hydroxy isocyanide

(Ans. C)

Sol. Carbonyl compound on addition with HCN gives a compound containing cyanohydrin group.

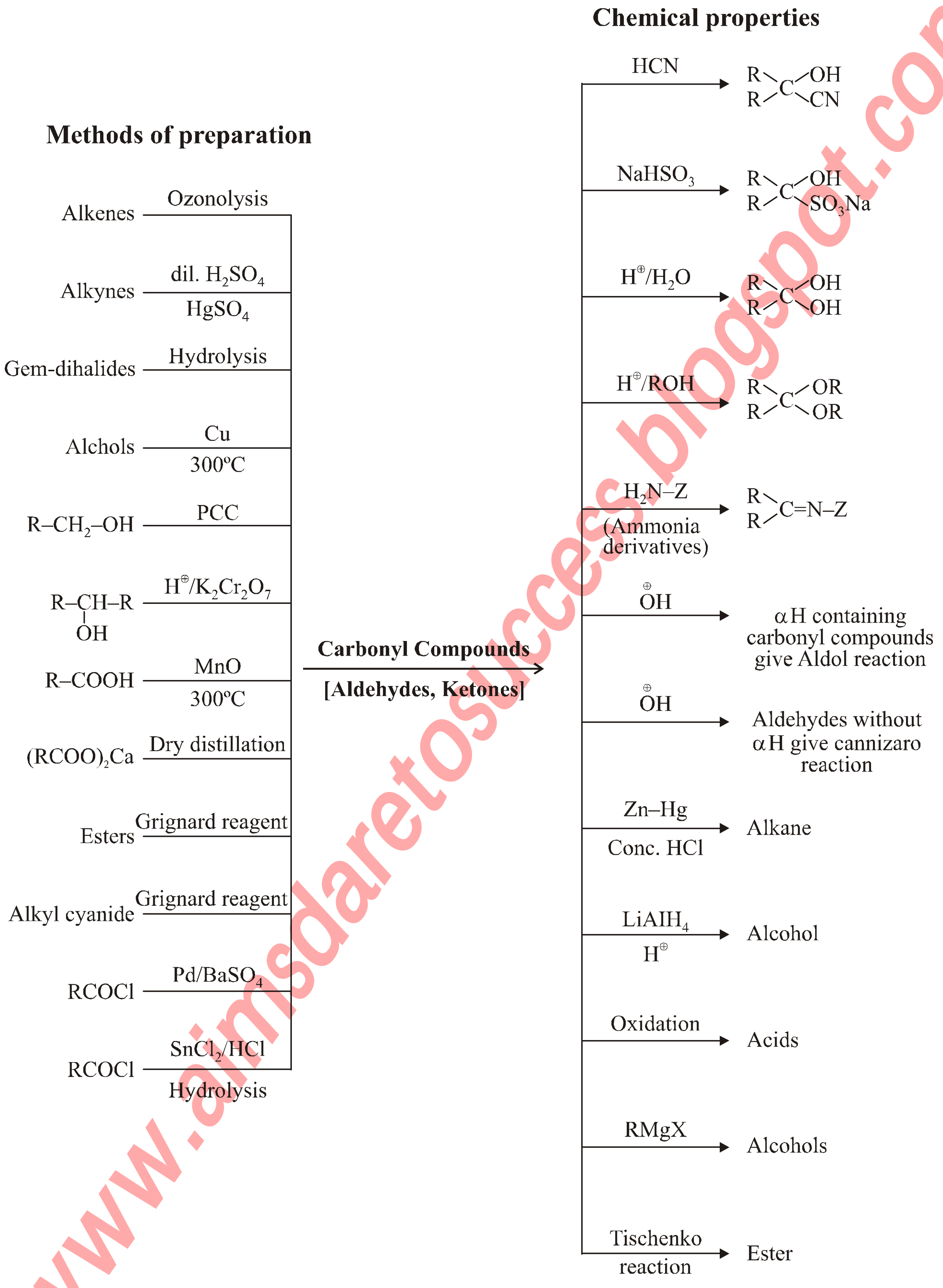
Ex.9 Butanone does not show any reaction with the reagent –

(A) $\phi - NHNH_2$ (B) CH_3NH_2

(C) $[Ag(NH_3)_2]^+$ (D) NH_2OH **(Ans. C)**

Sol. Tollen's reagent does not react with ketone.

CARBONYL COMPOUNDS



EXERCISE – I

Q.1 When propyne reacts with 20% H_2SO_4 & 1% $HgSO_4$, we get-
(A) Acetaldehyde (B) Propanaldehyde (C) Acetone (D) Formic acid

Q.2 The product formed by the reaction of propyne with dil. H_2SO_4 in the presence of Hg^{2+} can not be prepared by the following reaction-
(A) Dry distillation of calcium ethanoate
(B) By passing vapours of ethanoic acid over MnO at 300ºC
(C) By ozonolysis of 2- Butene
(D) By alkaline hydrolysis of isopropylidene chloride

Q.3 Except acetylene, other alkynes react with H_2O to give-
(A) Aldehyde (B) CH_3CHO (C) Ketones (D) Alkanal.

Q.4 When CH_3MgI reacts with CH_3CN and the product is hydrolysed, we get-
(A) Propanal (B) Acetone (C) Formaldehyde (D) Acetaldehyde

Q.5 Ethylidene chloride (CH_3CHCl_2) on hydrolysis with NaOH gives -
(A) CH_3CHO (B) CH_3COCH_3 (C) $CH_3CH(OH)_2$ (D) C_2H_5OH

Q.6 When calcium acetate is heated with calcium formate then, we get-
(A) Methanol (B) Acetic acid (C) Acetaldehyde (D) Acetone

Q.7 The reaction -

$$CH_3COCl + H_2 \xrightarrow[Pd/BaSO_4]{Xylene} CH_3CHO + HCl \text{ is}$$

(A) Stephen's reaction (B) Rosenmund reaction
(C) Hoffmann reaction (D) Cannizzaro's reaction

Q.8 Acetone will be obtained by the ozonolysis of -
(A) 1-Butene (B) 2-Butene (C) Isobutene (D) 2-Butyne

Q.9 Which fo the following forces is correctly described about boiling point of Aldehydes & ketones -
(A) Hydrogen bond (B) Vander wall force
(C) Dipole-dipole attraction (D) None of these

Q.10 The general order of reactivity of carbonyl compounds for nucleophilic addition reactions is -
(A) $H_2C = O > RCHO > ArCHO > R_2C = O > Ar_2C = O$
(B) $ArCHO > Ar_2C = O > RCHO > R_2C = O > H_2C = O$
(C) $Ar_2C = O > R_2C = O > ArCHO > RCHO > H_2C = O$
(D) $H_2C = O > R_2C = O > Ar_2C = O > RCHO > ArCHO$

Q.11 Reaction of ammonia derivative with carbonyl compound is an example of -
(A) Addition and Substitution
(B) Substitution and Elimination
(C) Addition and Elimination
(D) Addition and intramolecular substitution

Q.12 Acetone gives test with-
(A) 2,4 Dinitro phenyl hydrazine
(B) Fehling solution
(C) Schiff's reagent
(D) All

Q.13 Aldol condensation between the following compounds followed by dehydration gives methyl vinyl ketone-
(A) HCHO and CH_3COCH_3
(B) HCHO and CH_3CHO
(C) Two molecules of CH_3CHO
(D) Two molecules of CH_3COCH_3

Q.14 In Cannizzaro reaction-
(A) Aldehyde is converted into alcohol
(B) Alcohol is converted into aldehyde
(C) Primary amine is converted into isocyanide
(D) Acid is converted into amine

Q.15 Which is most difficult to oxidise-
(A) HCHO
(B) CH_3CHO
(C) CH_3COCH_3
(D) CH_3CH_2CHO

Q.16 Acetone shows similarity with acetaldehyde in reacting to-
(A) Schiff's reagent
(B) Fehling solution
(C) Grignard reagent
(D) Tollen's reagent

Q.17 For the reaction $RCH = O + 2[H] \rightarrow RCH_2OH$
the catalyst is-
(A) Ni only
(B) Pd. only
(C) Pt. only
(D) Any of the above

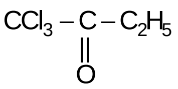
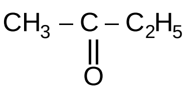
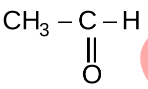
Q.18 Which of the following combinations give t-butyl alcohol when treated with Grignard reagent-
(A) $CH_3MgBr + CH_3COCH_3$
(B) $C_2H_5\,MgBr + CH_3COCH_3$
(C) $CH_3MgBr + (CH_3)_3C.\,OH$
(D) $CH_3MgBr + CH_3CH_2CHO$

Q.19 The conversion $CH_3CH_2CHO \longrightarrow CH_3CH_2CH_2OH$ can not be affected by:
(A) $NaBH_4$
(B) Zn/HCl
(C) H_2/Ni
(D) Na + alcohol

Q.20 Fehling's solution –B is-
(A) NH_4OH
(B) $Cu(OH)_2$
(C) CuO
(D) Cu_2O

Q.21 The best method for the conversion of ethanol to ethanal is-
(A) By passing ethanol vapours over Cu at 578 K
(B) By oxidation with acidic potassium dichromate
(C) By oxidation with mangenese dioxide at 300ºC
(D) By oxidation with acidic $KMnO_4$

Q.22 $(HCOO)_2Ca + (CH_3COO)_2Ca \xrightarrow{\text{Dry distillation}}$ "A" - Product A is–
(A) Propanone (B) Methanal (C) Ethanal (D) One of the above

Q.23 Least reactive towards nucleophilic additon is -
(A) $CH_2 = O$
(B) 
$CCl_3-\underset{\underset{O}{\|}}{C}-C_2H_5$
(C) 
$CH_3-\underset{\underset{O}{\|}}{C}-C_2H_5$
(D) 
$CH_3-\underset{\underset{O}{\|}}{C}-H$

Q.24 Stephen reaction is the reaction involving:
(A) Reduction of alkanoyl chloride with $Pd/BaSO_4$.
(B) Reduction of alkyl isocyanide with sodium and alcohol.
(C) Reduction of alkyl cyanide with $SnCl_2$ and HCl and hydrolysing the intermediate aldimine.
(D) Reduction of carbonyl compound with zinc amalgam and HCl.

Q.25 HCHO with conc. alkali forms two compounds. The change in oxidation number would be-
(A) (0 to –2) in both the compounds
(B) (0 to +2) in both the compounds
(C) (0 to +2) in one compound and (0 to –2) in the second compound
(D) All are correct

Q.26 For Cannizzaro's reaction. Which is necessary-
(A) Presence of α–C (B) Absence of α–C
(C) Presence of α–H (D) Absence of α–H

Q.27 Aldehydes and ketones can be reduced to corresponding hydrocarbons by-
(A) Refluxing with strong acids (B) Passing the vapours over PbO_2
(C) Refluxing with zinc amalgam (D) Refluxing with strong base

Q.28 Which of the following can be used to differentiate between ethanal and propanal-
(A) Ammonical $AgNO_3$
(B) Ammonical $AgNO_3$ in presence of tartrate ions
(C) I_2 in presence of base
(D) Ammonical $AgNO_3$ in presence of citrate ions

Q.29 The reaction,
$2RCHO \xrightarrow{\text{Al–elthoxide}} \underset{\text{Ester}}{RCOOCH_2R}$ is called-
(A) Tishenko reaction (B) Knoevangel reaction
(C) Cannizzaro reaction (D) HVZ reaction

Q.30 Which of the following does not turn schiff's reagent to pink-
(A) Formaldehyde (B) Benzaldehyde (C) Acetone (D) Acetaldehyde

EXERCISE –II

Q.1 Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon? **[AIEEE-2004]**

(A) Ethyl acetate (B) Acetic acid (C) Acetamide (D) Butan-2-one

Q.2 The best reagent to convert pent–3–en–2–ol into pent–3–en–2–one is - **[AIEEE-2005]**

(A) Acidic dichromate (B) Acidic permanganate
(C) Pyridinium chloro–chromate (D) Chromic anhydride in glacial acetic acid

Q.3 The increasing order of the rate of HCN addition to compounds A – D is - **[AIEEE 2006]**

(a) HCHO (b) CH_3COCH_3 (c) $PhCOCH_3$ (d) $PhCOCH_3$

(A) $d < b < c < a$ (B) $d < c < b < a$ (C) $c < d < b < a$ (D) $a < b < c < d$

Q.4 Which of the folowing on heating with aqueous KOH, produces acetaldehyde ? **[AIEEE 2009]**

(A) CH_3COCl (B) CH_3CH_2Cl (C) CH_2ClCH_2Cl (D) CH_3CHCl_2

Q.5 An aldehyde isomeric with allyl alcohol gives phenyl hydrazone. Pick out a ketone that too gives a phenyl hydrazone containing the same percentage of nitrogen:

(A) Methyl ethyl ketone (B) Dimethyl ketone
(C) 2– Butanone (D) 2–Methyl propanone

Q.6 Aldehydes and ketones form hydrocarbons by:

(A) The Clemmensen reduction (B) The Cannizzaro reaction
(C) The Rosenmund reduction (D) Aldol condensation

Q.7 Acetaldehyde oxidises:

(A) Fehling's solution. (B) Ammoniacal $AgNO_3$ solution
(C) NaOI. (D) None of these

Q.8 $C_6H_5CHO + CH_3COCH_3 \xrightarrow{OH^-} C_6H_5CH(OH)CH_2COCH_3 \longrightarrow C_6H_5CH = CHCOCH_3$ This reaction is known as:

(A) Aldol condensation (B) Cross aldol condensation
(C) The Claisen-Schmidt reaction (D) None of these

Q.9 Acetaldehyde on warming with fehling solution gives a red precipitate of:

(A) Elemental copper (B) Cuprous oxide
(C) Cupric oxide (D) Mixture of all of the above

Q.10 Fehling solution is made by mixing two separate solutions. One of which is a solution of copper sulphate only while the other contains:

(A) $NaHCO_3$ (B) Na_2CO_3 (C) $KNaC_4H_4O_6$ (D) $KHCO_3$

Q.11 Dry distillation of calcium formate and subsequent treatment with dilute KOH gives the mixture of:

(A) CH_3OH, HCOOK	(B)CH_3CHO, HCOOK
(C) HCHO, HCOOK	(D) None of the above

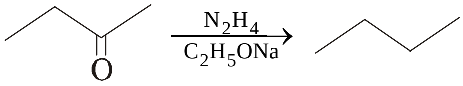
Q.12 The conversion $CH_3CHO \longrightarrow OHC - CHO$ can be effected by:

(A) CrO_3 (B) SeO_2 (C) Br_2/NaOH (D) $KMnO_4$

Q.13 Ammonia with formaldehyde gives the:

(A) Cyclic product	(B) Linear product
(C) Addition product	(D) Substitution product

Q.14 Match list I with list II and then select the correct answer from the codes given below the lists:

List I	**List II**
(1) $RCOR' \xrightarrow[HCl]{Zn/Hg} RCH_2R'$	(a) Meerwein-Ponndorf Verley reduction.
(2) 	(b) Clemmensen reduction
(3)  $R-\underset{R'}{\underset{\vert}{C}}=O$ + Aluminium $R-\underset{R'}{\underset{\vert}{CH}}-OH$	(c) Tischenko reaction iso propoxide
(4) $RCHO + Al(OC_2H_5)_3 \xrightarrow{Heat}$ Ester	(d) Wolff-Kishner reaction

Codes

	1	2	3	4
(A)	b	d	c	a
(B)	d	b	a	c
(C)	b	d	a	c
(D)	a	c	b	d

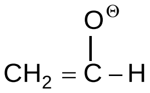
Q.15 Match List I with list II and then select the correct answer from the codes given below the lists:

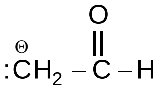
List I	List II
(1) C_6H_5CHO	(a) Mesitylene
(2) CH_3COCHO	(b) Paraldehyde
(3) CH_3COCH_3	(c) Iodoform reaction
(4) CH_3CHO	(d) Cannizzaro reaction

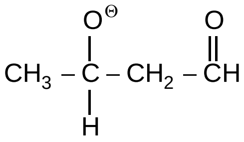
Codes

	1	2	3	4
(A)	d	c	b	a
(B)	d	b	c	a
(C)	a	c	b	d
(D)	d	c	a	b

Q.16 $CH_3\text{—}CHO \xrightarrow{\overset{\ominus}{OH}} CH_3CH(OH)CH_2CHO$ In the aldol condensation of acetaldehyde represented above, which of the following intermediate species are obtained ?

(A) 
$CH_2=\overset{O^{\ominus}}{\overset{|}{C}}-H$

(B) 
$\overset{\ominus}{:CH_2}-\overset{O}{\overset{\|}{C}}-H$

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

(D) All above

Q.17 Conversion of acetone into 2,3-dimethylbutane-2, 3-diol can be achieved by:
(A) Zn/Hg/HCl
(B) Wolff-Kishner reduction
(C) $Mg/Hg/H_2O$
(D) The conversion is not possible.

Q.18 Which of the following statements is wrong:
(A) All methyl ketones give a positive iodoform test.
(B) Acetaldehyde is the only aldehyde that gives iodoform test.
(C) All secondary alcohols give positive iodoform test.
(D) Any alcohol that can be oxidised to an acetyl group gives a positive iodoform test.

Q.19 Arrange $[(CH_3)_3C]_2CO$ (I), $[(CH_3)_2CH]_2C{=}O$ (II), $(CH_3)_2C{=}O$ (III) and CH_3CHO (IV) in order of reactivity towards nucleophilic attack:
(A) I > II > III > IV
(B) I > III > IV > II
(C) IV > III > II > I
(D) II > I > III > IV

Q.20 Which of the following statements is correct:
(A) All primary alcohol give iodoform reaction.
(B) All secondary alcohols give iodoform reaction.
(C) Ethanol is the only primary alkanol that gives positive iodoform test.
(D) All aldehydes with α hydrogen atoms give positive iodoform reaction:

Q.21 Both Fehling's solution and Benedict's solution give this compound when treated with acetaldehyde:
(A) CuO
(B) Cu_2O
(C) $Cu(OH)_2$
(D) $Cu(CO)_4$

Q.22 Aldehyde not containing α-hydrogen atom reacts with aqueous alkali to form:
(A) An α, β unsaturated aldehyde.
(B) An α, β unsaturated acid.
(C) Corresponding alcohol and corresponding carboxylate anion.
(D) Corresponding carboxylic acid.

Q.23 Formaldehyde reacts with 50% aqueous alkali to form:
(A) A mixture of methanol and sodium acetate.
(B) A mixture of ethanol and sodium formate.
(C) A mixture of methanol and sodium formate.
(D) A resinous mass.

Q.24 $CH_3CH=CH\text{-}CHO$ may be reduced to $CH_3CH=CHCH_2OH$ using:
(A) H_2/Pt (B) $NaBH_4$
(C) $[(CH_3)_2CHO]_3Al$ (D) Zn-Hg/HCl

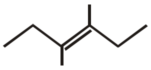
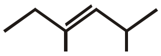
Q.25 How many aldols will be formed by CH_3CHO and $CH_3–CH_2–CHO$ –
(A) 2 (B) 3 (C) 4 (D) 1

Q.26 An organic compound reduces Tollens reagent and Fehling's solution. It can be –
(A) CH_3CH_2CHO (B) C_6H_5CHO (C) $CH_3COCH_2CH_3$ (D) $(CH_3)_3CCOCH_3$

Q.27 Methyl ethyl ketone can be reduced to n-butane by –
(A) Meerwein-Ponndorf reduction (B) Wolff-Kishner reduction
(C) Mg-Hg, H_2O (D) HI / red phosphorus at 423 K

Q.28 Ethyl cyanide is allowed to react with methylmagnesium iodide and subsequently acidified with dilute HCl. The product formed is -
(A) propanone (B) propanal (C) butanal (D) butanone

Q.29 Which of the following alkenes is most suitable for the preparation butanone by ozonolysis -

(A) 
(B) 
(C) 
(D) 

Q.30 In the reaction $CH_3CHO + HCN \rightarrow CH_3CHOHCN$ the product obtained is -
(A) a meso compound (B) a levorotatory compound
(C) a dextrorotatory compound (D) a recemic mixture

ANSWER KEY

EXERCISE – I

Q.1	C	Q.2	C	Q.3	C	Q.4	B	Q.5	A	Q.6	C	Q.7	B
Q.8	C	Q.9	C	Q.10	A	Q.11	C	Q.12	A	Q.13	A	Q.14	A
Q.15	C	Q.16	C	Q.17	D	Q.18	A	Q.19	B	Q.20	C	Q.21	A
Q.22	D	Q.23	C	Q.24	C	Q.25	C	Q.26	D	Q.27	C	Q.28	C
Q.29	A	Q.30	C										

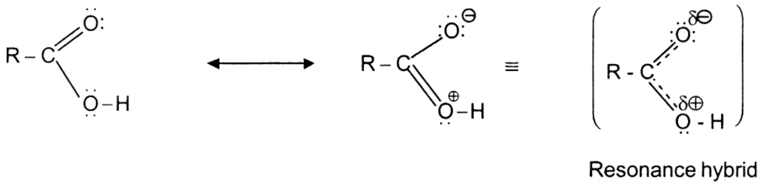
EXERCISE –II

Q.1	D	Q.2	D	Q.3	B	Q.4	D	Q.5	B	Q.6	A	Q.7	D
Q.8	C	Q.9	B	Q.10	C	Q.11	A	Q.12	B	Q.13	A	Q.14	C
Q.15	D	Q.16	D	Q.17	C	Q.18	C	Q.19	C	Q.20	C	Q.21	B
Q.22	C	Q.23	C	Q.24	C	Q.25	C	Q.26	A	Q.27	BD	Q.28	D
Q.29	A	Q.30	D										

CARBOXYLIC ACID & IT'S DERIVATIVES

1. GENERAL INTRODUCTION

The organic compounds containing carboxyl ($-\overset{\overset{O}{\|}}{C}-OH$) group are known as carboxylic acids and the term 'Carboxylic' was firstly proposed by scientist 'Bayer'.
Resonance hybrid structure of carboxylic acid group is



Resonance hybrid

due to resonance, the bond length value of both the bonds [C–O & C=O] are equal, which is 1.28 Å.

1.1 Classification :

On the basis of the group to which –COOH group is attached.

(a) Aliphatic carboxylic acid = $R-\overset{\overset{O}{\|}}{C}-OH$ (R = H atom or alkyl group).

(b) Aromatic carboxylic acid = $Ar-\overset{\overset{O}{\|}}{C}-OH$ (Ar = Aryl group)

1.2 On the basic of number of –COOH groups in their molecule.

		No. of –COOH group
(a)	Mono carboxylic acids	1
(b)	Dicarboxylic acids	2
(c)	Tricarboxylic acids	3

General formula is $C_nH_{2n}O_2$ or $C_nH_{2n+1}COOH$

Saturated and unsaturated mono carboxylic acids are also called fatty acids, because higher acids like palmitic acid, steric acid, oleic acid, etc. were obtained by hydrolysis of fats and oils.

Isomerism – Chain, positional, functional group and optical.

Hybridisation state of C in the carboxyl group in sp^2

2. METHOD OF PREPARATION

2.1 By the oxidation of alcohols, aldehydes and ketones :

(a) 1° Alcohol $\xrightarrow{[O]}$ corresponding carboxylic acids.

$$R-CH_2-OH + [O] \xrightarrow[K_2Cr_2O_7]{KMnO_4 \text{ or}} R-CHO \xrightarrow{[O]} R-\overset{\overset{O}{\|}}{C}-OH$$

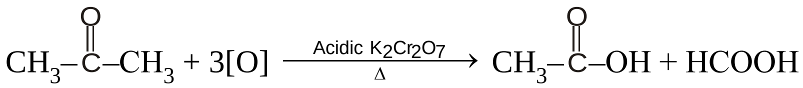
(b) Aldehyde $\xrightarrow{[O]}$ corresponding acids

$$R-CH{=}O + [O] \xrightarrow{\text{Acidic } K_2Cr_2O_7} R-\overset{\overset{O}{\|}}{C}-OH$$

(c) Ketones $\xrightarrow{[O]}$ mixture of acids of lesser no. of C atoms than the ketone.

$$R-\overset{\overset{O}{\|}}{C}-CH_2-R' + [O] \xrightarrow[\Delta]{\text{Acidic } K_2Cr_2O_7} R-\overset{\overset{O}{\|}}{C}-OH + R'-COOH$$

Ex.

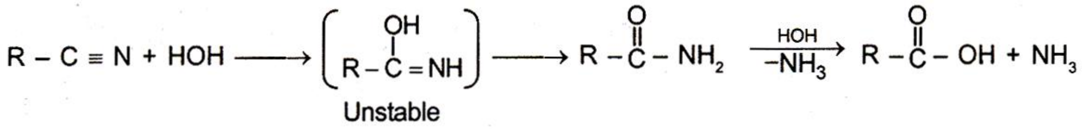


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 3[O] \xrightarrow[\Delta]{\text{Acidic } K_2Cr_2O_7} CH_3-\overset{\overset{O}{\|}}{C}-OH + HCOOH$$

$$HCOOH + [O] \longrightarrow CO_2 + H_2O$$

2.2 By the hydrolysis of cyanides (nitriles) :

Cyanides on complete hydrolysis in the presence of dilute HCl form carboxylic acids.



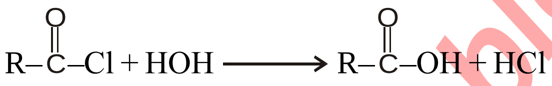
$$R-C\equiv N + HOH \longrightarrow \left(R-\overset{\overset{OH}{|}}{C}=NH\right) \longrightarrow R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[-NH_3]{HOH} R-\overset{\overset{O}{\|}}{C}-OH + NH_3$$

Unstable

2.3 From hydrolysis of acid derivatives :

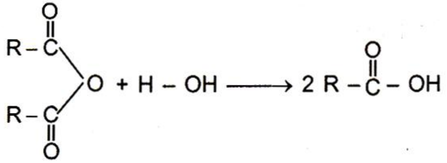
$$R-\overset{\overset{O}{\|}}{C}-Z + H-OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH + HZ$$

(a) **From acyl halides :**



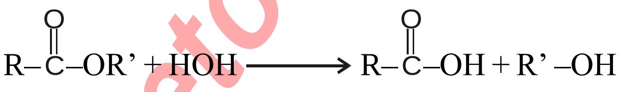
$$R-\overset{\overset{O}{\|}}{C}-Cl + HOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH + HCl$$

(b) **From acid anhydride :**



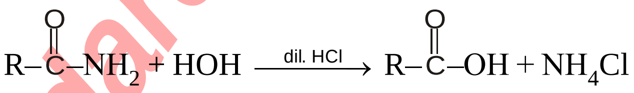
Note : Formic acid cannot be prepared by these two reactions (a & b) because it's corresponding formyl chloride and formic anhydride are unstable compounds.

(c) **From carboxylic ester :**



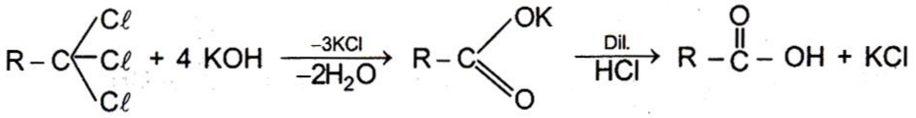
$$R-\overset{\overset{O}{\|}}{C}-OR' + HOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH + R'-OH$$

(d) **From acid amides :**



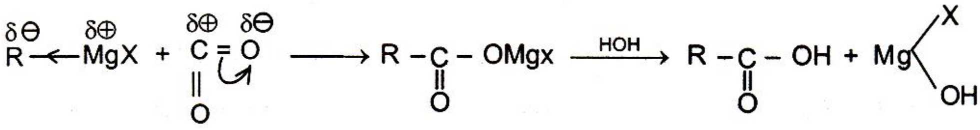
$$R-\overset{\overset{O}{\|}}{C}-NH_2 + HOH \xrightarrow{\text{dil. HCl}} R-\overset{\overset{O}{\|}}{C}-OH + NH_4Cl$$

2.4 By alkaline hydrolysis of alkylidyne trihalides :



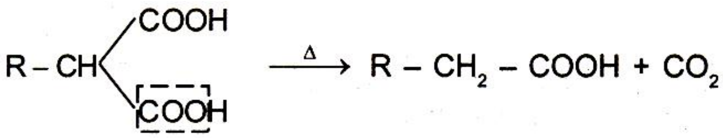
2.5 From carboxylation of grignard's reagent :

By passing CO_2 in ether Solution of Grignard's reagent



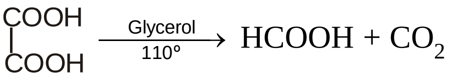
Note : Formic acid can not be prepared by this method.

2.6 Partial decarboxylation of gem dicarboxylic acids :



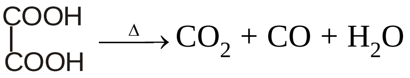
$$R-CH(COOH)_2 \xrightarrow{\Delta} R-CH_2-COOH + CO_2$$

Note : Formic acid is prepared from oxalic acid (laboratory method) by heating at about 110º in the presence of glycerol.



$$\begin{array}{l}COOH\\ |\\ COOH\end{array} \xrightarrow[110°]{Glycerol} HCOOH + CO_2$$

In absence of glycerol



$$\begin{array}{l}COOH\\ |\\ COOH\end{array} \xrightarrow{\Delta} CO_2 + CO + H_2O$$

2.7 Carbonylation of :

(a) Sodium alkoxides or sodium hydroxide :

$$H-O\,Na + CO \xrightarrow[High\ press]{High\ temp.} H-COONa \xrightarrow[HOH]{dil.\ HCl} H-\overset{O}{\overset{\|}{C}}-OH$$

$$R-ONa + CO \xrightarrow[High\ press]{High\ temp.} R-COONa \xrightarrow[HOH]{dil.\ HCl} R-\overset{O}{\overset{\|}{C}}-OH$$

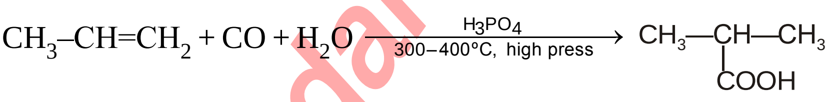
(b) Alcohols :

$$R-OH + CO \xrightarrow[High\ temp.\ \&\ press]{BF_3\,/\,HOH} R-\overset{O}{\overset{\|}{C}}-OH$$

$$H-OH + CO \xrightarrow[High\ temp.\ \&\ press]{BF_3\,/\,HOH} H-\overset{O}{\overset{\|}{C}}-OH$$

(c) Alkenes [Koch Reaction] :

$$CH_2=CH_2 + CO + H_2O \xrightarrow[300-400°C,\ high\ press]{H_3PO_4} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH \text{ (Propanoic acid)}$$



$$CH_3-CH=CH_2 + CO + H_2O \xrightarrow[300-400°C,\ high\ press]{H_3PO_4} CH_3-\underset{COOH}{\underset{|}{CH}}-CH_3 \text{ (2–methyl Propanoic acid)}$$

Note : Formic acid and acetic acid can not be prepared by this method.

2.8 Oxidation of alkenes and alkynes :

$$R-CH=CH-R' + 4[O] \xrightarrow[or\ Acidic\ K_2Cr_2O_7]{HNO_3\ or\ CrO_3} R-COOH + R'-COOH$$

$$CH_2=CH_2 + 4[O] \longrightarrow 2\,H\,COOH \xrightarrow{[O]} 2\,CO_2 + 2H_2O$$

$$CH_3-CH=CH_2 + 4\,[O] \longrightarrow CH_3\,COOH + CO_2 + H_2O$$

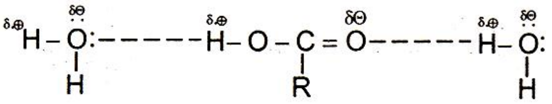
$$R-C\equiv C-R' + 3\,[O] + HOH \longrightarrow R-COOH + R'\,COOH$$

3. PHYSICAL POPERTIES

3.1 Physical State : C_1 to C_3 = Colour less pungent smelling liquids.
C_4 to C_9 = Liquids having goat's butter like smell.
C_{10} to C_{10+} = Colourless & odourless waxy solids.

3.2 Solubility : Up to C_4 = Highly soluble in water

With the increase in molecular weight of carboxylic acid, the solubility in water decreases.
Solubility of lower members of carboxylic acids family is due to the formation of hydrogen bond between –COOH group and water molecules.

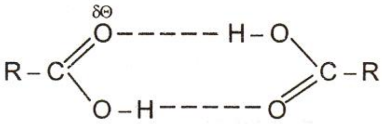


As the alkyl group increases in size in acids, the water repelling (hydrophobic) tendency of the hydrocarbon chain increases and it out weighs the effect of hydrogen bonding. This is why solubility decreases in higher members.

3.3 Boiling point (B.P.) :

B.P. of acids > B.P. of alcohols

Because, A carboxylic acid molecular can enter into hydrogen bonding at two different points. This leads to the formation of cyclic dimers in acids. This is the fact that lower acids occur as dimers in solution.

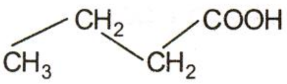


3.4 Melting point (M.P.) :

M.P. of carboxylic acids do not vary smoothly from one molecule to another

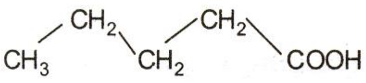
For first ten memebers M.P. of C_{2n} > M.P. of C_{2n+1}
(n = 1, 2, 3, 4, 5) (n = 0, 1, 2, 3, 4)

Reasons : In acids of even number of carbon atoms terminal $-CH_3$ and –COOH group lie on the opposite side of the carbon chain.



Provide more effective packing of the molecule in the lattice.

While in acids of odd no. of carbon atoms



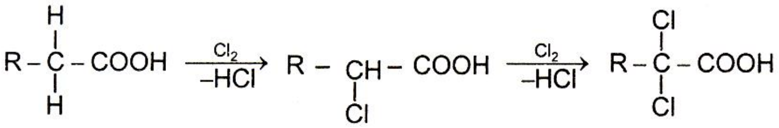
Less effective packing

4. CHEMICAL PROPERTIES : Carboxylic acids give following reactions :

4.1 Due to alkyl group
4.2 Due to acidic hydrogen
4.3 Due to >C = O group
4.4 Due to – OH group
4.5 Due to – COOH group
4.6 Special reaction of alkanoic acid

4.1 Reactions due to alkyl group :

Halogenation : Acids having α –H atom give this reaction. The α –H atoms are easily replaced by chlorine or bromine atoms, forming halogen derivatives of acids.



$$R-\underset{H}{\overset{H}{C}}-COOH \xrightarrow[-HCl]{Cl_2} R-\underset{Cl}{CH}-COOH \xrightarrow[-HCl]{Cl_2} R-\underset{Cl}{\overset{Cl}{C}}-COOH$$

Note : (i) The reaction is known as hell–volhard–Zelinisky (HVZ) reaction.

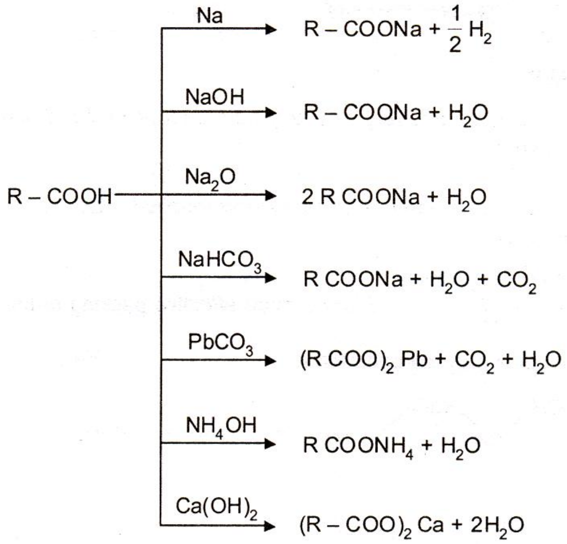
(ii) In the presence of phsophrous, monohalo product is formed as the main product.

$$R–CH_2–COOH + Br_2 \xrightarrow{P} R–CH(Br)–COOH + HBr$$

(iii) Formic acid does not shown HVZ reaction due to absence of alkyl group or α – H atom.

4.2 Due to acidic hydrogen :

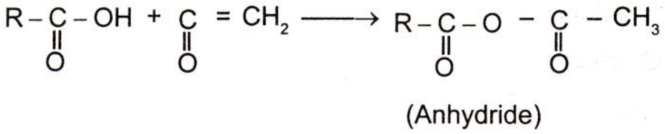
(a) **Salt Formation :** Carboxylic acids form salts with metals, metal oxide, hydroxides, carbonates, bicarbonates and compounds showing basic nature.



$$R-COOH \xrightarrow{Na} R-COONa + \frac{1}{2}H_2$$
$$R-COOH \xrightarrow{NaOH} R-COONa + H_2O$$
$$R-COOH \xrightarrow{Na_2O} 2\,R\,COONa + H_2O$$
$$R-COOH \xrightarrow{NaHCO_3} R\,COONa + H_2O + CO_2$$
$$R-COOH \xrightarrow{PbCO_3} (R\,COO)_2\,Pb + CO_2 + H_2O$$
$$R-COOH \xrightarrow{NH_4OH} R\,COONH_4 + H_2O$$
$$R-COOH \xrightarrow{Ca(OH)_2} (R-COO)_2\,Ca + 2H_2O$$

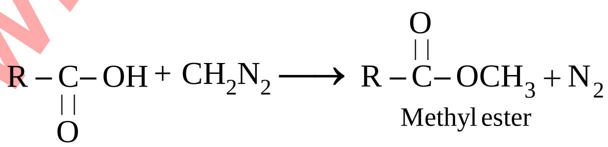
Note : Acids liberate CO_2 with $NaHCO_3$. This reaction is used to distinguish carboxylic acid from phenol which does not react with $NaHCO_3$.

(b) **Reaction with Ketene :**



$$R-\underset{O}{\underset{\|}{C}}-OH + \underset{O}{\underset{\|}{C}}=CH_2 \longrightarrow \underset{\text{(Anhydride)}}{R-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-CH_3}$$

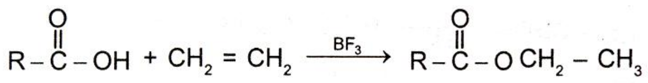
(c) **Reaction with diazomethane :**



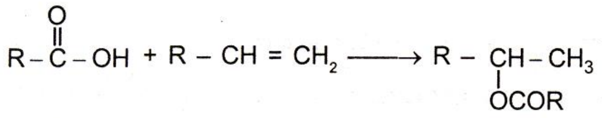
$$R-\underset{O}{\underset{\|}{C}}-OH + CH_2N_2 \longrightarrow \underset{\text{Methyl ester}}{R-\overset{O}{\overset{\|}{C}}-OCH_3} + N_2$$

Note : Diazomethane is a powerful methylating agent. So by this method methyl ester can be prepared.

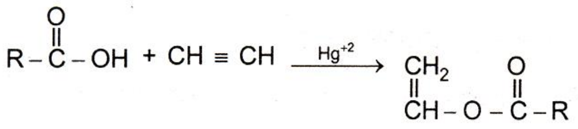
(d) **Reaction with alkene and alkyne :**



$$R-\overset{O}{\overset{\|}{C}}-OH + CH_2=CH_2 \xrightarrow{BF_3} R-\overset{O}{\overset{\|}{C}}-OCH_2-CH_3$$



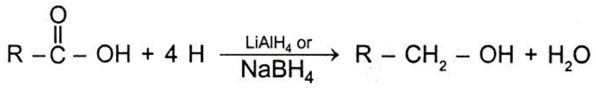
$$R-\overset{O}{\overset{\|}{C}}-OH + R-CH=CH_2 \longrightarrow R-\underset{OCOR}{\underset{|}{CH}}-CH_3$$



$$R-\overset{O}{\overset{\|}{C}}-OH + CH\equiv CH \xrightarrow{Hg^{+2}} \underset{CH-O-\overset{O}{\overset{\|}{C}}-R}{\overset{CH_2}{\|}}$$

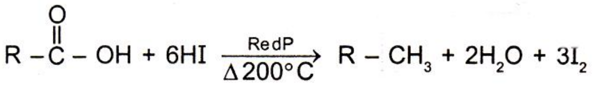
4.3 Reaction due to (>C = O) group :

(a)



$$R-\overset{O}{\overset{\|}{C}}-OH + 4\,H \xrightarrow[NaBH_4]{LiAlH_4\ or} R-CH_2-OH + H_2O$$

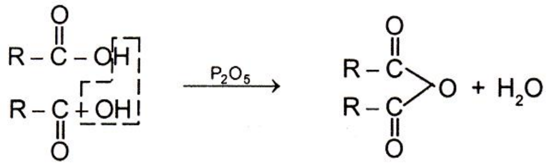
(b)



$$R-\overset{O}{\overset{\|}{C}}-OH + 6HI \xrightarrow[\Delta\,200^\circ C]{Red\,P} R-CH_3 + 2H_2O + 3I_2$$

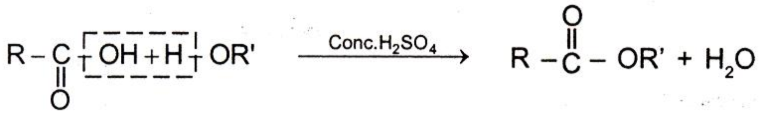
4.4 Reactions due to (–OH) group :

(a) **With P_2O_5 (Dehydrations)**



$$\begin{array}{l} R-\overset{O}{\overset{\|}{C}}-OH \\ R-\underset{O}{\underset{\|}{C}}-OH \end{array} \xrightarrow{P_2O_5} \begin{array}{l} R-\overset{O}{\overset{\|}{C}} \\ R-\underset{O}{\underset{\|}{C}} \end{array}\!\!>O + H_2O$$

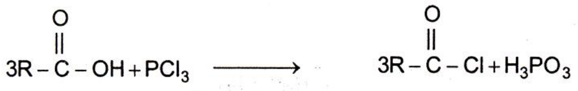
(b) **Esterification :**



$$R-\underset{O}{\underset{\|}{C}}-\boxed{OH+H}-OR' \xrightarrow{Conc.H_2SO_4} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

Note : The reaction is proton–catalysed esterification. In the reaction OH comes from the acid and H from the alcohol for release of H_2O.

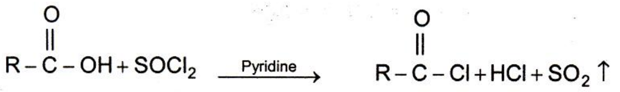
(c) **Reaction with Phosphrous Chlorides :**



$$3R-\overset{O}{\overset{\|}{C}}-OH+PCl_3 \longrightarrow 3R-\overset{O}{\overset{\|}{C}}-Cl+H_3PO_3$$

$$R-\overset{O}{\overset{\|}{C}}-OH+PCl_5 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl+HCl+POCl_3$$

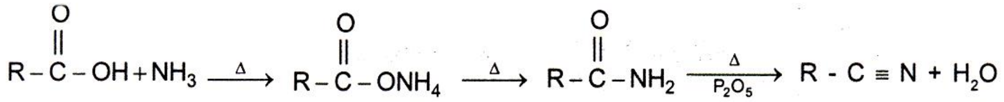
(d) **With Thionyl Chloride :**



$$R-\overset{O}{\overset{\|}{C}}-OH+SOCl_2 \xrightarrow{Pyridine} R-\overset{O}{\overset{\|}{C}}-Cl+HCl+SO_2\uparrow$$

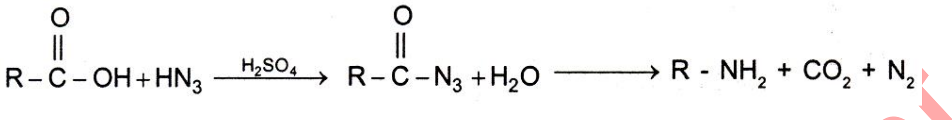
Note : In the reaction SO_2 is gas so escapes out and HCl is an acid, gets absorbed by basic pyridine and pure acyl chloride is left. So its is best method for preparing acyl chloride from acids.

(e) **Formation of acid Amides and Alkane Nitriles :**



$$R-\overset{\overset{\large O}{\|}}{C}-OH + NH_3 \xrightarrow{\Delta} R-\overset{\overset{\large O}{\|}}{C}-ONH_4 \xrightarrow{\Delta} R-\overset{\overset{\large O}{\|}}{C}-NH_2 \xrightarrow[P_2O_5]{\Delta} R-C\equiv N + H_2O$$

(f) **With Hydrazoic acid (Schmidt reaction) :** N_3H = Hydrazoic acid

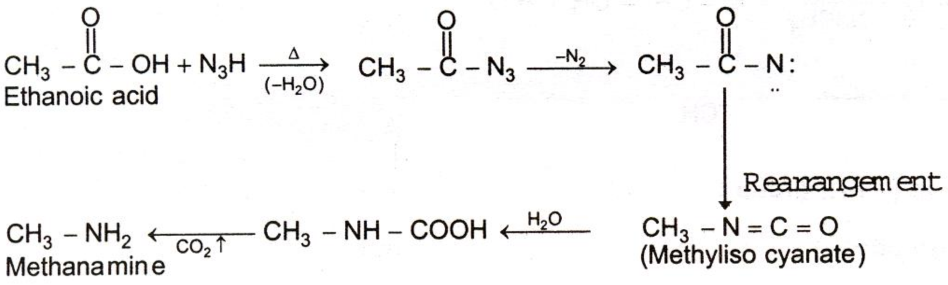


$$R-\overset{\overset{\large O}{\|}}{C}-OH + HN_3 \xrightarrow{H_2SO_4} R-\overset{\overset{\large O}{\|}}{C}-N_3 + H_2O \longrightarrow R-NH_2 + CO_2 + N_2$$

The reaction is a modification of "curtius reaction".

Ex. $CH_3-COOH + HN_3 \xrightarrow{H_2SO_4} CH_3-NH_2 + CO_2 + N_2$

Mechanism :



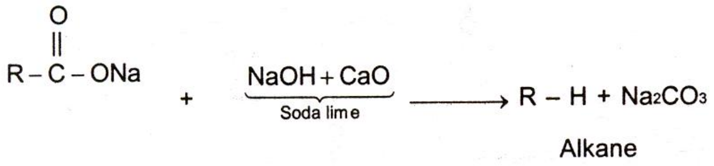
$$CH_3-\overset{\overset{\large O}{\|}}{C}-OH + N_3H \xrightarrow[(-H_2O)]{\Delta} CH_3-\overset{\overset{\large O}{\|}}{C}-N_3 \xrightarrow{-N_2} CH_3-\overset{\overset{\large O}{\|}}{C}-\ddot{N}:$$

Ethanoic acid

$$\xrightarrow{\text{Rearrangement}} CH_3-N=C=O \text{ (Methyliso cyanate)} \xrightarrow{H_2O} CH_3-NH-COOH \xrightarrow{CO_2\uparrow} CH_3-NH_2 \text{ (Methanamine)}$$

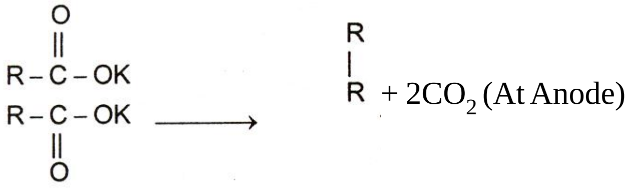
4.5 Reaction due to (–COOH) group :

(a) **Decarboxylation :**



$$R-\overset{\overset{\large O}{\|}}{C}-ONa + \underbrace{NaOH + CaO}_{\text{Soda lime}} \longrightarrow \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

(b) **Kolbe's electrolytic synthesis :**

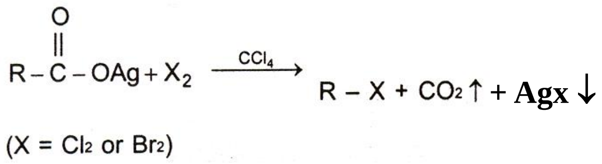


$$\begin{matrix} R-\overset{\overset{\large O}{\|}}{C}-OK \\ R-\underset{\underset{\large O}{\|}}{C}-OK \end{matrix} \longrightarrow \begin{matrix} R \\ | \\ R \end{matrix} + 2CO_2 \text{ (At Anode)}$$

$2K + 2H_2O \longrightarrow 2KOH + H_2$ (At Cathode)

Note : Kolbe synthesis undergoes free radical mechanism.

(c) **Hundsdiecker reaction :**

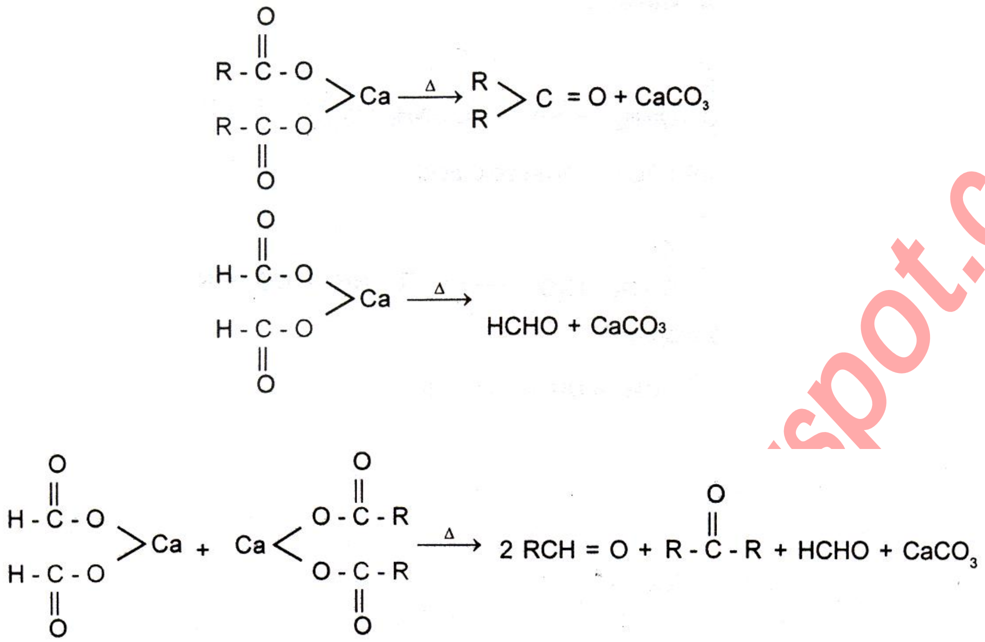


$$R-\overset{\overset{\large O}{\|}}{C}-OAg + X_2 \xrightarrow{CCl_4} R-X + CO_2\uparrow + Agx\downarrow$$

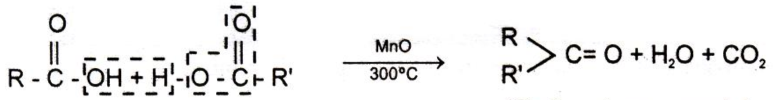
($X = Cl_2$ or Br_2)

Note : In the reaction decarboxylative halogenation of the acid takes place. The reaction is useful in stepping down a homologus series.

(d) **Formation of carbonyl compounds [Dry distillation of calcium salt] :**



(e) **With Manganous oxide :**



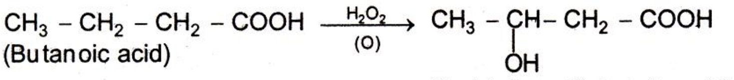
(Carbonyl compounds)

4.6 Special reaction of alkanoic acid :

(a) **Oxidation :**

→ By SeO_2 α keto acid is formed

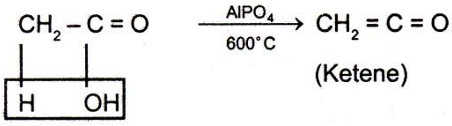
→ By H_2O_2 –OH group comes at β –C atom.



$$CH_3-CH_2-CH_2-COOH \xrightarrow[(O)]{H_2O_2} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-COOH$$

(Butanoic acid) (3 – Hydroxy Butanoic acid)

(b) **Pyrolysis :**

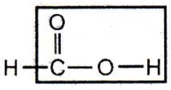


$$\underset{H}{CH_2}-\underset{OH}{C}=O \xrightarrow[600^{\circ}C]{AlPO_4} CH_2=C=O$$

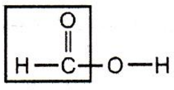
(Ketene)

5. SPECIAL FEATURES OF FORMIC ACID

(a) Formic acid shows acidic character due to the presence of –COOH group as well as shown reducing character due to the presence of –CHO group.



– COOH group



– CHO group

(b) It reduces Tollen's reagent and forms silver mirror.

(c) It reduces mercuric chloride and forms black ppt. of mercury.

(d) It decolourises the pink colour of acidic $KMnO_4$

(e) It forms brown ppt. of MnO_2 with basic $KMnO_4$

(f) It converts the orange colour of acidic $K_2Cr_2O_7$ into green colour.

(g) It reduces Fehling solution.

(h) Dehydration –HCOOH $\xrightarrow[\text{Conc. } H_2SO_4]{\Delta}$ $H_2O + CO_2$

(i) **Effect of heat :**

(a) $$HCOOH \xrightarrow[\Delta]{160°C} CO_2 + H_2$$

(b) $$2HCOONa \xrightarrow[\Delta]{380°C} 2\underset{\text{Sodium oxalate}}{\begin{array}{l}COONa\\|\\COONa\end{array}} + H_2$$

6. DISTINCTION BETWEEN FORMIC ACID AND ACETIC ACID

S. NO.	HCOOH	CH_3COOH
1.	Decomposed on heating to give carbon dioxide and hydrogen.	Stable
2.	With concentrated sulphuric acid gives carbon monoxide and water.	Stable
3.	With halogens, there is not action.	Substituted acids are formed.
4.	Reduces ammonical silver nitrate and Fehling's solution.	No action.
5.	Calcium salt on heating gives formaldehyde.	Calcium salt on heating gives acetone.
6.	Sodium salt on heating gives sodium oxalate hydrogen.	No action.
7.	Sodium salt + soda lime gives hydrogen on heating.	Methane is produced.
8.	Electrolysis of alkali solution gives hydrogen.	Ethane is obtained.
9.	Decolourises acidified $KMnO_4$ solution.	No action.
10.	Dichromate solution turns into green coloured solution.	No action.

7. FORMIC ACID (HCOOH)

1. Lab Reaction :

$$\begin{array}{l}COOH\\|\\COOH\end{array} \xrightarrow[110°]{\text{Glycerol}} HCOOH + CO_2$$

Note : BP of HCOOH is 100.5°, for removal of water from formic acid we can use $PbCO_3$ or PbO (Litharge) and H_2S.

$$2HCOOH + PbCO_3 \longrightarrow (HCOO)_2Pb + CO_2 + H_2O$$

$$(HCOO)_2Pb + H_2S \xrightarrow{100°C} 2HCOOH + PbS \text{ (PPT)}$$

2. Industrial method :

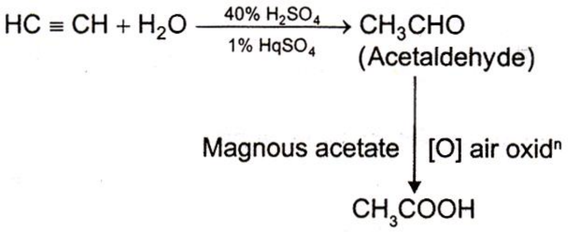
It is prepared on large scale by reaction CO with aqueous sodium hydroxide under pressure 1 atm and 473 K

$$CO + NaOH \xrightarrow[1atm]{473K} HCOONa \xrightarrow{H_2O} HCOOH + NaOH$$

8. ACETIC ACID CH_3COOH

Industrial methods :

(a) **From ethyne :**



$$\begin{tikzcd} HC \equiv CH + H_2O \arrow[r, "40\%\ H_2SO_4", "1\%\ HqSO_4"'] & CH_3CHO\ \text{(Acetaldehyde)} \arrow[d, "\text{Magnous acetate}"', "{[O]}\ \text{air oxid}^n"] \\ & CH_3COOH \end{tikzcd}$$

(b) **From ethyl alcohol**

(i) By dehydrogenation : $CH_3CH_2OH \xrightarrow[\substack{300°C \\ (-H_2)}]{Cu} CH_3CHO \xrightarrow[\text{(Magnous acetate)}]{[O]} CH_3COOH$

(ii) By fermentation (Quick vinegar process)

$$CH_3CH_2OH + O_2 \xrightarrow[\text{(Mycoderma acetail)}]{\text{Acetobector bacteria}} CH_3COOH + H_2O$$

[dilute form 8 – 10% Called **VINEGAR**]

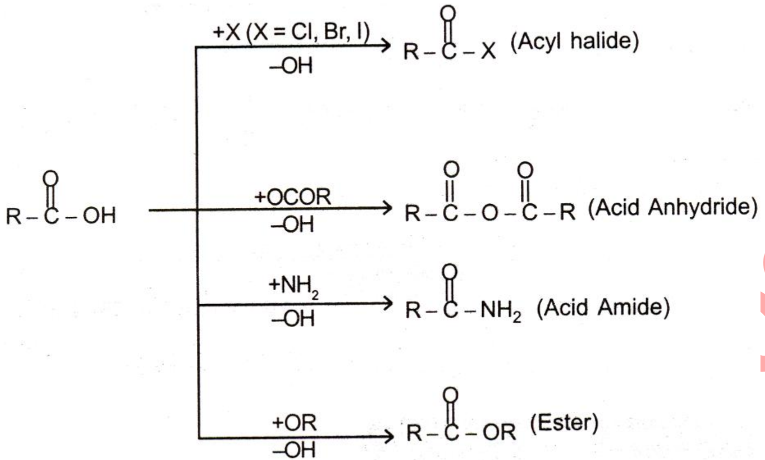
(iii) From CH_3OH

$$CH_3OH + CO \xrightarrow[\text{or Rh}]{BF_3} CH_3COOH$$

ACID DERIVATIVES

1. GENERAL INTRODUCTION

Replacement of –OH group of the –COOH group in a carboxylic acid by an atom or by any other functional group give rise to certain new families of compounds. These compounds are called acid dervatives.

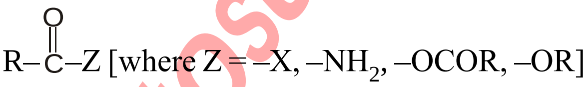


Acyl chlorides are the most important acid halides. The first member of this family is acetyl chloride because formylchloride is unstable.

Similarly acetic anhydride is the representative member of the acid anhydrides family, because formic anhydride is unstable.

The first two members of Acid Amide family are formamide and Acetamide. Acetamide is an important acid amide.

Esters have functional group isomerism with acids.

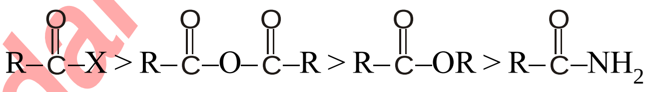


$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}Z}\ [\text{where } Z = -X, -NH_2, -OCOR, -OR]$$

* Order of basic character of group Z

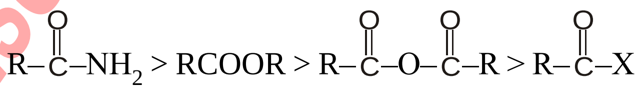
$$X^- < O^-COR < {}^-OR < NH_2^-$$

* Reactivity order/Rate of hydrodysis



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}X > R{-}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}R > R{-}\overset{\overset{O}{\|}}{C}{-}OR > R{-}\overset{\overset{O}{\|}}{C}{-}NH_2}$$

* Order of stability



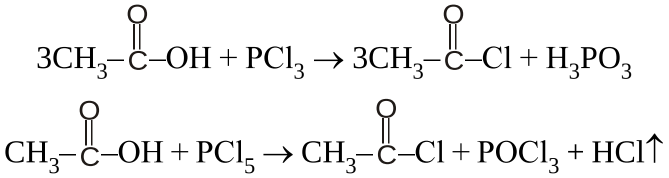
$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 > RCOOR > R{-}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}R > R{-}\overset{\overset{O}{\|}}{C}{-}X}$$

Derivatives regenerate the parent acid on hydrolysis.

2. ACETYL CHLORIDE $[\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}Cl}]$

2.1 Method of preparation :

Laboratory method :



$$\mathrm{3CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH + PCl_3 \rightarrow 3CH_3{-}\overset{\overset{O}{\|}}{C}{-}Cl + H_3PO_3}$$

$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH + PCl_5 \rightarrow CH_3{-}\overset{\overset{O}{\|}}{C}{-}Cl + POCl_3 + HCl\uparrow}$$

$$\mathrm{CH_3COOH + SOCl_2 \rightarrow CH_3{-}CO{-}Cl + SO_2 + HCl\uparrow}$$

From Sodiumacetate :

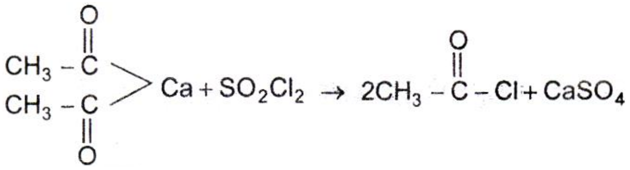
$$CH_3\text{–}COONa + PCl_5 \rightarrow CH_3\text{–}CO\text{–}Cl + POCl_3 + NaCl$$

$$3CH_3\text{–}COONa + PCl_3 \rightarrow 3CH_3\text{–}CO\text{–}Cl + Na_3PO_3$$

$$2CH_3\text{–}COONa + POCl_3 \rightarrow 2CH_3\text{–}CO\text{–}Cl + NaPO_3 + NaCl$$

$$CH_3\text{–}COONa + SOCl_2 \rightarrow CH_3\text{–}CO\text{–}Cl + SO_2 + NaCl$$

By the reaction of sulpuryl chloride on calcium ethanoate :



$$(CH_3COO)_2Ca + SO_2Cl_2 \rightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-Cl + CaSO_4$$

2.2 Physical Properties :

(i) Colourless liquid, having pungent odour.

(ii) Slowly soluble in water, soluble in organic solvents like $CHCl_3$, CCl_4, $CH_3\text{–}CO\text{–}CH_3$, etc.

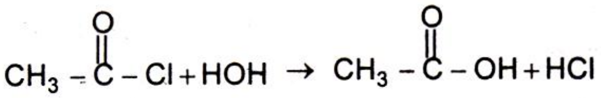
(iii) Produces bilster on skin and its vapour causes irritation in eyes.

(iv) Boiling point is 51ºC.

(v) Fumes strongly in moist air.

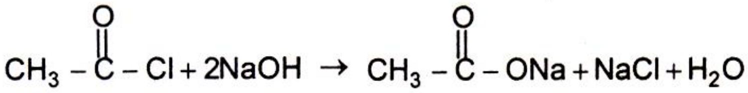
2.3 Chemical properties :

(1) Hydrolysis :



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + HOH \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + HCl$$

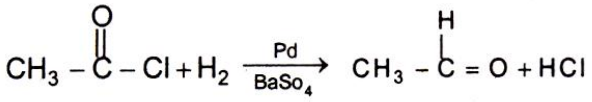
on alkaline hydrolysis



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + 2NaOH \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONa + NaCl + H_2O$$

(2) Reduction :

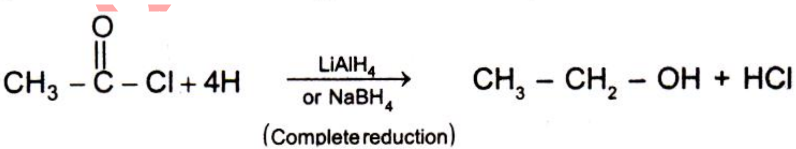
(i)



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[BaSo_4]{Pd} CH_3-\overset{H}{\overset{|}{C}}=O + HCl$$

(Rosenmund's reduction, partial reduction)

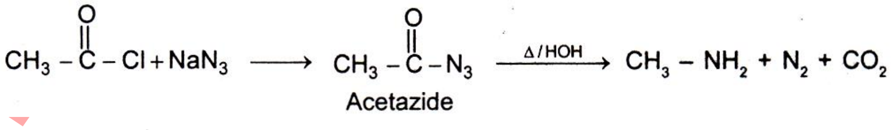
(ii)



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + 4H \xrightarrow[\text{or } NaBH_4]{LiAlH_4} CH_3-CH_2-OH + HCl$$

(Complete reduction)

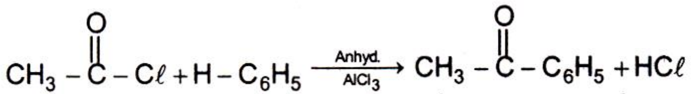
(3) Curtius Reaction :



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + NaN_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow{\Delta/HOH} CH_3-NH_2 + N_2 + CO_2$$

Acetazide

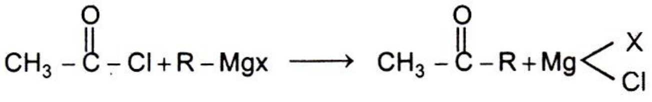
(4) Friedel Craft's reaction :



$$CH_3-\overset{O}{\overset{\|}{C}}-C\ell + H-C_6H_5 \xrightarrow[AlCl_3]{Anhyd.} CH_3-\overset{O}{\overset{\|}{C}}-C_6H_5 + HC\ell$$

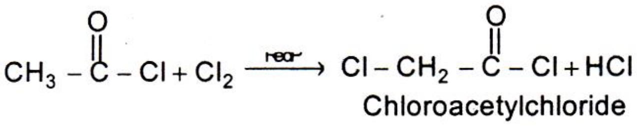
(Acetophenone)

(5) With Grignard's reagent :



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+R-MgX \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-R+Mg\begin{matrix}X\\Cl\end{matrix}$$

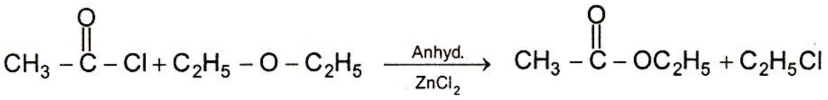
(6) Halogenation :



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+Cl_2 \xrightarrow{\text{heat}} Cl-CH_2-\overset{O}{\overset{\|}{C}}-Cl+HCl$$

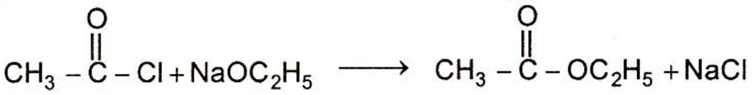
Chloroacetylchloride

(7) With Ether :



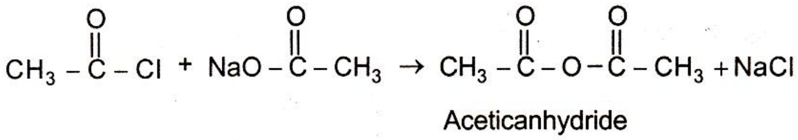
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+C_2H_5-O-C_2H_5 \xrightarrow[ZnCl_2]{\text{Anhyd.}} CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+C_2H_5Cl$$

(8) With Sodium Ethoxide :



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+NaOC_2H_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+NaCl$$

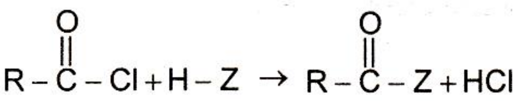
(9) With Sodium Acetate :



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + NaO-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+NaCl$$

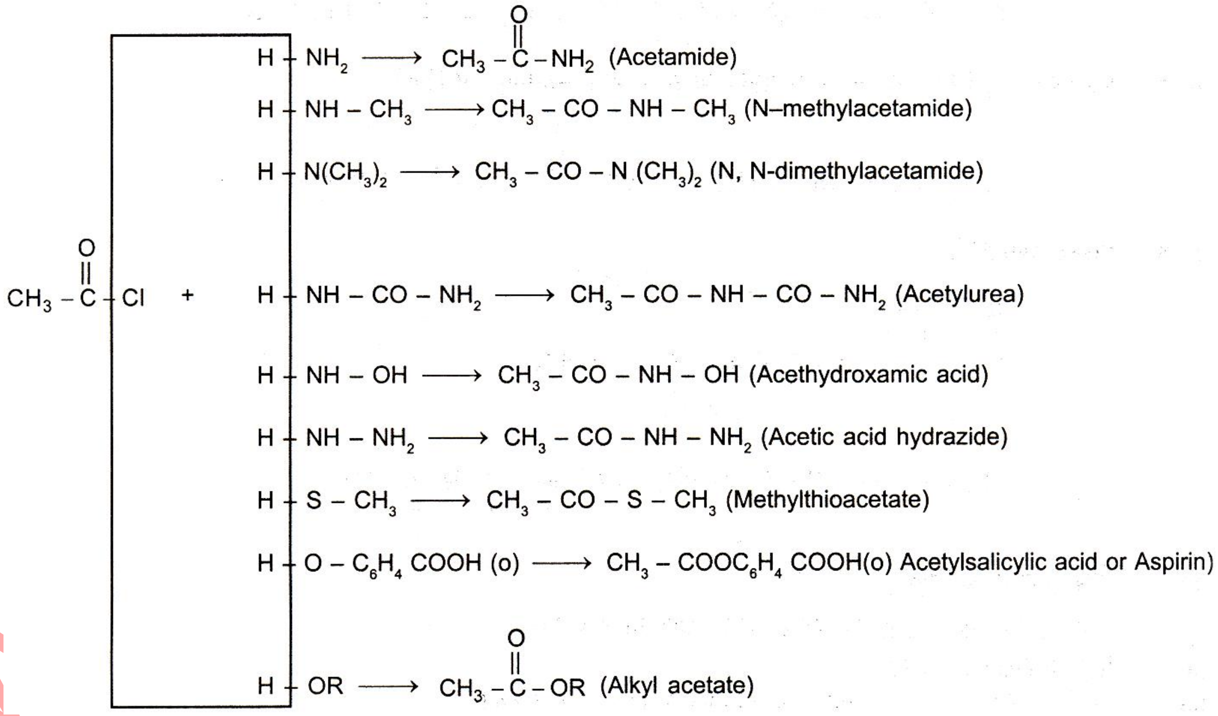
Aceticanhydride

(10) Acetylation of Compounds having reactive hydrogen atom :



$$R-\overset{O}{\overset{\|}{C}}-Cl+H-Z \rightarrow R-\overset{O}{\overset{\|}{C}}-Z+HCl$$

Ex.



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \; + \; H-NH_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \text{ (Acetamide)}$$

$$H-NH-CH_3 \longrightarrow CH_3-CO-NH-CH_3 \text{ (N–methylacetamide)}$$

$$H-N(CH_3)_2 \longrightarrow CH_3-CO-N(CH_3)_2 \text{ (N, N-dimethylacetamide)}$$

$$H-NH-CO-NH_2 \longrightarrow CH_3-CO-NH-CO-NH_2 \text{ (Acetylurea)}$$

$$H-NH-OH \longrightarrow CH_3-CO-NH-OH \text{ (Acethydroxamic acid)}$$

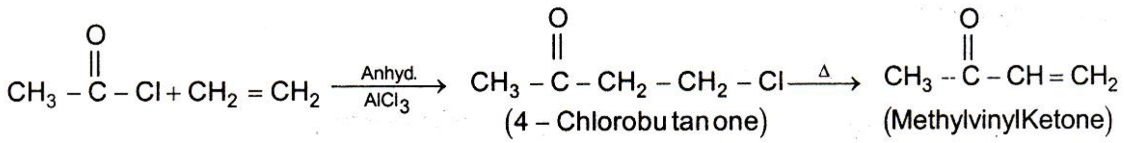
$$H-NH-NH_2 \longrightarrow CH_3-CO-NH-NH_2 \text{ (Acetic acid hydrazide)}$$

$$H-S-CH_3 \longrightarrow CH_3-CO-S-CH_3 \text{ (Methylthioacetate)}$$

$$H-O-C_6H_4\,COOH\,(o) \longrightarrow CH_3-COOC_6H_4\,COOH(o) \text{ Acetylsalicylic acid or Aspirin)}$$

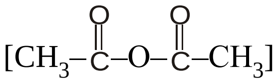
$$H-OR \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OR \text{ (Alkyl acetate)}$$

(11) With Alkene :

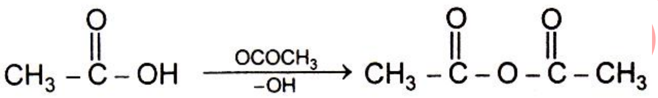


$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+CH_2=CH_2\xrightarrow[AlCl_3]{Anhyd.}\underset{(4-Chlorobutanone)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-Cl}\xrightarrow{\Delta}\underset{(Methylvinyl Ketone)}{CH_3-\overset{O}{\overset{\|}{C}}-CH=CH_2}$$

3. ACETIC ANHYDRIDE



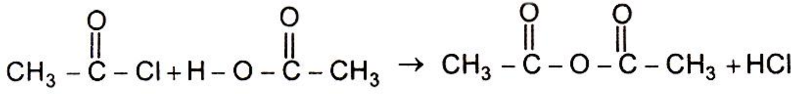
$$[CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3]$$



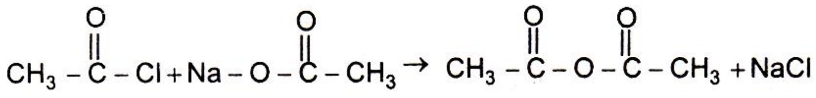
$$CH_3-\overset{O}{\overset{\|}{C}}-OH\xrightarrow[-OH]{OCOCH_3}CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$$

3.1 Method of prepatation :

From Acetyl chloride :



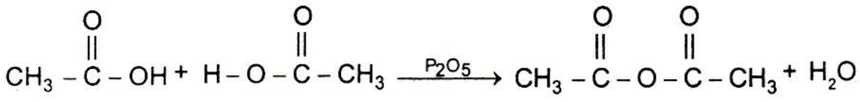
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+H-O-\overset{O}{\overset{\|}{C}}-CH_3\rightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+HCl$$



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+Na-O-\overset{O}{\overset{\|}{C}}-CH_3\rightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+NaCl$$

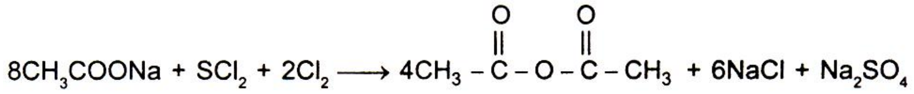
(Laboratory Method)

From Acetic acid :



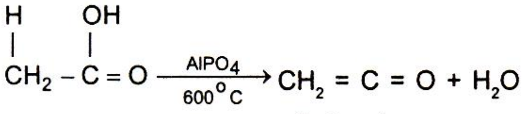
$$CH_3-\overset{O}{\overset{\|}{C}}-OH+H-O-\overset{O}{\overset{\|}{C}}-CH_3\xrightarrow{P_2O_5}CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+H_2O$$

By passing chlorine in a mixture of SCl_2 and sodium acetate :

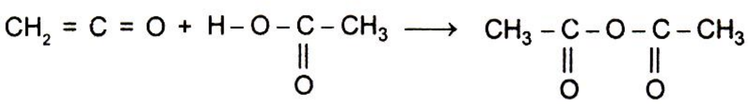


$$8CH_3COONa+SCl_2+2Cl_2\longrightarrow 4CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3+6NaCl+Na_2SO_4$$

From Ketene :



$$\overset{H}{\overset{|}{CH_2}}-\overset{OH}{\overset{|}{C}}=O\xrightarrow[600^\circ C]{AlPO_4}\underset{(ketene)}{CH_2=C=O}+H_2O$$



$$CH_2=C=O+H-O-\underset{O}{\underset{\|}{C}}-CH_3\longrightarrow CH_3-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-CH_3$$

3.2 Physical Properties :

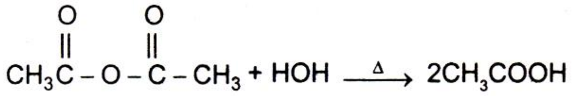
(i) It is colourless liquid having pungent vinegar like odour.

(ii) Boiling point is 138ºC.

(iii) Slowly soluble in cold water, but readily soluble in hot water

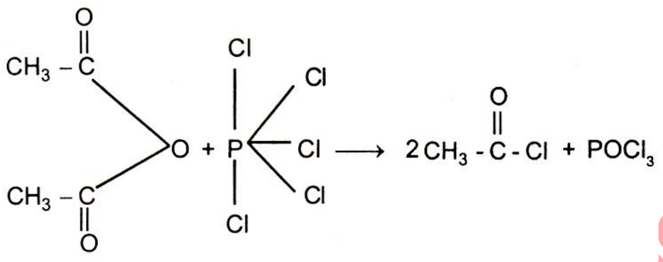
3.3 Chemical Properties :

Hydrolysis :

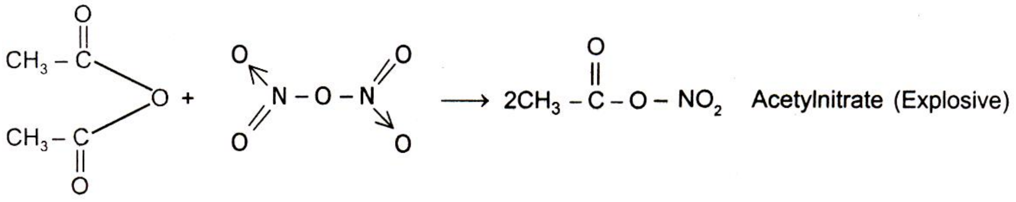


$$CH_3\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + HOH \xrightarrow{\Delta} 2CH_3COOH$$

With PCl_5 :

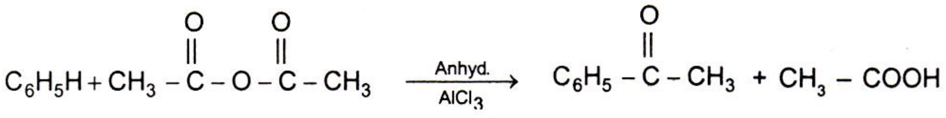


With N_2O_5 :



Acetylnitrate (Explosive)

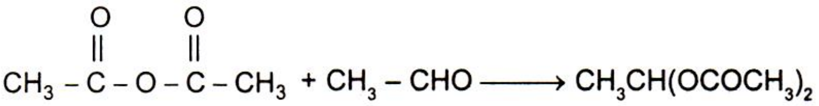
With Benzene [Friedel–Craft's Reaction] :



$$C_6H_5H + CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[AlCl_3]{Anhyd.} C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-COOH$$

Acetophenone

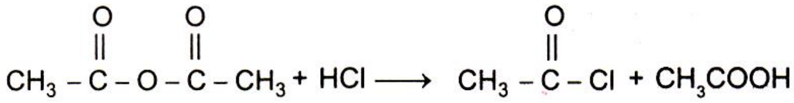
With Acetaldehyde :



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-CHO \longrightarrow CH_3CH(OCOCH_3)_2$$

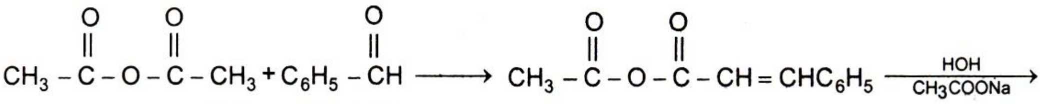
Ethylidene diacetate

With Dry HCl gas :



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + HCl \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3COOH$$

Perkin's Reaction :



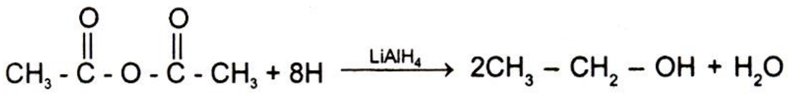
$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + C_6H_5-\overset{O}{\overset{\|}{C}H} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH=CHC_6H_5 \xrightarrow[CH_3COONa]{HOH}$$

(Benzaldehyde)

$$\rightarrow C_6H_5-CH=CH\text{-}COOH + CH_3COOH$$

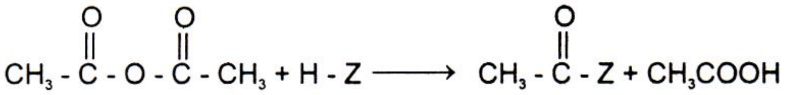
(Cinnamic acid)

Reduction :



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + 8H \xrightarrow{LiAlH_4} 2CH_3-CH_2-OH + H_2O$$

With Compounds having reactive H–atom :

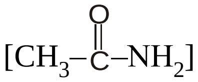


$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H-Z \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Z + CH_3COOH$$

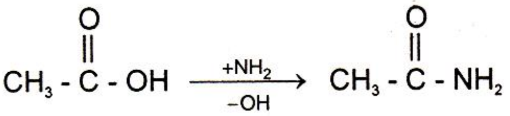
Acetylderivative

Note : Products are similar as in case of Acetyl chloride.

4. ACETAMIDE



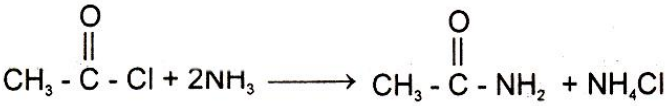
$$[CH_3-\overset{O}{\overset{\|}{C}}-NH_2]$$



$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-OH]{+NH_2} CH_3-\overset{O}{\overset{\|}{C}}-NH_2$$

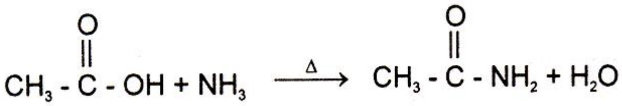
4.1 Method of Preparation :

From Acetychloride :



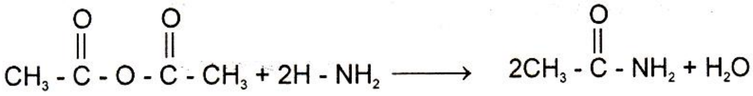
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + 2NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + NH_4Cl$$

From Acetic Acid :



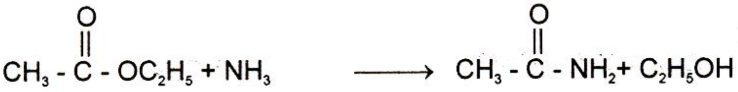
$$CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3 \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

From acetic Anhydride :



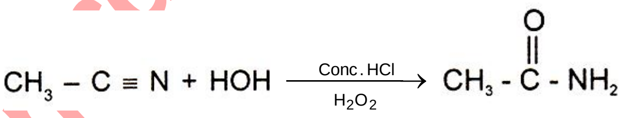
$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + 2H-NH_2 \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

From Ethyl Acetate :



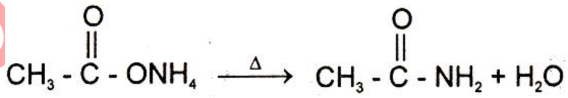
$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + C_2H_5OH$$

Partial hydrolysis of Acetonitrile :



$$CH_3-C\equiv N + HOH \xrightarrow[H_2O_2]{Conc.\,HCl} CH_3-\overset{O}{\overset{\|}{C}}-NH_2$$

By thermal decomposition of Ammonium acetate :



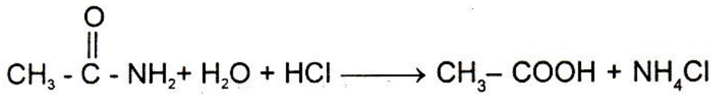
$$CH_3-\overset{O}{\overset{\|}{C}}-ONH_4 \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

4.2 Physical properties :

(i) It is a hygroscopic white crystalline solid.
(ii) It has faint smell in pure state, but a rat like smell in impure state.
(iii) It is soluble in water and alcohol, but sparingly soluble in ether.
(iv) Melting point 82ºC and boiling point is 222ºC.

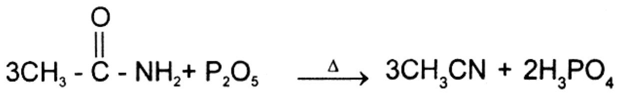
4.3 Chemical properties :

Hydrolysis :

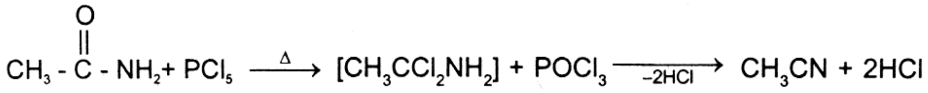


$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2+H_2O+HCl\longrightarrow CH_3-COOH+NH_4Cl$$

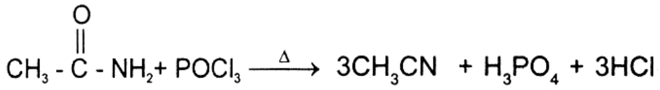
Dehydration :



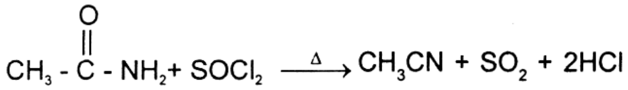
$$3CH_3-\overset{\overset{O}{\|}}{C}-NH_2+P_2O_5\xrightarrow{\Delta}3CH_3CN+2H_3PO_4$$



$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2+PCl_5\xrightarrow{\Delta}[CH_3CCl_2NH_2]+POCl_3\xrightarrow[-2HCl]{}CH_3CN+2HCl$$



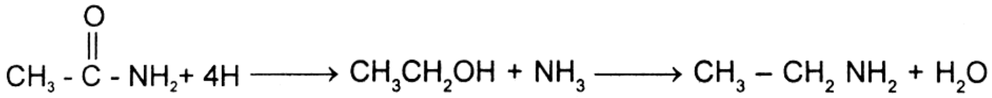
$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2+POCl_3\xrightarrow{\Delta}3CH_3CN+H_3PO_4+3HCl$$



$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2+SOCl_2\xrightarrow{\Delta}CH_3CN+SO_2+2HCl$$

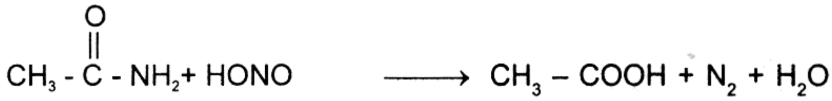
Reduction :

Reducing Agent : Metal Catalyst + H_2, Na + Ethanol, $LiAlH_4$ etc.



$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2+4H\longrightarrow CH_3CH_2OH+NH_3\longrightarrow CH_3-CH_2\,NH_2+H_2O$$

With Nitrous Acid :

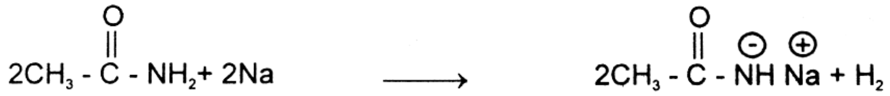


$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2+HONO\longrightarrow CH_3-COOH+N_2+H_2O$$

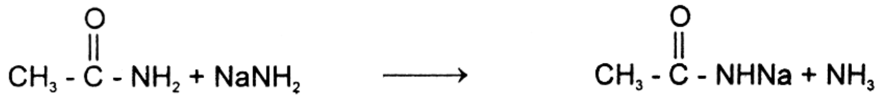
Amphoter character :

Acetamids forms salts on reacting with strong bases as well as strong acids. Therefore it behaves like a weak base as well as weak acid. i.e. it shows amphoteric character.

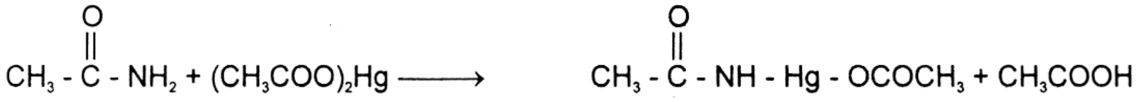
(i) **Weak acidic behaviour :**



$$2CH_3-\overset{\overset{O}{\|}}{C}-NH_2+2Na\longrightarrow 2CH_3-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{NH}\,\overset{\oplus}{Na}+H_2$$



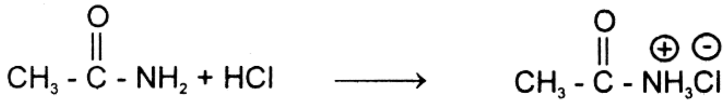
$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2+NaNH_2\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NHNa+NH_3$$



$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2+(CH_3COO)_2Hg\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH-Hg-OCOCH_3+CH_3COOH$$

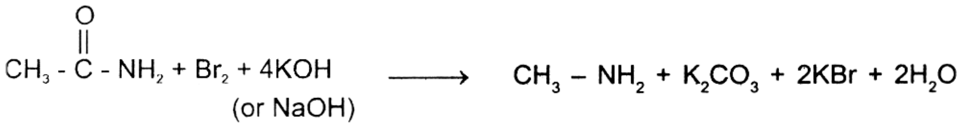
Acetamidomercuriacetate

(ii) **Weak basic behaviour :**



$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2+HCl\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\overset{\oplus}{NH_3}\overset{\ominus}{Cl}$$

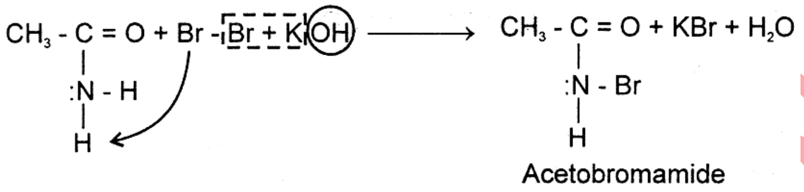
Hofmann Bromamide Reaction or Hypobromite Reaction :



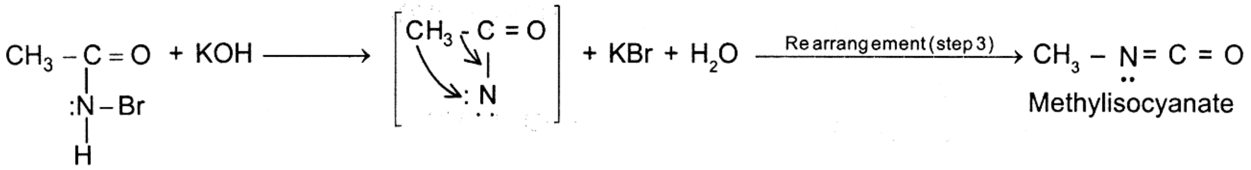
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4KOH \text{ (or NaOH)} \longrightarrow CH_3-NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

Slightly Mechanism :

Bromination :



Dehydrobromination :

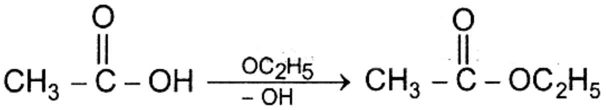


Hydrolysis :

$$CH_3-N=C=O + 2KOH \longrightarrow \underset{\text{Methylamine}}{CH_3-NH_2} + K_2CO_3$$

Note : In the reaction decrease of one carbon atom takes place. Therfore it can be used in decending down a homlogous series and it is also called Hofmann degradation.

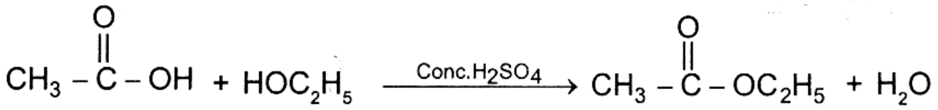
5. ETHYLACETATE AND ACETIC ESTER [$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5$]



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[-OH]{OC_2H_5} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5$$

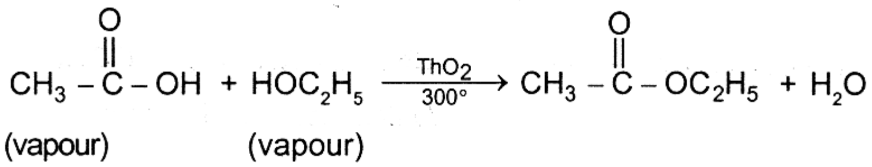
5.1 Methods of preparation :

By liquid phase Esterification :



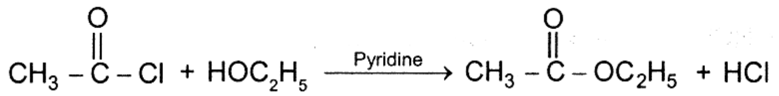
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HOC_2H_5 \xrightarrow{Conc.H_2SO_4} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + H_2O$$

By vapour phase Esterification :

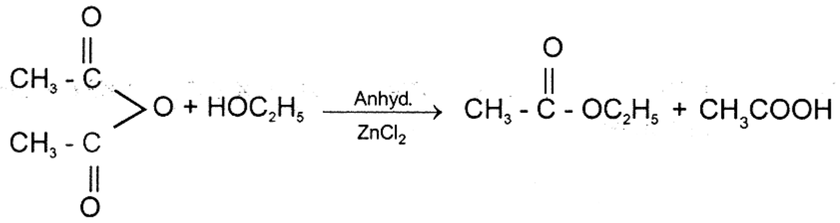


$$\underset{\text{(vapour)}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{(vapour)}}{HOC_2H_5} \xrightarrow[300^\circ]{ThO_2} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + H_2O$$

By Aceylation of Ethanol :

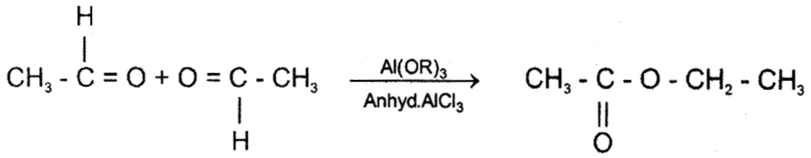


$$CH_3-\overset{\overset{O}{\parallel}}{C}-Cl + HOC_2H_5 \xrightarrow{\text{Pyridine}} CH_3-\overset{\overset{O}{\parallel}}{C}-OC_2H_5 + HCl$$



$$(CH_3-\overset{\overset{O}{\parallel}}{C})_2O + HOC_2H_5 \xrightarrow[\text{ZnCl}_2]{\text{Anhyd.}} CH_3-\overset{\overset{O}{\parallel}}{C}-OC_2H_5 + CH_3COOH$$

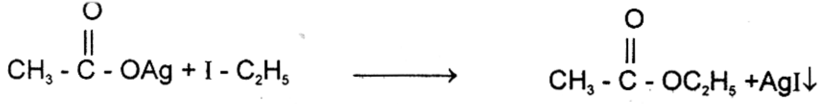
Tischenko Reaction :



$$CH_3-\overset{\overset{H}{|}}{C}=O + O=\underset{\underset{H}{|}}{C}-CH_3 \xrightarrow[\text{Anhyd.AlCl}_3]{\text{Al(OR)}_3} CH_3-\underset{\underset{O}{\parallel}}{C}-O-CH_2-CH_3$$

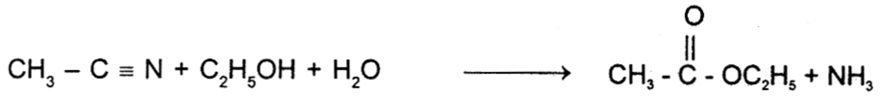
Ethyl acetate

Ethylation of Silver halides :



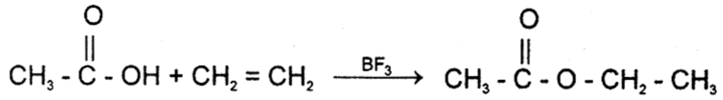
$$CH_3-\overset{\overset{O}{\parallel}}{C}-OAg + I-C_2H_5 \longrightarrow CH_3-\overset{\overset{O}{\parallel}}{C}-OC_2H_5 + AgI\downarrow$$

Ethanolysis of Ethanenitrile :



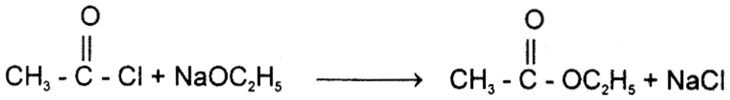
$$CH_3-C\equiv N + C_2H_5OH + H_2O \longrightarrow CH_3-\overset{\overset{O}{\parallel}}{C}-OC_2H_5 + NH_3$$

By addition of Acetic acid on Ethylene :



$$CH_3-\overset{\overset{O}{\parallel}}{C}-OH + CH_2=CH_2 \xrightarrow{BF_3} CH_3-\overset{\overset{O}{\parallel}}{C}-O-CH_2-CH_3$$

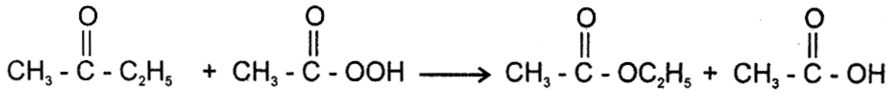
By reaction of sodium Ethoxide on Acetyl chloride :



$$CH_3-\overset{\overset{O}{\parallel}}{C}-Cl + NaOC_2H_5 \longrightarrow CH_3-\overset{\overset{O}{\parallel}}{C}-OC_2H_5 + NaCl$$

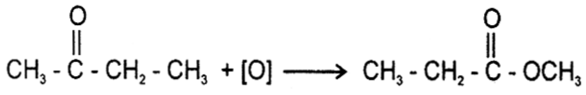
Baeyer–Villiger Oxidation :

Ethyl acetate is formed on reacting butanone with a peracid, Methyl propionate is also formed in small amounts.



$$CH_3-\overset{\overset{O}{\parallel}}{C}-C_2H_5 + CH_3-\overset{\overset{O}{\parallel}}{C}-OOH \longrightarrow CH_3-\overset{\overset{O}{\parallel}}{C}-OC_2H_5 + CH_3-\overset{\overset{O}{\parallel}}{C}-OH$$

Peracetic acid



$$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_3 + [O] \longrightarrow CH_3-CH_2-\overset{\overset{O}{\parallel}}{C}-OCH_3$$

Methyl propionate

5.2 Physical Properties :

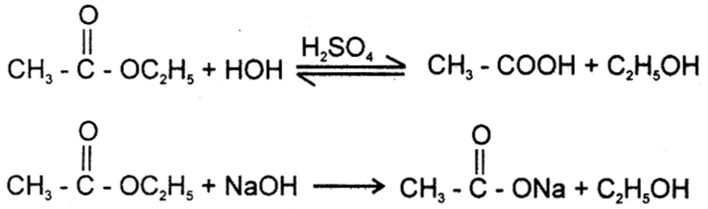
(i) Colourless, sweet smelling steamvolatile, inflammable liquid.

(ii) Very sparingly soluble in water, but soluble in organic solvents.

(iii) Boiling point 78°.

5.3 Chemical Properties :

Hydrolysis :

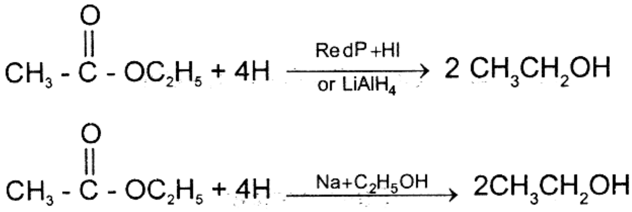


$$CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5 + HOH \xrightleftharpoons{H_2SO_4} CH_3-COOH + C_2H_5OH$$

$$CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5 + NaOH \longrightarrow CH_3-\overset{O}{\overset{||}{C}}-ONa + C_2H_5OH$$

Note : In esters caustic alkalies hydrolysis is rapid and complete. Alkaline hydrolysis of esters is called "Saponification".

Reduction :

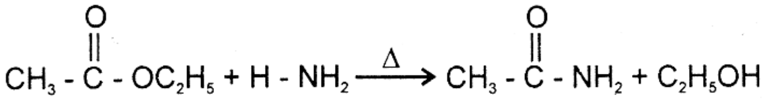


$$CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5 + 4H \xrightarrow[\text{or } LiAlH_4]{\text{Red P + HI}} 2\ CH_3CH_2OH$$

$$CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5 + 4H \xrightarrow{Na + C_2H_5OH} 2CH_3CH_2OH$$

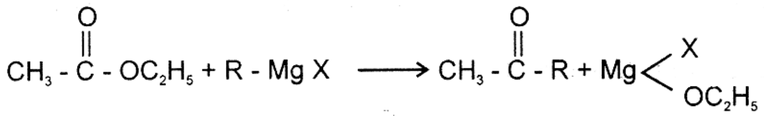
(Bouveault-Blanc reduction)

Ammonolysis :



$$CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5 + H-NH_2 \xrightarrow{\Delta} CH_3-\overset{O}{\overset{||}{C}}-NH_2 + C_2H_5OH$$

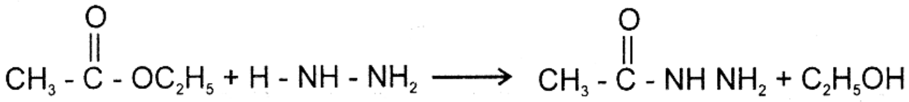
With Grignard's Reagent :



$$CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5 + R-Mg\,X \longrightarrow CH_3-\overset{O}{\overset{||}{C}}-R + Mg\begin{matrix} X \\ OC_2H_5 \end{matrix}$$

Note : The product will be tertiary alcohol when 2 mole of Grignard's reagent are taken.

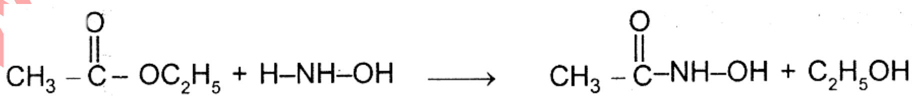
With Hydazine :



$$CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5 + H-NH-NH_2 \longrightarrow CH_3-\overset{O}{\overset{||}{C}}-NH\,NH_2 + C_2H_5OH$$

Acetyl hydrazine

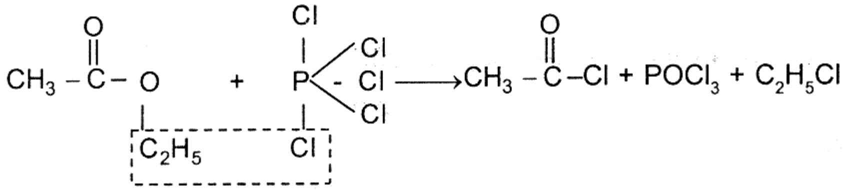
With Hydroxyl Amine :



$$CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5 + H-NH-OH \longrightarrow CH_3-\overset{O}{\overset{||}{C}}-NH-OH + C_2H_5OH$$

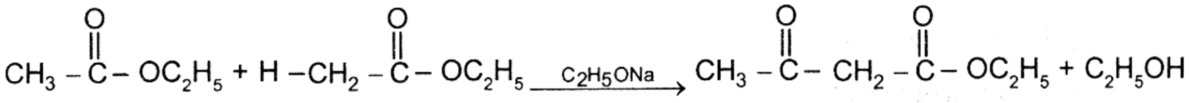
Acetyl hydraxomic acid

With PCl_5 :



$$CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 + PCl_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + C_2H_5Cl$$

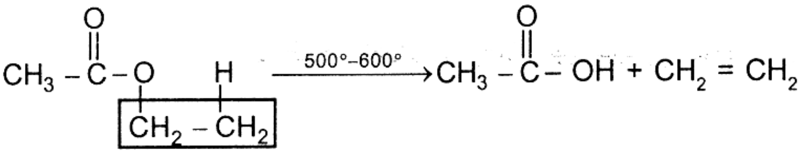
Claisen Ester Condensation :



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{C_2H_5ONa} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + C_2H_5OH$$

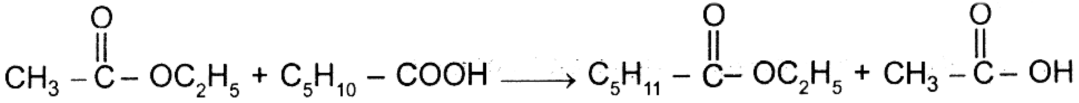
Acetoaceticester

Pyrolysis or Thermal decomposition :



$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-H \xrightarrow{500°-600°} CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_2=CH_2$$

Acidolysis :



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + C_5H_{10}-COOH \longrightarrow C_5H_{11}-\overset{O}{\overset{\|}{C}}-OC_2H_5 + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

BENZOIC ACID

BENZOIC ACID (C_6H_5COOH)

Benzoic aicd was first obtained by Schiele from gum benzoin. It is also present in Peru balsam and Tolu balsam in the form of its benzyl ester (benzyl benzoate).

$C_6H_5COOCH_2C_6H_5$ Benzyl Benzoate

In combined form it is found as benzoylglycine in horse urine.

$C_6H_5CONHCH_2COOH$ Benzoylglycine

1.1 PREPARATION

(1) Oxidation of Benzyl Alcohol :

Benzoic acid is formed on permanganate oxidation of benzyl alcohol.

$C_6H_5CH_2OH$ (Benzyl alcohol) + [O] $\longrightarrow$ C_6H_5CHO(Benzaldehyde) $\xrightarrow{[O]}$ C_6H_5COOH (Benzoic acid)

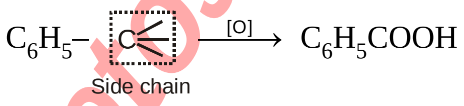
(2) Oxidation of Benzaldehyde :

Oxidation of benzaldehyde takes place very readily and benzoic acid is formed.

$$C_6H_5CHO \xrightarrow{[O]} C_6H_5COOH$$

(3) Oxidation of Aralkanes and Their Derivatives :

A side chain (alkyl group or substituent alkyl group) bonded directly to the benzene ring is converted to a carboxyl group on oxidation. Dilute nitric acid or chromic acid or alkaline permangante can be used as oxidant.



Benzoic acid is obtained on oxidation of many compounds like aralkanes (toluene, ethylbenzene, n–propylbenzene, cumene, etc.) and their oxygenated derivatives (benzyl alcohol, benzaldehyde, acetophenone, benzophenone, etc.) halogenated derivatives (benzyl chloride, benzal chloride, benzotrichloride etc) nitrogenated derivatives (cyanobenzene benzamide, etc.)

(4) Carboxylation of Grignard's Reagents :

Benzoic acid is formed on hydrolysis of the product obtained by passing carbon dioxide in ethereal solution of phenylmagnesium bromide.

$$C_6H_5MgBr \xrightarrow{CO_2} C_6H_5COOMgBr \xrightarrow{HOH} C_6H_5COOH$$

(5) Carboxylation of Benzene :

Benzoic acid is obtained on heating benzene and carbon dioxide in nitrobenzene medium in the presence of anhydrous aluminium chloride.

$$C_6H_5H + CO_2 \xrightarrow{AlCl_3} C_6H_5COOH$$

(6) Alkaline Hydrolysis of Benzotrichloride :

Benzoic acid is formed on hydrolysis of benzotrichloride by lime water in the presence of iron catalyst.

$$C_6H_5CCl_3\ (\text{Benzotrichloride})\ 3\ OH^- \xrightarrow[\text{Fe}]{Ca(OH)_2} C_6H_5COOH + H_2O + 3\ Cl^-$$

(7) Hydrolysis of Benzoyl Chloride :

Benzoic acid is obtained by hyrolysis of benzoyl chloride

$$C_6H_5COCl + HOH \longrightarrow C_6H_5COOH + HCl$$

Benzoyl chloride is prepared by Friedel–Crafts chlororformylation of benzene, Benzoic acid is obtained in 60% yield by the method.

$$C_6H_5H + \underset{\text{Phosgene}}{Cl–CO–Cl} \xrightarrow{AlCl_3} C_6H_5COCl + HCl$$

(8) Hydrolysis of Cyanobenzene :

Benzoic acid is formed on hydrolysis of cyanobenzene i.e., benzonitrile by dilute hydrochloric acid.

$$C_6H_5CN + 2HOH + HCl \longrightarrow C_6H_5COOH + NH_4Cl$$

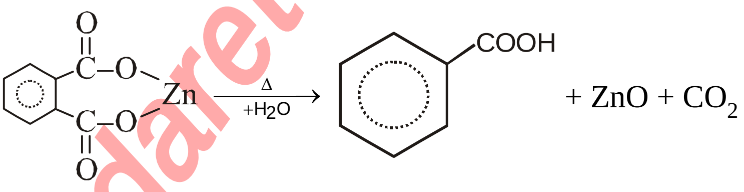
(9) Dehydroxylation of Hydroxybenzoic Acid :

Benzoic acid is formed on dry distillation of o–, m– or p–hydroxybenzoic acid with zinc dust. The ortho isomer is called salicylic acid.

$$HO–C_6H_4–COOH + Zn \longrightarrow \underset{\text{Benzoic acid}}{H–C_6H_4–COOH} + ZnO$$

(10) Decarboxylation of Phthalic Acid :

o–Benzendicarboxylic acid is called phthalic acid. On heating its zinc of nickel or chromium salt at 200–300º with water vapours, benzoic acid is formed by partial decarboxylation.



Zinc phthalate

(11) Hydrolysis of Benzoic Acid Derivatives :

Benzoic acid is formed on hydrolysis of esters, anhydride, acid chloride and amide of benzoic acid.

$$C_6H_5CO–Z + HOH \longrightarrow C_6H_5COOH + Z–H$$

Benzoyl chloride and benzoic anhydride very readily get hydrolysed by water, but with little bit more diffucilty as compared to aliphatic acid chlorides. Hydrolysis by alkali takes place faster.

$$C_6H_5COCl + H_2O \longrightarrow C_6H_5COOH + HCl$$

$$(C_6H_5CO)_2O + H_2O \longrightarrow 2C_6H_5COOH$$

Hydrolysis of benzoic esters takes place on heating with an alkali.

$$C_6H_5COOEt + NaOH \longrightarrow C_6H_5COONa + EtOH$$

Hydrolysis of benzamide takes place on boiling with dilute acid or alkali solution.

$$C_6H_5CONH_2 + H_2O + HCl \longrightarrow C_6H_5COOH + NH_4Cl$$

$$C_6H_5CONH_2 + NaOH \longrightarrow C_6H_5COONa + NH_3$$

Liberation of ammonia gas on heating the solution after adding sodium hydroxide solution is the test for amides.

1.2 PHYSICAL PROPERTIES

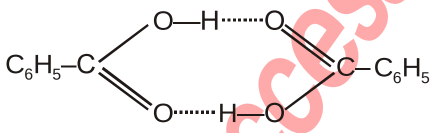
Benzoic acid is a crystalline solid (melting point 122º) which is sparingly soluble in cold water, but readily soluble in hot water. It is also soluble in organic solvents like alcohol ether, etc. Its acid strength is more than that of the alkanoic acids due to weak negative inductive effect of phenyl group.

1.3 RESONANCE IN BENZOIC ACID

The COOH group present in benzoic acid is a strong electron–attracting group due to which the benzene ring is deactivated and rate of S_E reaction decreases as compared to unsubstitued benzene. Therefore, the COOH group exerts a deactivating effect on the benzene ring.

Dimerisation in Benzoic Acid due to Hydrogen Bonding :

Benzoic acid in liquid phase (in benzene solution or in molten form) exists in the form of a dimer by association due to intermolecular hydrogen bonding in the same fashion as in alkanoic acids. This is the reason why the experimental value of the molecular weight of benzoic acid is twice the calculated value.



Hydrogen bonded dimer of benzoic acid

1.4 REACTIONS

Benzoic acid gives the following two types of reactions.

(A) Reactions due to COOH group

(B) Reactions due to C_6H_5 group

(A) Reaction Due to Carboxyl Group :

1. With Bases :

Many alkaline compounds form benzoate salts on reacting with benzoic aicd.

$$C_6H_5COOH + NaOH \longrightarrow C_6H_5COONa + H_2O$$

$$2C_6H_5COOH + Na_2CO_3 \longrightarrow 2C_6H_5COONa + H_2O + CO_2$$

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2$$

Phenol (a weak acid) does not react with sodium bicarbonate, whereas benzoic acid gives effervescence of CO_2, although both are acidic organic compounds toward litmus. Therefore, distinction between phenol and carboxylic acids can be done by using $NaHCO_3$.

$$2C_6H_5COOH + Ca(OH)_2 \longrightarrow (C_6H_5COO)_2Ca$$

$$C_6H_5COOH + NH_3 \longrightarrow C_6H_5COONH_4$$

$$C_6H_5COOH + NH_4OH \longrightarrow C_6H_5COONH_4 + H_2O$$

2. With Alcohols :

An alkyl benzoate is formed by esterification on heating a mixture benzoic acid and an alkanol in the presence of a few drops of concentrated H_2SO_4.

$$C_6H_5COOH + HOR \xrightarrow[\Delta]{H^+} C_6H_4COOR + H_2O$$

3. **With Inorganic Chloride :**

Benzoyl chloride is formed on the reaction of benzoic acid with phosphrous pentachloride or phsophrous trichloride or thionyl chloride.

$$C_6H_5COOH + PCl_5 \longrightarrow C_6H_5COCl + POCl_3 + HCl$$
$$3C_6H_5COOH + PCl_3 \longrightarrow C_6H_5COCl + H_3PO_4$$
$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl \text{ (Benzoyl chloride)} + SO_2 + HCl$$

4. **With P_2O_5 :**

Benzoic anhydride is formed on heating benzoic acid with P_2O_5.

$$2C_6H_5COOH \xrightarrow[\Delta]{P_2O_5} (C_6H_5CO)_2O + H_2O$$

Acetic anhydride also dehydrates two molecules of benzoic acid to give benzoic anhydride.

5. **With Ammonia :**

Benzamide is formed on heating benzoic acid with ammonia.

$$C_6H_5COOH + NH_3 \longrightarrow [C_6H_5COONH_4] \xrightarrow[-H_2O]{\Delta} C_6H_5CONH_2$$

Benzonitrile or cyanobenzne can be obtained by heating benzamide with P_2O_5.

$$C_6H_5CONH_2 \xrightarrow[\Delta]{P_2O_5} C_6H_5CN + H_2O$$

6. **With Soda Lime :**

Benzene is obtained on dry distillation of sodium salt of benzoic acid with sodalime.

$$C_6H_5COONa + NaOH \xrightarrow{\Delta} C_6H_6 + Na_2CO_3$$

7. **Dry Distillation of Calcium Salt :**

Benzophenone is obtained on dry distillation of calcium salt of benzoic acid.

$$(C_6H_5COO)_2Ca \xrightarrow{\Delta} C_6H_5COC_6H_5 + CaCO_3$$

8. **Hunsdiecker Reaction :**

Bromobenzene is formed on heating the silver salt of benzoic acid with bromine in carbon tetrachloride solution

$$C_6H_5COOAg + Br_2 \xrightarrow{CCl_4} C_6H_5Br + CO_2 + AgBr$$

9. **Reduction by Lithium Aluminium Hydride :**

Benzyl alcohol is formed on reduction of benzoic acid by lithium aluminium hydride ($LiAlH_4$).

$$C_6H_5COOH + 4H \xrightarrow{LiAlH_4} C_6H_5CH_2OH + H_2O$$

10. **Reduction by Sodium and Ethanol :**

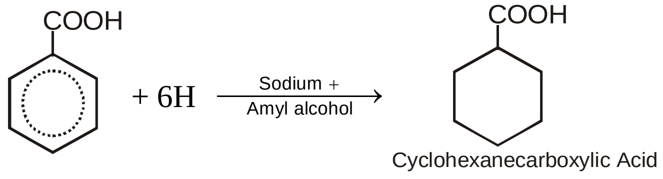
Toluene is formed on reduction of benzoic acid by sodium and ethanol.

$$C_6H_5COOH + 6H \xrightarrow[EtOH]{Na} C_6H_5CH_3 + 2H_2O$$

(B) Readuction Due to Aromatic Ring :

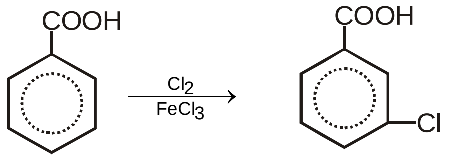
Hydrogenation by Sodium and Amyl Alcohol :

The COOH group is not affected on reduction of benzoic acid by sodium and amyl alcohol but benzene ring of benzoic acid is completely hydrogenated to form Cyclohexanecarboxylic acid.

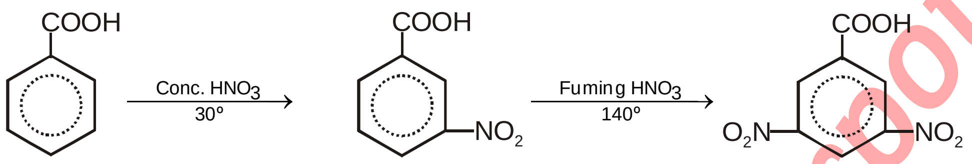


Aromatic Electrophilic Substitution Reaction :

Meta substitution products are formed on halogenation nitration and sulphonation of benzoic acid.

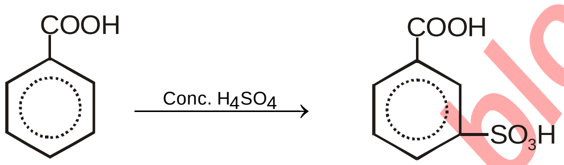


m-Chlorobenzoic acid



m-nitrobenzoic

3,5-Dinitrobenzoic acid



m-Sulphobenzoic acid

Note : Due to the presence of a deactivating m–directing COOH group in benzoic acid, the latter does not give Friedel–Crafts reaction.

1.5 TESTS

1. Formation of Ferric salt :

A red–brown precipitate is obtained on adding a small amount of neutral ferric chloride solution in benzoic acid solution.

2. Esterification :

A sweet odour of ethyl benzoate is perceived on heating benzoic acid after adding a few drops of ethyl alcohol and concentrated sulphuric acid.

3. Decarboxylation :

Inflammable vapours of benzene are liberated out on heating benzoic acid after mixing it thoroughly with soda lime.

1.6 USES

Benzoic acid is used as follows :

1. As a germicide.
2. Benzoic acid and its salts are used in the form of medicines.
3. Sodium benzoate is used as a preservative of canned food products.
4. Benzoic acid is used in the manufacture of many synthetic dyes, like aniline blue dye.
5. Ethyl ester of benzoic acid (ethyl benzoate) is used as a flavouring agent.

EXERCISE -I

Q.1 In the reaction sequence :

$$CH_3{-}C{\equiv}C{-}H \xrightarrow{CH_3MgBr} CH_4 + (A) \xrightarrow[(ii)\,H_2O/H^{\oplus}]{(i)\,CO_2} (B)$$

(B) will be:

(A) $CH_3{-}C{\equiv}C{-}CH_3$ (B) $CH_3{-}C{\equiv}C{-}MgBr$

(C) $CH_3{-}C{\equiv}C{-}COOH$ (D) $CH_3{-}CH{=}CH{-}COOH$

Q.2 Hydrolysis of 1,1, 1-trichloro derivative (A) of alkane gives a molecule (B) on alkaline hydrolysis which produces red coloration with aqueous $FeCl_3$. The compound (A) is -

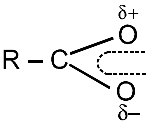
(A) $CH_3CH_2CCl_3$ (B) CH_3CCl_3 (C) $CHCl_3$ (D) None

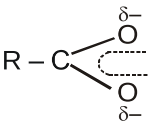
Q.3 In the given reaction :

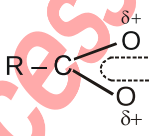
$$CH_3CHO \xrightarrow[(ii)\,H_2O/H^{\oplus}/\Delta]{(i)\,NaCN/HCl} (A) \xrightarrow[\text{reagent}]{\text{Fenton}} (B),\ \ (B) \text{ will be :}$$

(A) Acetic acid (B) Oxalic acid (C) Pyruvic acid (D) Citric acid

Q.4 Which of the following is the best representation of the structure of the carboxylate ion -

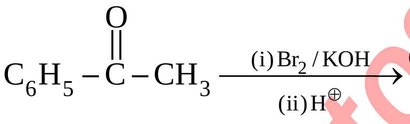
(A) 

(B) 

(C) 

(D) None of these

Q.5 In the given reaction :



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[(ii)\,H^{\oplus}]{(i)\,Br_2/KOH} CHBr_3 + [X],\ [X] \text{ will be:}$$

(A) $C_6H_5{-}CHO$ (B) C_6H_5COOH (C) $C_6H_5{-}CH_2OH$ (D) CH_3COOH

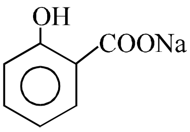
Q.6 Identify Z in the sequence

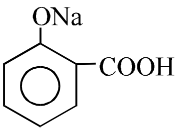
$$CH_3COONH_4 \xrightarrow[(ii)\,P_2O_5]{(i)\,heat} Y \xrightarrow{H_2O(H^+)} Z \text{ -}$$

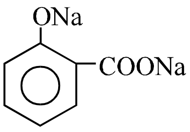
(A) $CH_3CH_2CONH_2$ (B) CH_3CN (C) CH_3COOH (D) $(CH_3CO)_2O$

Q.7 Sodium bicarbocate reacts with salicylic acid to form:

(A) C_6H_5ONa

(B) 

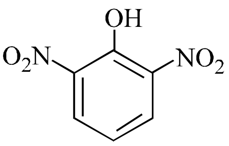
(C) 

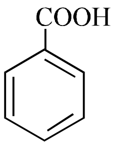
(D) 

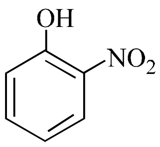
Q.8 Which one of the following reacts with Grignard reagent to form an addition product which can be hydrolysed to a carboxylic acid?

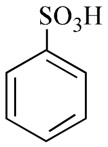
(A) O_2 (B) CO_2 (C) SO_2 (D) None

Q.9 Which of the following will not be soluble in sodium bicarbonate solution?

(A) 

(B) 

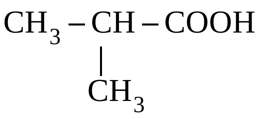
(C) 

(D) 

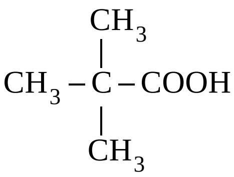
Q.10 Consider the given reaction :

$$RCOOAg \xrightarrow{Br_2/\Delta} R\text{–}Br$$

which one of the following acid will give maximum yield of R–Br in the above reaction?

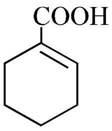
(A) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$

(B) $CH_3\text{–}CH_2\text{–}CH_2\text{–}COOH$

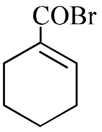
(C) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-COOH$

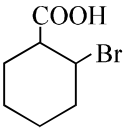
(D) All will give same yield

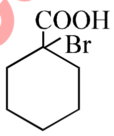
Q.11 In the given reaction:

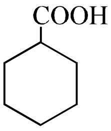


$\xrightarrow{HBr}$ [X], [X] will be:

(A) 

(B) 

(C) 

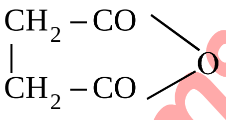
(D) 

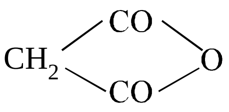
Q.12 In the given reaction :

$$CH_3\text{–}COOH \xrightarrow[\substack{(ii)\ NaCN \\ (iii)\ H_2O/H^{\oplus}/\Delta}]{(i)\ Br_2/red\ P} [X],\ [X] \text{ will be:}$$

(A) CH_3COOH

(B) $COOH\text{–}CH_2\text{–}CH_2\text{–}COOH$

(C) 

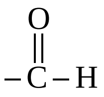
(D) 

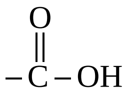
Q.13 Which of the following is a polyprotic acid -

(A) Acetic acid (B) Benzoic acid (C) Salicylic acid (D) Oxalic acid

Q.14 Reducing property of formic acid is due to the presence of :

(A) – OH

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

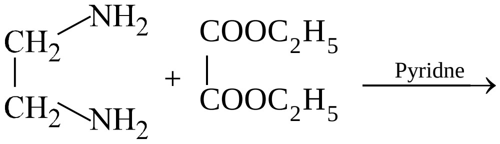
(C) 
$-\overset{\overset{O}{||}}{C}-OH$

(D) All of these

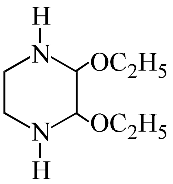
Q.15 The Hell-Volhard Zelinsky reaction is used for preparing a/an -

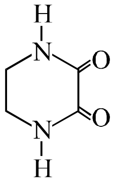
(A) β-Haloacid (B) γ-Haloacid (C) Acid halide (D) α-Haloacid

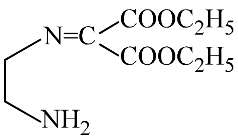
Q.16 In the given reaction:

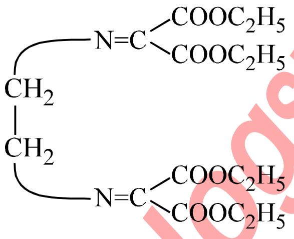


[X], [X] will be :

(A) 

(B) 

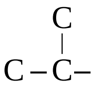
(C) 

(D) 

Q.17 Select the compound which does not give acetic acid on hydrolysis -

(A) CH_3CCl_3 (B) CH_3CN (C) CH_3COCl (D) CH_3CH_2Cl

Q.18 Which of the following skeleton gives the strongest acid if COOH is attached to the free valency -

(A) 

$C-\overset{\overset{C}{|}}{C}-$

(B) $C-C-C-$ (C) $H-$ (D) $C-C-$

Q.19 $A \xleftarrow[HI]{red\ P} CH_3COOH \xrightarrow{LiAlH_4} B$. What is not true for A and B -

(A) A is hydrocarbon of general formula C_nH_{2n+2} while B belongs to alkanol

(B) A can be obtained by reducing CH_3CH_2Cl while B by its hydrolysis

(C) A is alkene while B is alkanal

(D) A and B both belongs to different homologous series

Q.20 The product A, B, C and D in the reaction $A + B \xleftarrow{Heat} H-COOH \xrightarrow[H_2SO_4]{Heat} C + D$ are given by the set -

(A) CO, H_2O, CO_2, H_2 (B) CO_2, H_2O, CO, H_2

(C) CO_2, H_2, CO, H_2O (D) CO, H_2, CO_2, H_2O

Q.21 Ozonolysis of fatty acid is carried out to ascertain -

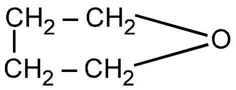
(A) Number of –OH group (B) Number of – COOH group

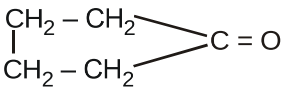
(C) Position of carbonyl group (D) Position of double bond

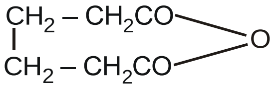
Q.22 Dry distillation of calcium acetate gives -

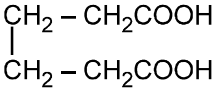
(A) Acetaldehyde (B) Acetone (C) Ethane (D) Propane

Q.23 Which of the following products is formed when adipic acid is heated -

(A) 

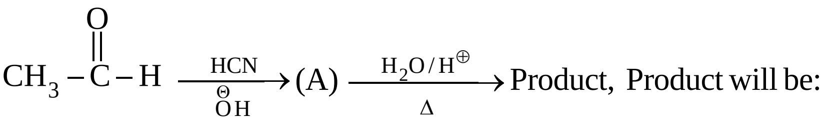
(B) 

(C) 

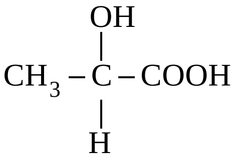
(D) 

$$\begin{matrix} CH_2 - CH_2COOH \\ | \\ CH_2 - CH_2COOH \end{matrix}$$

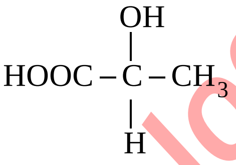
Q.24 In the reaction sequence :



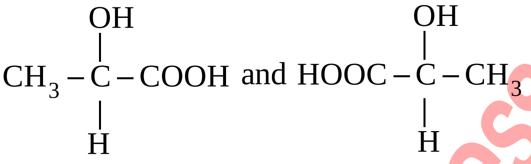
$$CH_3-\overset{\overset{\large O}{||}}{C}-H \xrightarrow[\overset{\ominus}{O}H]{HCN} (A) \xrightarrow[\Delta]{H_2O/H^{\oplus}} \text{Product, Product will be:}$$

(A) 

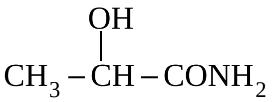
$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-COOH$$

(B) 

$$HOOC-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

(C) Mixture of 

$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-COOH \text{ and } HOOC-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

(D) 

$$CH_3-\overset{\overset{OH}{|}}{CH}-CONH_2$$

Q.25 Which of the following compounds gives carbondioxide with $NaHCO_3$?
(A) Acetic acid (B) Hexanol (C) Phenol (D) Acetylene

Q.26 When malonic acid is heated, it gives -
(A) Formic acid (B) Oxalic acid (C) Acetic anhydride (D) Acetic acid

Q.27 Amongst the acids,
(i) $CH \equiv CCOOH$ (ii) $CH_2 = CHCOOH$ and (iii) CH_3CH_2COOH,
the acid strength follows the sequence
(A) (i) < (ii) > (iii) (B) (i) > (ii) > (iii) (C) (i) = (ii) = (iii) (D) (i) = (ii) > (iii)

Q.28 Formic acid reacts with PCl_5 to form -
(A) Acetyl chloride (B) Methyl chloride
(C) Carbon monoxide and hydrogen chloride (D) formyl chloride

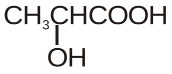
Q.29 Which one of the following reactions can be used for the preparation of β-hydroxy ester:
(A) Perkin reaction (B) Reformatsky reaction
(C) Aldol condensation (D) Claisen condensation

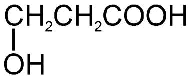
Q.30 Kolbe's electrolysis of aqueous potassium ethanoate leads to the formation of -
(A) Ethene (B) Methane (C) Ethane (D) Ethyne

EXERCISE -II

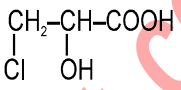
Q.1 End product of the following reaction is – **[AIEEE-2002]**

$$CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} \xrightarrow{\text{Alcoholic KOH}}$$

(A)  $CH_3CH(OH)COOH$

(B)  $CH_2(OH)CH_2COOH$

(C) $CH_2=CHCOOH$

(D)  $CH_2(Cl)-CH(OH)-COOH$

Q.2 In the anion HCOO— the two carbon-oxygen bonds are found to be of equal length. What is the reason for it ? **[AIEEE-2003]**
(A) The anion HCOO— has two resonating structures
(B) The anion is obtained by removal of a proton from the acid molecule
(C) Electronic orbitals of carbon atom are hybridised
(D) The C=O bond is weaker than the C—O bond

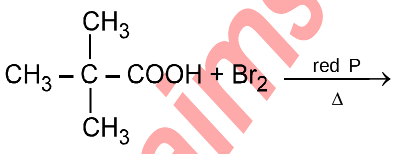
Q.3 Which one of the following does not have sp^2 hybridized carbon ? **[AIEEE-2004]**
(A) Acetone (B) Acetic acid (C) Acetonitrile (D) Acetamide

Q.4 Consider the acidity of the carboxylic acids : **[AIEEE-2004]**
(a) PhCOOH (b) o – $NO_2C_6H_4COOH$
(c) p – $NO_2C_6H_4COOH$ (d) m – $NO_2C_6H_4COOH$
Which of the following order is correct ?
(A) a > b > c > d (B) b > d > c > a (C) b > d > a > c (D) b > c > d > a

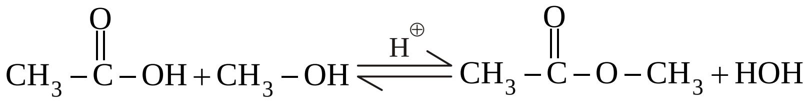
Q.5 The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is – **[AIEEE-2007]**
(A) benzophenone (B) acetophenone (C) benzoic acid (D) benzyl alcohol

Q.6 A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was : **[AIEEE-2009]**
(A) CH_3OH (B) HCHO (C) CH_3COCH_3 (D) CH_3COOH

Q.7 Acetic acid can be used for the preparation of :
(A) Ethane (B) Methane (C) Acetone (D) ethanol

Q.8  $CH_3-C(CH_3)_2-COOH + Br_2 \xrightarrow[\Delta]{\text{red P}}$ [Product] The product of the above reaction is -
(A) β-Dibromo acid (B) β,β' - Dibromo acid
(C) β,β',β''-Tribromo acid (D) No reaction takes place

Q.9 Consider the following reaction:

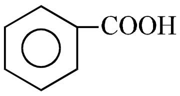
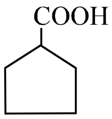
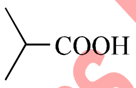
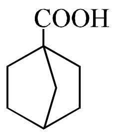


$$CH_3-\overset{\overset{O}{\|}}{C}-OH+CH_3-OH \overset{H^{\oplus}}{\rightleftharpoons} CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3+HOH$$

True about the above reaction is:
(A) Product is having smell like fruits
(B) Nucleophilic addition followed by elimination reaction
(C) follows $A_{AC'}$ mechanism
(D) it is irriversible reaction

Q.10 HVZ reaction is specific for -
(A) Replacement of β - hydrogen (B) Replacement of α - hydrogen
(C) Replacement of β - carbons (D) Replacement of α - carbons

Q.11 Which one of the following compounds will give HVZ reaction?

(A)  (B)  (C)  (D) 

Q.12 Acetic acid vapours when passed over aluminium phosphate forms -
(A) CH_3CHO (B) Ketene (C) C_2H_6 (D) C_2H_4

Q.13 Acetic anhydride is used as:
(A) Solvent (B) Dehydrating agent
(C) Acetylating agent (D) Antiseptic

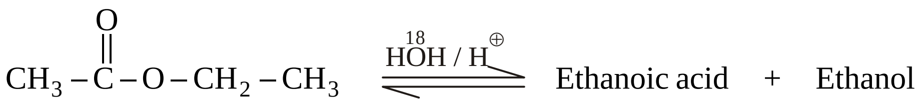
Q.14 Arrange the following compounds in decreasing order of acidity -
$ClCH_2CH_2CH_2COOH$ (I) $CH_3CHClCH_2COOH$ (II) $CH_3CH_2CHClCOOH$ (III)
(A) I > II > III (B) III > II > I (C) I > III > II (D) III > I > II

Q.15 Which compound will liberate CO_2 from $NaHCO_3$ solution:
(A) $CH_3CO\ NH_2$ (B) CH_3NH_2 (C) $(CH_3)_4N^+OH^-$ (D) $CH_3N^+H_3Cl^-$

Q.16 Arrange $OHCH_2COOH$ (I), $HOCH_2CH_2COOH$ (II) and CH_3COOH (III) in order of acidity -
(A) I > II > III (B) III > II > I (C) I > III > II (D) II > III > I

Q.17 Hofmann Bromamide degradation is given by:
(A) Imide (B) Acid chloride (C) Acid anhydride (D) Amide

Q.18 The rate of esterfication of HCOOH (I), CH_3COOH (II), $(CH_3)_2CHCOOH$ (III) and $(CH_3)_3CCOOH$ (IV) with ethanol follows in the order -
(A) IV > III > II > I (B) I > II > III > IV (C) II > I > IV > III (D) III > IV > I > II

Q.19 

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3 \xrightleftharpoons{H\overset{18}{O}H\,/\,H^{\oplus}} \text{Ethanoic acid} + \text{Ethanol}$$

Isotopic oxygen of water will be present with

(A) Ethanoic acid

(B) Ethanol

(C) After some time it will also be present in some molecules of ester

(D) None of these

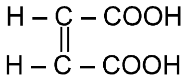
Q.20 In the electrolysis of the aqueous solution of CH_3CH_2COONa, anion goes to anode the possibility of formation of following compounds takes place -

(A) $CH_3-CH_2-CH_2-CH_3$ (B) $CH_2=CH_2$, CH_3-CH_3

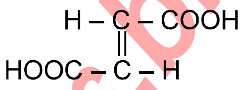
(C) $CH_3CH_2COOC_2H_5$ (D) All the above

Q.21 Which of the following organic acid decolourises bromine water as well as forms anhydride -

(A) HOOC – COOH (B) HOOC – CH_2 – COOH

(C) 

$$\begin{matrix} H-C-COOH \\ \| \\ H-C-COOH \end{matrix}$$

(D) 

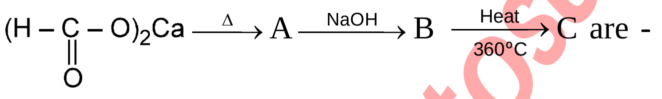
$$\begin{matrix} H-C-COOH \\ \| \\ HOOC-C-H \end{matrix}$$

Q.22 The general formula of dicarboxylic acid is -

(A) $(COOH)_2$ (B) $(CH_2)_n(COOH)_2$

(C) $(CH_2)_{n-2}\ (COOH)_2$ (D) $(CH_2)_{n-1}\ (COOH)_2$

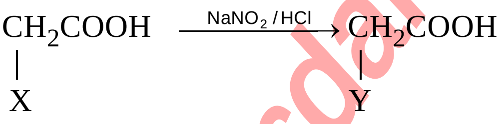
Q.23 The product A, B and C in the reaction sequence



$$(H-\underset{\underset{\displaystyle O}{\|}}{C}-O)_2Ca \xrightarrow{\Delta} A \xrightarrow{NaOH} B \xrightarrow[360°C]{Heat} C \text{ are -}$$

(A) HCHO, HCOONa, CH_3OH (B) HCHO, Na_2CO_3, $NaHCO_3$

(C) HCHO, HCOONa, $(COONa)_2$ (D) HCHO, HCOONa, Na_2CO_3

Q.24 

$$\underset{\underset{\displaystyle X}{|}}{CH_2COOH} \xrightarrow{NaNO_2\,/\,HCl} \underset{\underset{\displaystyle Y}{|}}{CH_2COOH}$$

glycine glycollic acid

Here X and Y respectively are -

(A) OH, NH_2 (B) NH_2, OH (C) Cl, OH (D) None

Q.25 The carboxylic acid that does not undergo HVZ reaction is -

(A) CH_3COOH (B) $(CH_3)_2CHCOOH$

(C) $CH_3CH_2CH_2CH_2COOH$ (D) $(CH_3)_3C\ COOH$

Q.26 The end product 'C' in the following sequence of chemical reactions is

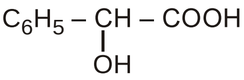
$CH_3COOH \xrightarrow{CaCO_3} A \xrightarrow{heat} B \xrightarrow{NH_2OH} C$ -

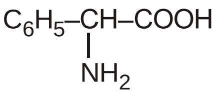
(A) Acetaldehyde oxime (B) Formaldehyde oxime

(C) Methyl nitrate (D) Acetoxime

Q.27 Which of the following carboxylic acids undergoes decarboxylation easily?

(A) $C_6H_5–CO–CH_2–COOH$ (B) $C_6H_5–CO–COOH$

(C) 
$C_6H_5-\underset{OH}{CH}-COOH$

(D) 
$C_6H_5–\underset{NH_2}{CH}–COOH$

Q.28 $CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} a \xrightarrow{\text{Alc.KOH}} b$

The compound b is -

(A) CH_3CH_2OH (B) CH_3CH_2COCl (C) $CH_2=CHCOOH$ (D) $CH_3–CHCl–COOH$

Q.29 A compound undergoes the following sequence of reactions :

$$C_3H_5N \xrightarrow{\text{Hydrolysis}} \underset{(a)}{C_3H_6O_2} \xrightarrow{Cl_2/P} \underset{(b)}{C_3H_5O_2Cl} \xrightarrow{NH_3} \underset{(c)}{C_3H_7NO_2}$$

The compound C is -

(A) 1-Nitropropane (B) 2-Nitropropane

(C) 2-Aminopropanoic acid (D) 2-Hydroxypropanamide

Q.30 $R – CH_2 – CH_2OH$ can be converted into RCH_2CH_2COOH. The correct sequence of reagent is

(A) PBr_3, KCN, H^+ (B) PBr_3, KCN, H_2

(C) KCN, H^+ (D) HCN, PBr_3, H^+

ANSWER KEY

EXERCISE -I

Q.1	C	Q.2	B	Q.3	C	Q.4	B	Q.5	B	Q.6	C	Q.7	B
Q.8	B	Q.9	C	Q.10	B	Q.11	B	Q.12	A	Q.13	D	Q.14	B
Q.15	D	Q.16	B	Q.17	D	Q.18	C	Q.19	C	Q.20	C	Q.21	D
Q.22	B	Q.23	B	Q.24	C	Q.25	A	Q.26	D	Q.27	B	Q.28	C
Q.29	B	Q.30	C										

EXERCISE -II

Q.1	C	Q.2	A	Q.3	C	Q.4	B	Q.5	C	Q.6	D		
Q.7	ABCD	Q.8	D	Q.9	AB	Q.10	B	Q.11	BC	Q.12	B		
Q.13	ABC	Q.14	B	Q.15	D	Q.16	A	Q.17	AD	Q.18	B	Q.19	AC
Q.20	D	Q.21	C	Q.22	B	Q.23	C	Q.24	B	Q.25	D	Q.26	D
Q.27	A	Q.28	C	Q.29	C	Q.30	A						

NITROGEN COMPOUNDS

1. GENERAL CHARACTERISTICS

(a) If a hydrogen atom of NH_3 is replaced by an alkyl group then it is called primary amine and possess $–NH_2$(amino) group.

(b) Amines are called alkyl derivative of NH_3.

(c) Aliphatic amine was discovered by **'Wurtz'.**

(d) If two hydrogen atoms of NH_3 are replaced then it is called secondary amine and it posses > NH (Imino) group.

(e) If all hydrogen atoms of NH_3 are replaced then it is called tert. amine and has a nitrilo N group.

(f) N is in sp^3 hybridisation and tetrahedral geometry.

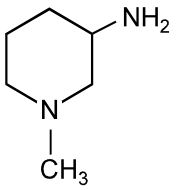
(g) Bond angle increases from ammonia to 3° amines.

NH_3 (107°) < RNH_2 < R_2NH < R_3N

(h) Aliphatic and aromatic amine shows chain, position, functional and metamerism.

GENERAL CHARACTERISTICS :

Ex.1 Compound is a -



(A) 1° and 3° amine (B) Only primary amine
(C) 2° and 3° amine (D) Only secondary amine **(Ans.A)**

Sol. 3–Amino–N–methylpiperidine contains primary and tertiary amino groups.

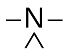
Ex.2 The third member of homologous series of dimethyl amine -
(A) $CH_3–CH_2–NH–CH_2–CH_3$ (B) $CH_3–NH–CH_2–CH_2–CH_{3–}$
(C) $CH_3–NH–CH(CH_3)_2$ (D) 2^{nd} and 3^{rd} are correct **(Ans.D)**

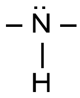
Sol. Compounds 2^{nd} and 3^{rd} contains $CH_3–NH–$ group.

Ex.3 Tertiary butyl amine is a-
(A) 1° Amine (B) 2° Amine
(C) 3° Amine (D) Quaternary salt **(Ans.A)**

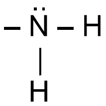
Sol. $(CH_3)_3C–NH_2$ is primary amine

Ex.4 N–atom in quaternary ammonium halide will have the form-

(A) 
$-\overset{\oplus}{N}-$

(B) 
$-\ddot{N}-$ with H below

(C) 
$\ddot{N}\lessdot$

(D) 
$-\ddot{N}-H$ with H below **(Ans.A)**

Sol. Quaternary ammonium halide is an ionic compound. Hence N carries positive charge.

Ex.5 $-CONH_2 \xrightarrow{\text{Reduction}} -CH_2NH_2$

In above reaction hybridisation state of carbon changes from ..... → ....

(A) $sp \longrightarrow sp^2$ (B) $sp \longrightarrow sp^3$

(C) $sp^2 \longrightarrow sp^3$ (D) $sp^2 \longrightarrow sp$ **(Ans.C)**

Sol. Hybridisation state of carbon changes from sp^2 to sp^3.

2. METHODS OF PREPARATION

2.1 From Alkylchloride :

$$R-Cl + H-NH_2 \xrightarrow[200°C]{Cu_2O} R-NH_2 + HCl$$

Note : In the above reaction Cu_2O neutralises the evolved HCl in form of $Cu_2Cl_2 + H_2O$ otherwise HCl forms additional salt with amines.

2.2 From Grignard reagent :

$$R-Mg-Cl + Cl-NH_2 \longrightarrow R-NH_2 + MgCl_2$$

2.3 From Alcohol :

$$R-OH + H-NH_2 \xrightarrow[-H_2O]{300°C} R-NH_2 + H_2O$$

2.4 By Aldehyde or Ketone (reaction with H_2 and NH_3 in presence of catalyst) :

Primary amine can be produced by passing a mixture of aldehyde or ketone and large excess of ammonia and hydrogen under pressure (20-150 atm) over raney nickel catalyst at 40-150ºC.

$$R_1R_2C=O + NH_3 \xrightarrow{Ni} R_1R_2CHNH_2$$

Note: Small amount of secondary and tertiary amines are also produced in this method as by products.

2.5 By reaction of Aldehyde or Ketones (with ammonium formate or with formamide and subsequent hydrolysis of product)

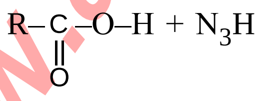
Aldehyde and ketones when react with ammonium formate or formamide or the formyl derivative of primary amine on hydrolysis yields primary amine and formate ions.

$$\rangle C=O + \underset{\text{(ammonium formate)}}{2HCO_2NH_4} \longrightarrow \rangle CH-NHCHO + 2H_2O + NH_3 + CO_2$$

$$\rangle C=O + 2HCONH_2 \longrightarrow \rangle CH-NH-CHO + CO_2 + NH_3$$

$$\rangle CH-NH-CHO \xrightarrow[\text{in alkaline medium}]{2H_2O} \rangle CH-NH_2 + HCOO^{\ominus}$$

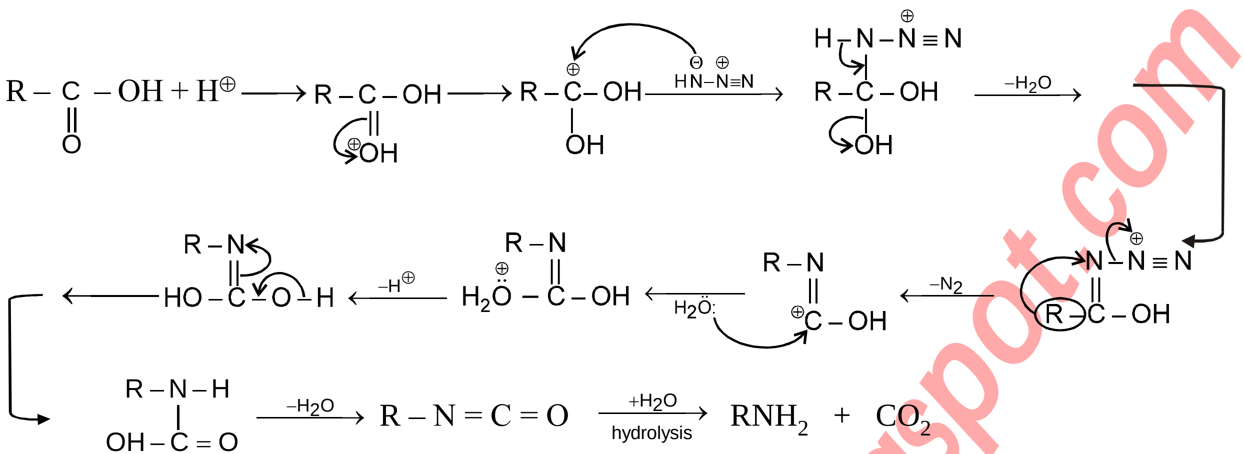
2.6 From Alkanoic acid (Schimdt Reaction) :



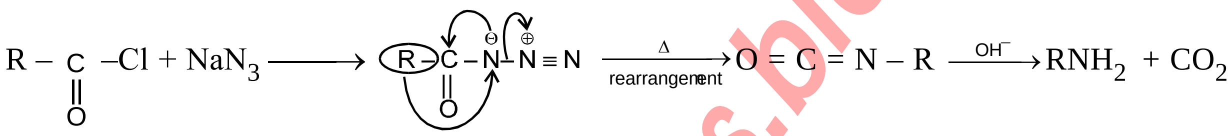
$$R-\underset{\underset{O}{\|}}{C}-O-H + N_3H \xrightarrow{conc.\ H_2SO_4} RNH_2 + N_2 + CO_2$$

Note : Alkyl isocyanate can also be produced by heating the mixture of acyl halide and sodium azide, alkylisocyanate, once it is formed, can easily be hydrolysed into primary amine and CO_2.

Mechanism : –

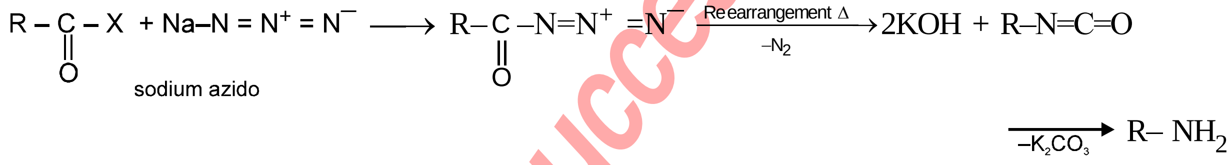


alkyl isocyanate



$$R-\underset{\underset{O}{\|}}{C}-Cl + NaN_3 \longrightarrow R-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{N}-\overset{\oplus}{N}\equiv N \xrightarrow[\text{rearrangement}]{\Delta} O=C=N-R \xrightarrow{OH^-} RNH_2 + CO_2$$

2.7 From Acyl halide :

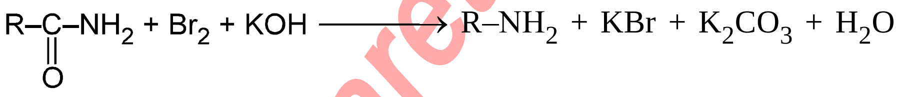


$$R-\underset{\underset{O}{\|}}{C}-X + Na-N=N^+=N^- \longrightarrow R-\underset{\underset{O}{\|}}{C}-N=N^+=N^- \xrightarrow[-N_2]{\text{Rearrangement }\Delta} 2KOH + R-N=C=O \xrightarrow{-K_2CO_3} R-NH_2$$

sodium azido

Note : It is a good method for preparation of alkyl amine. Reaction is called '**Curtius Reaction**'.

2.8 From Alkanamide :



$$R-\underset{\underset{O}{\|}}{C}-NH_2 + Br_2 + KOH \longrightarrow R-NH_2 + KBr + K_2CO_3 + H_2O$$

Note : The reaction is called '**Hoffmann Bromamide reaction**' discussed earlier.

2.9 By Alkyl cyanide (By reduction) :

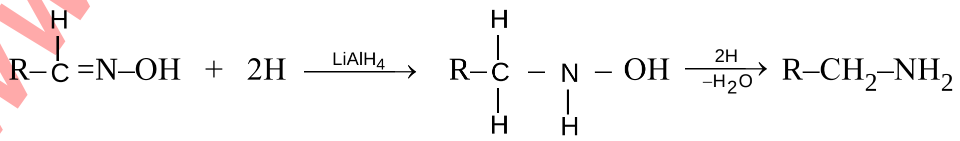
$$R-C\equiv N + 4H \xrightarrow[\text{Na+Et OH}]{LiAlH_4} R-CH_2-NH_2$$

Note : When (Na + Et.OH) is used as reducing agent then reaction is called '**Mandius Reaction**'.

2.10 From Alkyl isocyanate (Alkaline Hydrolysis) :

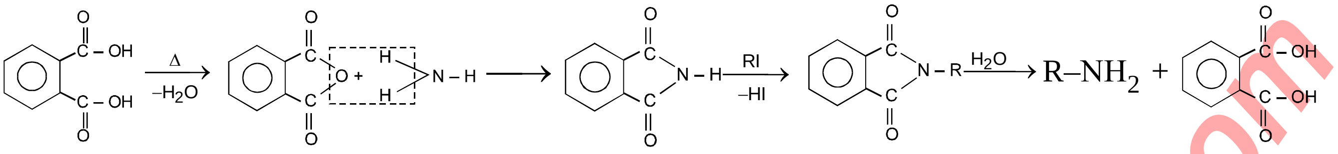
$$R-N=C=O + 2KOH \longrightarrow R-NH_2 + K_2CO_3$$

2.11 From Aldoxime (By Reduction) :



$$R-\overset{H}{\overset{|}{C}}=N-OH + 2H \xrightarrow{LiAlH_4} R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{N}-OH \xrightarrow[-H_2O]{2H} R-CH_2-NH_2$$

2.12 From Phthalic acid :



phthalic anhydride phthalimide N–alkyl phthalimide

Note : It is the best method for preparation of aliphatic amines. The reaction is called '**Gabriel-Phthalimide reaction**'.

2.13 By reduction of Nitro compounds :

Nitro alkanes are reduced catalytically to primary amine.

(a) By $LiAlH_4$

(b) By Metal and acid (commonly used Sn + HCl or Fe + HCl)

$$RNO_2 \xrightarrow[4H]{\text{reduction}} RNH_2 + 2H_2O$$

Note : (i) When reduction with metal is carried out in neutral solution e.g. with Zn dust & NH_4Cl solution, nitro compounds are converted into N-alkyl hydroxyl amine.

$$RNO_2 \xrightarrow[NH_4Cl]{Zn^+} \underset{\text{N-alkylhydroxyl amine}}{RNHOH} + 2H_2O$$

(ii) When reduction of nitroalkane is carried out with $SnCl_2$ and conc. HCl, a mixture of N-alkyl hydroxyl amine and oxime are produced.

$$RCH_2NO_2 \xrightarrow[\text{conc. HCl}]{SnCl_2+} \underset{\text{N-Alkyl hydroxy amine}}{RCH_2NHOH} + \underset{\text{Oxime}}{RCH = NOH}$$

3. PHYSICAL PROPERTIES

(a) Like ammonia, amines are polar compounds and except 3° amines can form intermoleculer H-bonds that's why they have higher boiling points.

(b) Unlike other organic compounds, amines are much more soluble in water. Because All amines form a stronger H- bond with water.

(c) Solubility in water follow the order.

$1^o > 2^o > 3^o$ amine.

This is all due to H- Bonding.

(d) Boiling points of amines are lesser than alcohols and acids of comparable mol. weight. Because H- bonding in amines is less pronounced in 1° and 2° than that in alcohols and carboxylic acids. Because nitrogen is less electronegative than oxygen.

Thus every question regarding boiling point can be answered on the basis of H - bonding.

(e) Boiling points of 1°, 2° and 3° amines follow the order.

$1^o > 2^o > 3^o$ amine.

4. CHEMICAL PROPERTIES

(a) Almost all chemical properties and reactions of amines are governed by basicity of amines.

(b) A lone pair of electron on nitrogen atom in each of amines and ammonia makes them basic in nature.

(c) Alkyl groups are electron releasing group which increases electron density on nitrogen atom thus, we can expect the order of basicity of ammonia

1° , 2° and 3° amines to be

3° > 2° > 1° > ammonia

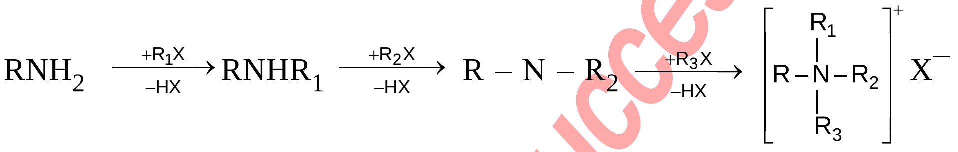
(d) Some other factors like steric effect, Solvation or hydration and mainly crowding on nitrogen atom by three bulky alkyl groups, decreases the basicity of 3° amines to a great extent and order follows -

$$\underset{(2^\circ)}{R_2NH} > \underset{(1^\circ)}{RNH_2} > \underset{(3^\circ)}{R_3N} > \underset{(\text{ammonia})}{NH_3}$$

(e) This can be also explained on basis of lesser capacity of 3° amine to form H- bonds with water which stabilizes R_2N^+H on because it has only one H-atom

5. CHEMICAL REACTIONS

5.1 Alkylation :



$$RNH_2 \xrightarrow[-HX]{+R_1X} RNHR_1 \xrightarrow[-HX]{+R_2X} R-N-R_2 \xrightarrow[-HX]{+R_3X} \left[R-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{N}}-R_2 \right]^+ X^-$$

(quartenary amm. salts.)

5.2 Reaction with Grignard reagent :

Since primary and secondary amines have active hydrogen, they on reaction with Grignard reagent give alkanes

$$RNH_2 + CH_3MgBr \xrightarrow{\text{ether}} CH_4 + RNH.MgBr$$

$$R_2NH + CH_3MgBr \xrightarrow{\text{ether}} CH_4 + R_2N.Mg\ Br$$

Note : Tertiary do not react because of absence of active hydrogen.

5.3 Reaction with Aldehydes and Ketone:

$$RNH_2 + CH_3CHO \longrightarrow RN = CHCH_3 + H_2O$$

(schiff's base or anil's base)

5.4 Acylation :

1° and 2° amines react with acetyl chloride or acetic anhydride to form acetyl derivatives.

$$R–NH_2 + CH_3COCl \longrightarrow RNHCOCH_3 + HCl$$

$$R–NH_2 + (CH_3CO)_2O \longrightarrow RNHCOCH_3 + CH_3COOH$$

$$(CH_3)_2NH + CH_3COCl \longrightarrow (CH_3)_2N – COCH_3 + HCl$$

Note : (a) Tertiary amines donot undergo this reaction because of absence of replacable H- atom.

(b) When Benzoyl chloride is used in place of acetyl chloride reaction is called '**Schotten - Baumann**' reaction.

5.5 **Oxidation :** All three are oxidised in different ways depending upon conditions of oxidation.

(a) **Primary Amine :** Oxidised to aldehydes and ketones.

$$RCH_2NH_2 \xrightarrow[KMnO_4]{[O]} R\text{-}CH=NH \xrightarrow{H_2O} R\text{-}CHO + NH_3$$

aldimine aldehyde

$$R_2CHNH_2 \xrightarrow[KMnO_4]{[O]} R_2C=NH \xrightarrow{H_2O} R_2C=O + NH_3$$

ketimine ketone

(b) **Secondary Amine :**

$$2R_2NH \xrightarrow[KMnO_4]{[O]} R_2N\text{-}NR_2$$

(tetra-alkyl hydrazine)

$$R_2NH \xrightarrow{\text{caro's acid}} R_2N\text{-}OH$$

(dialkyl hydroxylamine)

(c) **Tertiary Amine :** Resistant to $KMnO_4$ but oxidised by neutral and aqueous H_2O_2 in cold to form trialkyl amine oxide.

Note: **(i)** $NH_2\text{-}NH_2$ is called hydrazine

(ii) $NH_2\text{-}OH$ is called Hydroxylamine

5.6 **Salt formation:** Amine forms salt with mineral acids

$$RNH_2 \xrightarrow{+HCl} [RNH_3]^+ Cl^-$$

$$R_2NH + HCl \longrightarrow [R_2NH_2]^+ Cl^-$$

$$R_3N + HCl \longrightarrow [R_3NH]^+ Cl^-$$

These salts may undergo dealkylation at higher temp.

For example : $C_2H_5NH_3^+Cl^- \xrightarrow[\Delta]{} C_2H_5Cl + NH_3$

5.7 **Reaction with HNO$_2$:** This reaction distinguishes 1°, 2° and 3° alcohols.

(a) **Primary Amine :** Except methyl amine, reaction happens at ordinary temp. to evolve N_2 Gas.

$$CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2 + H_2O$$

Methylamine reacts in different way:

$$CH_3NH_2 + 2HNO_2 \longrightarrow CH_3\text{-}O\text{-}N=O + N_2 + H_2O$$

methyl nitrite

$$2CH_3NH_2 + 2HNO_2 \longrightarrow CH_3\text{-}O\text{-}CH_3 + 2N_2 + 3H_2O$$

dimethyl ether

(b) **Secondary Amine :** Form nitroso amines with HNO_2 (No N_2 gas is evolved)

$$R_2NH + HNO_2 \longrightarrow R_2-N-N=O + H_2O$$

(yellow)

Note : These nitroso amines formed, on warming with phenol and conc. H_2SO_4 give a brown or red colour changing to blue or green on further addition of an alkali, colour changes to red . This test is called **Libermann's nitroso test** and used for identification of 2° amines.

(c) **Tertiary Amine :** These are inert to HNO_2 but being basic in nature forms salts with it.

$$(CH_3)_3N + HNO_2 \longrightarrow (CH_3)_3\ N\text{ - }HONO$$

5.8 Reaction with water : Amine gives alkyl ammonium hydroxides which dissociate into ions-

$$RNH_2 + H_2O \rightleftharpoons RNH_3OH \rightleftharpoons RNH_3^+ + OH^-$$

5.9 Isocyanide test or Carbylamine reaction :

Primary amines when heated with chloroform and ethanolic KOH solution, alkyl isocyanides is produced which have characteristic foul smell. This reaction is characteristic to the primary amine. This test is known as **carbyl amine test or isocyanide test**.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$$

The reaction proceeds via the formtion of dichloro carbene ($:CCl_2$). In the absence of any lewis base catalyst when $HCCl_3$ reacts only with base, $:CCl_2$ also produced, which is rapidly hydrolysed into CO, HCO_2^- and Cl^-.

$$CHCl_3 + OH^{\ominus} \longrightarrow \underset{\text{(dichloro carbene)}}{:CCl_2} + H_2O + Cl^{\ominus}$$

$$RNH_2 + :CCl_2 \longrightarrow \underset{\text{(alkyl isocyanide)}}{R - \overset{\oplus}{N} \equiv \overset{\ominus}{C}} + 2HCl$$

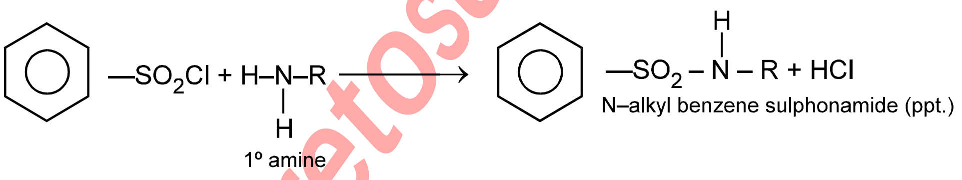
$$:CCl_2 \xrightarrow[H_2O]{OH^{\ominus}} CO + HCO_2^{\ominus} + 2Cl^{\ominus}$$

5.10 Reaction with Hinsberg reagent : This is a method for seperation of 1° , 2° and 3° amines Hinsberg Reagent is

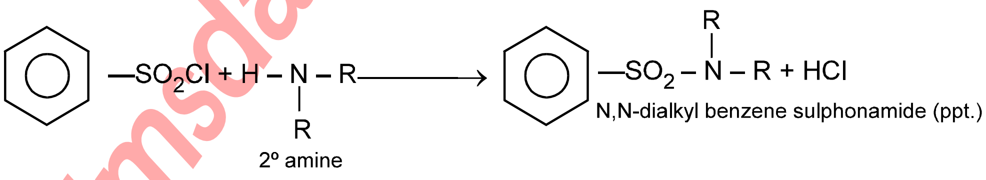
$C_6H_5\text{-}SO_2\text{-}Cl$. (Benzene sulphonyl chloride)

$$RNH_2 + Cl - SO_2\text{-}C_6H_5 \longrightarrow R\text{-}NH\text{-}SO_2\text{-}C_6H_5 + HCl$$

(a) Primary amines form N—Alkyl benzene sulphonamide

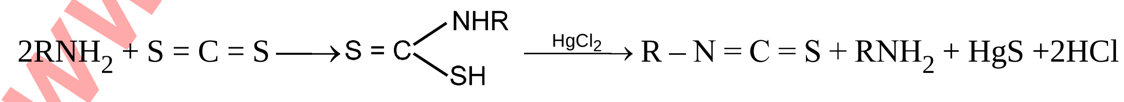


(b) Secondary amines form N, N-dialkyl benzene sulphonamide



(c) Tertiary amines do not react because they do not possess a replacable Hydrogen atom.

5.11 Mustard oil reaction: A 1° amine reacts with CS_2 and then with $HgCl_2$ to form iso thiocyanate having pungent smell of mustard oil.



$$2RNH_2 + S = C = S \longrightarrow S = C\begin{smallmatrix} NHR \\ SH \end{smallmatrix} \xrightarrow{HgCl_2} R - N = C = S + RNH_2 + HgS + 2HCl$$

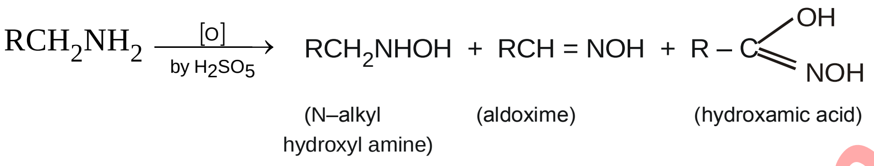
alkyl isothiocyanate

5.12 Reaction with Nitrosyl chloride (TILDEN'S REAGENT) :

$$R\text{–}NH_2 + NOCl \longrightarrow R\text{-}Cl + N_2 + H_2O$$

5.13 Reaction with Caro's acid [H_2SO_5] :

With caro's acid, the oxidation products of primary amine are also dependent on the nature of the alkyl group present in the amine.



$$RCH_2NH_2 \xrightarrow[\text{by } H_2SO_5]{[O]} RCH_2NHOH + RCH=NOH + R-C\begin{matrix}OH\\NOH\end{matrix}$$

(N–alkyl hydroxyl amine) (aldoxime) (hydroxamic acid)

$$R_2CHNH_2 \xrightarrow[\text{by } H_2SO_5]{[O]} R_2C=NOH \text{ (ketoxime)}$$

$$R_3CNH_2 \xrightarrow[\text{by } H_2SO_5]{[O]} R_3CNO \text{ (nitrosoalkane)}$$

CHEMICAL REACTION

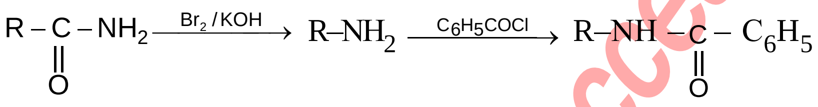
Ex.6 The smell of mustard oil is given by the compounds -

(A) Carbylaminoalkane (B) RNCS

(C) RCNO (D) RCNS **(Ans. B)**

Sol. Alkyl isothiocyanate gives the smell of mustard oil.

Ex.7



$$R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2/KOH} R\text{–}NH_2 \xrightarrow{C_6H_5COCl} R\text{–}NH-\underset{\underset{O}{\|}}{C}-C_6H_5$$

The reactions involved in the above reaction sequence are -

(A) Stephen and Schotten Boumann (B) Hofmann and Schotten Boumann

(C) Hofmann and Cannizaro (D) Gabriel and Schotten Boumann

(Ans. B)

Ex.8 When 1-propane amine is treated with $NaNO_2$ and HCl the products will be -

(A) 1-propanol, 2-propanol

(B) Propene

(C) 2-Chloropropane, 1-chloropropane

(D) All of these **(Ans. D)**

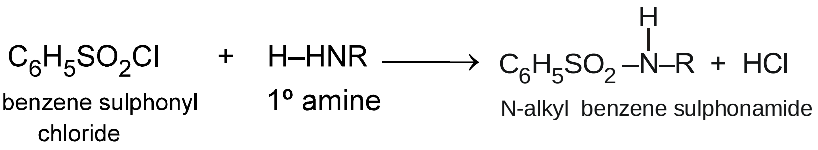
Sol. The products formed in the reaction between $CH_3CH_2CH_2NH_2$ and HNO_2 are
1- Propanol, 2 propanol, propene,
1-Chloropropane and 2-chloropropane

6. SEPERATION OF MIXTURES OF AMINES

6.1 Hinsberg method :

This involves the treatment of the mixture with benzene sulphonyl chloride (Hinsberg Reagent) and KOH.

(a) The primary amine forms N–alkyl benzene sulphonamide which forms a salt with KOH, which is soluble in water.



$$C_6H_5SO_2Cl + H\text{–}HNR \longrightarrow C_6H_5SO_2\text{–}\overset{\overset{H}{|}}{N}\text{–}R + HCl$$

benzene sulphonyl chloride; 1° amine; N-alkyl benzene sulphonamide

(b) The secondary amine gives N, N- dialkyl benzene sulphonamide which is insoluble in KOH solution

(c) The tertiary amine does not react at all.

6.2 Hofmann method :

This involves the treatment of the mixture with diethyl oxalate.

(a) The primary amine forms a dialkyloxamide, which is a solid

(b) The secondary amine forms a dialkyl oxamic ester, which is an oily liquid.

(c) The tertiary amine does not react at all.

6.3 Fractional distillation :

The mixture of primary, secondary and tertiary amines, may be separated by fractional distillation because their B.P's. are quite different . This method is extensively used in industry.

CYANIDES, ISOCYANIDES, ALKYL NITRITES AND NITRO ALKANES

1.1 GENERAL CHARACTERISTICS :

(a) Compounds having the formula RCN are called alkyl cyanides or as nitriles of the acid which they produce on hydrolysis.

(b) According to IUPAC system, cyanides are named as alkane nitriles, i.e., in the name of parent hydrocarbon 'nitrile' is suffixed. In naming the hydrocarbon part, carbon of the — CN group is also counted.

Formula	As cyanide	IUPAC name
CH_3CN (Acetonitrile)	Methyl cyanide	Ethane nitrile
C_2H_5CN (Propiononitrile)	Ethyl cyanide	Propane nitrile
C_3H_7CN	Propyl cyanide	Butane nitrile
C_4H_9CN	Butyl cyanide	Pentane nitrile

(c) The compounds having the formula RNC are called isocyanide or isonitriles. The nomenclature of isocyanides is similar to cyanides.

Formula	As isocyanides (Comman name)	IUPAC names
CH_3NC	Methyl isocyanide (Methyl isonitrile)	Methylcarbylamine (Carbylamino methane)
C_2H_5NC	Ethyl isocyanide (Ethyl isonitrile)	Ethyl carbylamine (Carbylamino ethane)
C_3H_7NC	Propyl isocyanide (Propyl isonitrile)	Propyl carbylamine (Carbylamino propane)

(d) Isocyanides are also named as alkane isonitrile.

CH_3NC	Methane isonitrile
C_2H_5NC	Ethane isonitrile
C_3H_7NC	Propane isonitrile

(e) Hydrogen cyanide is known to exist as a tautomeric mixture. (Diad forms)

$$H - C \equiv N \rightleftharpoons H - N \equiv C$$

Hence, it forms two types of alkyl derivatives which are known as alkyl cyanides and alkyl isocyanides.

$R - C \equiv N$	$R - N \equiv C$
Alkyl cyanide	Alkyl isocyanide

1.2 ALKYL CYANIDES

Methods of Preparation

(i) **From alkyl halides :** The alkyl cyanides are prepared by refluxing an alcoholic solution of an alkyl halide with potassium cyanide. The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.

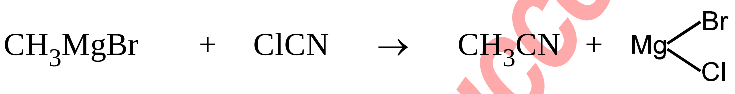
$$RX + KCN \text{ (or NaCN)} \rightarrow RCN + RNC$$

Alkyl halide	Nitrile (Major product)	Isonitrile (Minor product)

(ii) **From Grignard reagent :** Grignard reagent reacts with cyanogen chloride to form alkyl cyanides.

$$RMgX + ClCN \rightarrow RCN + Mg\begin{smallmatrix}X\\Cl\end{smallmatrix}$$

Grignard reagent Alkyl Cyanide



$$CH_3MgBr + ClCN \rightarrow CH_3CN + Mg\begin{smallmatrix}Br\\Cl\end{smallmatrix}$$

Methyl magnisium bromide Cyanogen chloride Methylcyanide

(iii) **From acid amides** : Pure nitriles are obtained by dehydration of acid amides with phosphorus pentoxide. Amides are distilled with phosphorus pentoxide, P_2O_5.

$$RCONH_2 \xrightarrow[-H_2O]{P_2O_5} RCN$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{P_2O_5} \underset{\text{Methyl cyanide}}{CH_3CN} + H_2O$$

Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at 500°C.

$$\underset{\text{Acid}}{RCOOH} + NH_3 \longrightarrow \underset{\text{Ammonium Salt}}{RCOO\overset{+}{N}H_4} \xrightarrow[-H_2O]{Al_2O_3, 500°C} \underset{\text{Amide}}{RCONH_2} \xrightarrow[-H_2O]{Al_2O_3} \underset{\text{Alkyl Cyanide}}{RCN}$$

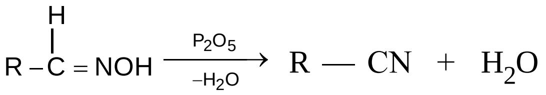
(iv) **From primary amines :** Primary amines are dehydrogenated when passed over copper or nickel at high temperature to form alkyl cyanides. This is also a commercial method.

$$\underset{\text{Primary amine}}{RCH_2NH_2} \xrightarrow[500°C]{\text{Cu or Ni}} RCN + 2H_2$$

$$CH_3CH_2NH_2 \xrightarrow[500°C]{Cu\ or\ Ni} CH_3CN + 2H_2$$

Ethylamine Methyl cyanide

(v) **From oximes :** Aldoximes are converted into alkyl cyanides when distilled with phosphorus pentoxide or acetic anhydride. The dehydration of aldoximes occurs.



$$R-\overset{\overset{\large H}{|}}{C}=NOH \xrightarrow[-H_2O]{P_2O_5} R-CN + H_2O$$

Aldoxime Alkyl cyanide

1.3 Physical properties :

(a) Lower members containing upto 15 carbon atoms are liquids, while higher members of carbon atoms in the molecule.

(b) Alkyl cyanides are neutral substances with pleasant odour, similar to bitter almonds.

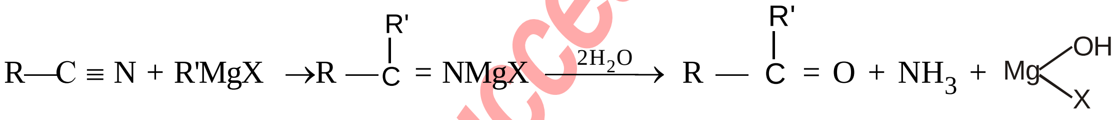
(c) They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the molecule are solid.

(d) They are soluble in organic solvents.

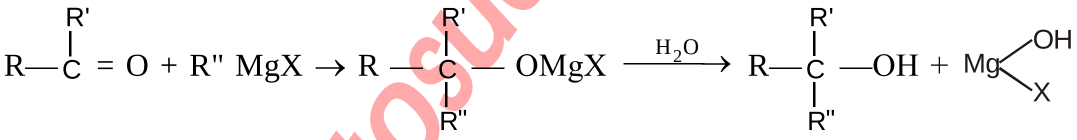
(e) They are poisonous but less poisonous than HCN.

1.4 Chemical properties :

(i) **Reaction with Grignard reagent :** With Grignard's reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.



$$R-C\equiv N + R'MgX \rightarrow R-\overset{\overset{R'}{|}}{C}=NMgX \xrightarrow{2H_2O} R-\overset{\overset{R'}{|}}{C}=O + NH_3 + Mg\begin{matrix}OH\\X\end{matrix}$$



$$R-\overset{\overset{R'}{|}}{C}=O + R''MgX \rightarrow R-\underset{\underset{R''}{|}}{\overset{\overset{R'}{|}}{C}}-OMgX \xrightarrow{H_2O} R-\underset{\underset{R''}{|}}{\overset{\overset{R'}{|}}{C}}-OH + Mg\begin{matrix}OH\\X\end{matrix}$$

Tertiary alcohol

(ii) **Reduction :** When reduced with hydrogen in presence of Pt or Ni, or $LiAlH_4$ (Lithium aluminium hydride) or sodium and alcohol, alkyl cyanides yield primary amines.

$$RCN \xrightarrow{4H} RCH_2NH_2$$

Alkyl cyanide Primary amine

However, when a solution of alkyl cyanides in ether is reduced with stannous chloride and hydrochloric acid and then steam distilled, an aldehyde is formed (**Stephen's reaction**).

$$R-C\equiv N \xrightarrow[{[2H]}]{SnCl_2/HCl} RCH=NH.HCl \xrightarrow{H_2O} RCHO + NH_4Cl$$

Imine hydrochloride Aldehyde

(iii) **Hydrolysis :** Alkyl cyanides are hydrolysed by both acid and alkalies. On partial hydrolysis amides are formed while on complete hydrolysis acids are obtained.

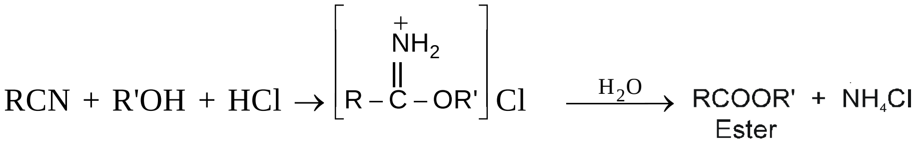
$$RCN \xrightarrow[H^+]{H_2O} RCONH_2 \xrightarrow[H^+]{H_2O} RCOOH + NH_3$$

Alkyl cyanide Amide Acid

$$CH_3CN \xrightarrow[H^+]{H_2O} CH_3CONH_2 \xrightarrow[H^+]{H_2O} CH_3COOH + NH_3$$

Methyl cyanide Acetamide Acetic acid

(iv) **Alcoholysis :** When an alkyl cyanide is refluxed with an anhydrous alcohol in presence of dry HCl, an imido ester is formed, which on hydrolysis with water forms ester.



$$RCN + R'OH + HCl \rightarrow \left[R-\overset{\overset{+}{NH_2}}{\overset{\|}{C}}-OR' \right] Cl \xrightarrow{H_2O} \underset{\text{Ester}}{RCOOR'} + NH_4Cl$$

Uses : Alkyl cyanides are important intermediates in the laboratory synthesis of a large number of compounds like acids, amides, ester, amines, etc.

1.5 ALKYL ISOCYANIDES

Methods of Preparation

(i) **From alkyl halides :** The isocyanides are prepared by refluxing an alkyl halide solution in alcohol with silver cyanide. The isonitrile is the main product but small amount of nitrile is also formed.

$$\underset{\text{Alkyl halide}}{R - X} + AgCN \longrightarrow \underset{\substack{\text{Isocyanide}\\\text{(Isonitrile)}\\\text{Main product}}}{RNC} + \underset{\substack{\text{Cyanide}\\\text{(Nitrile)}\\\text{Minor product}}}{RCN}$$

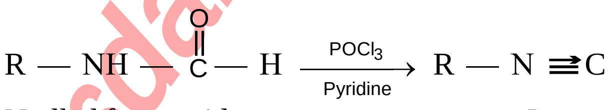
$$\underset{\text{Methyl chloride}}{CH_3Cl} + AgCN \longrightarrow \underset{\substack{\text{Methyl isocyanide}\\\text{(Main product)}}}{CH_3NC} + CH_3CN$$

This method is, thus, suitable for preparing isocyanides.

(ii) **From Primary Amines : (Carbylamine reaction) :** Alkyl isocyanides may be prepared by heating primary amines with chloroform and alcoholic potash.

$$\underset{\substack{\text{Primary}\\\text{amine}}}{RNH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \rightarrow \underset{\text{Isocyanide}}{RNC} + 3KCl + 3H_2O$$

(iii) **From N-alkyl formamides :** N-alkyl formamides when dehydrated with $POCl_3$ in presence of pyridine give isocyanides.



$$\underset{\text{N-alkyl formamide}}{R - NH - \overset{\overset{O}{\|}}{C} - H} \xrightarrow[\text{Pyridine}]{POCl_3} \underset{\text{Isocyanide}}{R - N \equiv C}$$

Physical properties :

(a) Alkyl isocyanides are colourless, unpleasant smelling liquids.

(b) They are insoluble in water but freely soluble in organic solvents.

(c) The boiling points of isonitiriles are lower than corresponding alkyl cyanides.

(d) Isonitriles are much more poisonous than isomeric cyanides.

Chemical properties :

(i) **Hydrolysis** : Alkyl isocyanides are hydrolysed by dilute mineral acids (but not by alkalies) to form primary amines.

$$\underset{\text{Alkyl isocyanide}}{RN \equiv C} + 2H_2O \xrightarrow{H^+} \underset{\text{Primary amine}}{RNH_2} + \underset{\text{Formic acid}}{HCOOH}$$

(ii) **Reduction :** When reduced with nascent hydrogen or hydrogen in presence of nickel, isocyanides form secondary amines containing methyl as one of the alkyl groups.

$$R - N \equiv C \;+\; 4H \longrightarrow RNHCH_3$$

Alkyl isocyanide Secondary amine

(iii) **Action of heat :** When heated for sometime at 250°C, a small amount of isonitrile changes into isomeric nitrile.

$$RNC \xrightarrow{\text{heat}} RCN$$

(iv) **Addition reaction :** Alkyl isocyanide give addition reactions due to presence of unshared electron pair on carbon atom.

$$R : N :::C : \text{ or } R - \overset{+}{N} \equiv \overset{-}{C}$$

The following are some of the addition reactions shown by alkyl isocyanides.

$RNC + X_2 \longrightarrow RNCX_2$ Alkyl iminocarbonyl halide

(Halogen)

$RNC + S \longrightarrow RNCS$ Alkyl isothiocyanate

$RNC + HgO \longrightarrow RNCO + Hg$

(Alkyl isocyanate)

Distinction between Ethyl Cyanide and Ethyl Isocyanide

Test	Ethyl Cyanide (C_2H_5CN)	Ethyl isocyanide (C_2H_5NC)
1. Odour	Not unpleasant	Extremely unpleasant
2. Solublity in water	Soluble	Insoluble
3. Hydrolysis	Yields propionic aci	Produces ethyl amine
4.Reduction	Gives propylamine	Gives ethylmethylamine
	(Primary amine)	(Secondary amine)
5.Heating at 250°C	No effect	Changes to ethyl cyanide

CYNIDES AND ISOCYNIDES :

Ex.9 Alkyl halide reacts with AgCN to form –

(A) Alcohol (B) Cyanide (C) Isocyanide (D) Both B & C

(Ans.D)

Sol. In the above reaction major product is Isocyanide and minor product is Cyanide.

Ex.10 Amide on heating with P_2O_5 gives –

(A) Alkane nitrile (B) Alkyl halide (C) Amine (D) None **(Ans.A)**

Sol. See text.

SOLVED EXAMPLES

Ex.1 An example of a primary amine is -

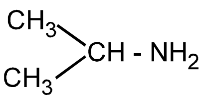
(A) n-Propylamine (B) Isopropylamine

(C) t-Butyl amine (D) All of above **(Ans.D)**

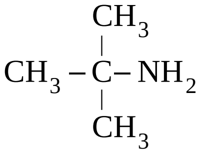
Sol. All the compounds given above are examples of primary amine.

$CH_3\ CH_2\ CH_2-NH_2$

n-propyl amine



Iso propyl amine



$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-NH_2$$

t – butyl amine

Ex.2 For the elimination of $-\overset{O}{\overset{||}{C}}-$ group of amide following reaction is used -

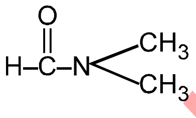
(A) Hoffmann hypobromite reaction (B) Kolbe reaction

(C) Hunsdiecker reaction (D) Liebermann's reaction **(Ans.A)**

Sol. For the formation of RNH_2 from $RCONH_2$, NaOH and Br_2 are used as reagent. It is called Hofmann hypobromite reaction.

Ex.3 Which of the following is hydrolysed to give secondary amine -

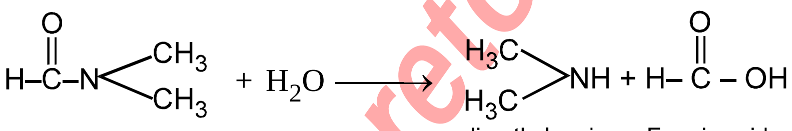
(A) Alkyl cyanide (B)



(C) Nitro paraffins (D) Acid amide

(Ans.B)

Sol. The compound H-CO - N $(CH_3)_2$ on hydrolysis produces secondary amine .



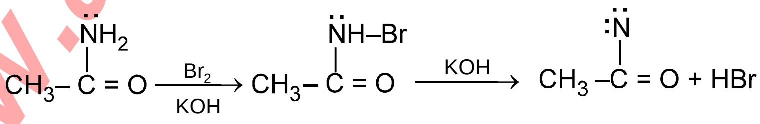
dimethyl amine Formic acid

Ex.4 The structure of intermediate acetyl nitrene is -

(A) $CH_3-CO-\overset{+}{N}:$ (B) $CH_3-CO-\bar{N}:$ (C) $CH_3-CO-\underset{..}{N}:$ (D) $CH_3-CO=N:$

(Ans.C)

Sol. The structure of intermediate acetyl nitrene is CH_3–CO–N. It is formed by the following reaction



Ex.5 In hypobromite reaction of amide, carbonyl carbon atom is lost as -

(A) CO (B) CO_2 (C) CO_3^{-2} (D) None of above

(Ans.C)

Sol. In hypobromite reaction of amide, carbonyl carbon atom is lost as CO_3^{-2} ion. The reaction takes place as follows:

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + H_2O$$

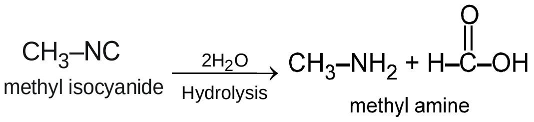
K_2CO_3 is an ionic compound and ionizes as K^+ and CO_3^{-2} ions.

Ex.6 Which one of the following will give primary amine on hydrolysis-

(A) Nitroparaffins (B) Alkyl cyanide (C) Amide (D) Alkyl isocyanide

(Ans.D)

Sol. Alkyl isocyanide on hydrolysis produces a primary amine. The reaction takes place as follows.



$$\underset{\text{methyl isocyanide}}{CH_3{-}NC} \xrightarrow[\text{Hydrolysis}]{2H_2O} \underset{\text{methyl amine}}{CH_3{-}NH_2} + H{-}\overset{\overset{O}{\|}}{C}{-}OH$$

Ex.7 The correct set of the products obtained in the following reactions-

(1) $RCN \xrightarrow{\text{reduction}}$ (2) $RCN \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr}$

(3) $RNC \xrightarrow{\text{hydrolysis}}$ (4) $RNH_2 \xrightarrow{HNO_2}$

The answer is-

	1	2	3	4
(A)	2° Amine	Methyl ketone	1° Amine	Alcohol
(B)	1° Amine	Methyl ketone	1° Amine	Alcohol
(C)	2° Amine	Methyl ketone	2° Amine	Acid
(D)	2° Amine	Methyl ketone	2° Amine	Aldehyde

(Ans.B)

Sol. The products of the reaction 1, 2, 3 and 4 respectively are : 1° amine, methyl ketone, 1° amine and alcohol.

Ex.8 The reaction of an alkyl cyanide with sodium and alcohol to form an alkyl amine is known by the name of -

(A) Mendius reaction (B) Hofmann's reaction

(C) Gabriel reaction (D) Ammonolysis **(Ans.A)**

Sol. Cyanoalkanes are reduced to primary amines in the presence of Na and ethanol. It is called Mendius reacion

$$R\text{-}C \equiv N + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{alkyl amine}}{RCH_2{-}NH_2}$$

Ex.9 Formaldoxime on reaction with Na/EtOH gives –

(A) 1° Amine (B) 2° Amine (C) 3° Amine (D) All above

(Ans.A)

Sol. Formaldoxime on reaction with Na/EtOH gives

1° amine. The reaction is representated as follows :

$$\underset{\text{formaldoxime}}{H{-}CH{=}N{-}OH} \xrightarrow[4H]{Na/EtOH} \underset{\text{methyl amine}}{CH_3NH_2} + H_2O$$

This method is used for the preparation of primary amines.

Ex.10 Which of the following compounds on reduction gives an amine -

(A) Alkyl cyanide (B) Aldoxime (C) Alkyl isocyanide (D) All above

(Ans.D)

Sol. All the given compounds like alkyl cyanide, aldoxime, alkyl isocyanide on reduction gives an amine

$CH_3{-}C{\equiv}N \xrightarrow[Sn/HCl]{4H} CH_3\ CH_2NH_2$

acetonitrile ethyl amine

$CH_3{-}CH{=}NOH \xrightarrow[H_2O]{4H} CH_3{-}CH_2{-}NH_2 + H_2$

acetaldoxime ethyl amine

$CH_3{-}NC \xrightarrow[Sn/HCl]{4H} CH_3{-}NH{-}CH_3$

methyl isocyanide dimethyl amine

(2° amine)

Ex.11 An alkyl amine is prepared by the following reaction -

$RCOOH + N_3H \xrightarrow{Conc.\ H_2SO_4} RNH_2 + CO_2 + N_2$

Name of the above reaction is :

(A) Schmidt reaction (B) Stephan's reaction

(C) Schotton-Baumann reaction (D) Reimer- tiemann reaction **(Ans.A)**

Sol. The given reaction is represented as :

$RCOOH + N_3H \xrightarrow{Conc.\ H_2SO_4} RNH_2 + CO_2 + N_2$

alkanoic acid hydrazoic acid alkylamine

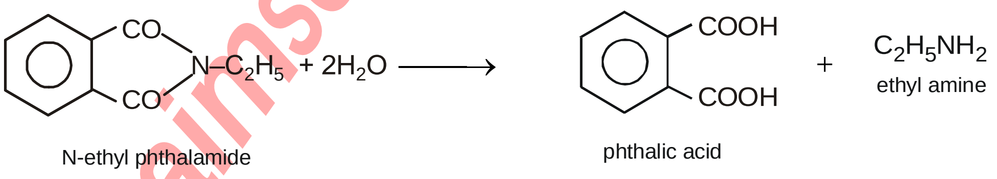
The above reaction is known as Schmidt reaction. This is an important method of preparing primary amines.

Ex.12 N-Ethyl pthalimide on hydrolysis gives -

(A) Methyl alcohol (B) Ethyl amine

(C) Dimethyl amine (D) Diethyl amine **(Ans.B)**

Sol. N- ethyl pthalimide on hydrolysis forms ethylamine. It is called Gabriel phthalimide reaction. It is an important method of preparing primary amines.

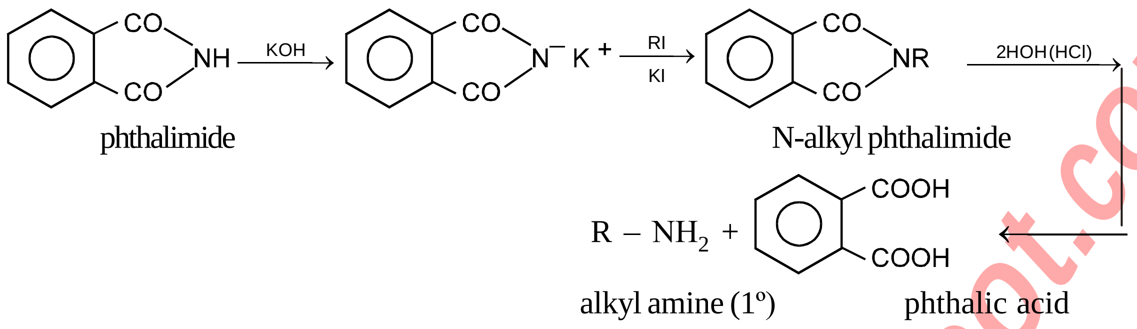


Ex.13 Gabriel phthalimide reaction is used to prepare -

(A) Primary amine (B) Secondry amine

(C) Tertiary amine (D) All of above **(Ans.A)**

Sol. Gabriel phthalimide reaction is used to prepare primary amine.



Ex.14 Assign number 1 for least to 4 for most to indicate the relative base strength of the following-

I	II	III	IV
$C_6H_5NH_2$	$p–NO_2C_6H_4NH_2$	$m–NO_2C_6H_4NH_2$	$p–CH_3OC_6H_4NH_2$

	I	II	III	IV
(A)	2	3	1	4
(B)	1	2	3	4
(C)	2	3	4	1
(D)	4	1	2	3

(Ans.A)

Sol. $p–NO_2C_6H_4NH_2$ is the least basic due to electron withdrawing group at the p–position (in conjugation with NH_2 group) $p–CH_3OC_6H_4NH_2$ is the most basic due to interaction of lone pair of electron on oxygen atom of $–OCH_3$ group with the benzene ring. As such lone pair of electron on $–NH_2$ group is more available.

Ex.15 Which compound is soluble in water-

(A) $[(CH_3)_2NH_2]^+ Cl^–$ (B) $[CH_3NH_3]^+ Cl^–$

(C) $[(CH_3)_3NH]^+ Cl^–$ (D) All the above **(Ans.D)**

Sol. Amines salt are soluble in water.

Ex.16 Which compound will liberate CO_2 from $NaHCO_3$ solution-

(A) $CH_3CO\ NH_2$ (B) CH_3NH_2 (C) $(CH_3)_4\ N^+OH^–$ (D) $CH_3N^+H_3Cl^–$

(Ans.D)

Sol. The compound which will liberate CO_2 from $NaHCO_3$ solution is $CH_3N^+\ H_3Cl^–$. The reaction takes place as follows:

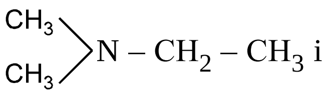
$CH_3N^+H_3Cl^– + NaHCO_3 \longrightarrow CH_3–NH_2 + NaCl + H_2O + CO_2\uparrow$
methyl amine methyl amine
hydrogen chloride

Ex.17 Which amine will not react with nitrous acid -

(A) Methyl amine (B) Ethyl amine

(C) Dimethyl amine (D) N, N Dimethyl ethane amine **(Ans.D)**

Sol. Primary and secondary amines react with HNO_2, while tertiary amines do not react with HNO_2. Since N, N dimethyl ethane amine



$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>N-CH_2-CH_3$ is a tertiary amine, hence it will not react with HNO_2.

Ex.18 Which gas will be evolved out when $[CH_3CH_2NH_2 + (CH_3)_2CHNH_2]$ is treated with sodium nitrite and HCl -

(A) Chlorine (B) Ammonia (C) Nitrogen (D) NO_2 **(Ans.C)**

Sol. Primary amine and HNO_2 produces nitrogen gas.

$$RNH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O$$

Ex.19 Which of the following compound cannot be produced if 1-propane amine is treated with $NaNO_2$ and HCl -

(A) Propane -1-ol (B) Propane-2-ol

(C) 2-Chloropropane (D) 2-Propaneamine **(Ans.D)**

Sol. In the reaction,

$CH_3–CH_2–\overset{\oplus}{C}H_2$ and $CH_3–\overset{\oplus}{C}H–CH_3$,

carbonium ions are formed.

As such 1-propanol, 2-propanol, 2-chloro-propane, 1-chloropropane and propene are the products while 2-propaneamine is not obtained.

Ex.20 In the following sequence of reactions the product B, will be

$$C_2H_5MgBr \xrightarrow{ClNH_2} A \xrightarrow[HCl]{NaNO_2} B$$

(A) C_2H_5OH (B) $C_2H_5NO_2$ (C) C_2H_2 (D) All of the above

(Ans.A)

Sol. In the given sequence of reactions, the product B, will be ethanol. The reaction takes place as

$$C_2H_5MgBr \xrightarrow[MgBrCl]{ClNH_2} C_2H_5NH_2 \xrightarrow[NaNO_2/HCl]{HONO} \underset{\text{‘B’}}{C_2H_5OH} + N_2 + H_2O$$

Ex.21 Which set of the following compounds on reaction with an alkyl amine gives schiff's base :

(A) HCHO, C_6H_5CHO, CH_3CHO (B) HCHO, NH_2OH, NH_2 - NH_2

(C) CH_3CHO, NH_2OH, NH_2-NH_2 (D) CH_3COCH_3, C_2H_5OH **(Ans.A)**

Sol. The aldehydes e.g. HCHO, C_6H_5CHO and CH_3CHO on reaction with alkylamine gives schiff's base

$$\underset{\text{benzaldehyde}}{C_6H_5CHO} + \underset{\text{methylamine}}{H_2NCH_3} \longrightarrow \underset{\text{schiff's base}}{C_6H_5CH = N - CH_3} + H_2O$$

Ex.22 Which of the following does not give a sulphur compound with a 1° amine -

(A) Hinsberg reaction (B) Mustard oil reaction

(C) Schotton - Baumann reaction (D) Con. H_2SO_4 **(Ans.C)**

Sol. In Schotton - Baumann reaction a sulphur compound is not produced with a 1° amine

$$\underset{\text{alkyl amine}}{R - NH_2} + \underset{\text{benzoyl chloride}}{Cl - CO - C_6H_5} \xrightarrow{NaOH} \underset{\text{N-alkyl benzamide}}{R– NHCOC_6H_5} + HCl$$

Ex.23 Ethylamine on oxidation with acidified $KMnO_4$ gives-

(A) Acetaldehyde (B) Ethylamine oxide

(C) Ethanol (D) Acetamide **(Ans.A)**

Sol. Oxidation of ethylamine gives acetaldehyde.

Ex.24 Mustard oil reaction is given by -

(A) Primary amine (B) Urea (C) Secondary amine (D) Acid amide

(Ans.A)

Sol. Mustard oil reaction is given by primary amine. It is known as Hoffmann's mustard oil reaction

$$R - NH_2 + S = C = S + HgCl_2 \xrightarrow{\qquad} R - N = C = S + HgS\downarrow + 2HCl$$

alkyl isothiocyanate

This compound alkyl isothiocyanate has a smell resembling that of mustard oil.

Ex.25 Which of the following compounds has a smell of mustard oil

(A) Alkyl cyanate (B) Alkyl thiocyanate

(C) Alkyl isothiocyanate (D) alkyl isocyanate **(Ans.C)**

Sol. A primary amine condenses with CS_2 in the presence of $HgCl_2$ to form an alkyl isothiocyanate. This compound has a smell resembling that of mustard oil. It is called as Hofmann's mustard oil reaction

$$R - NH_2 + S = C = S + HgCl_2 \xrightarrow{\qquad} R - N = C = S + HgS\downarrow + 2HCl$$

alkyl amine alkyl isothiocyanate

Ex.26 Which of the following amine does not react with Hinsberg reagent -

(A) Neopentyl amine (B) Isopropyl amine

(C) Triethyl amine (D) Ethyl methyl amine **(Ans.C)**

Sol. Triethyl amine is tertiary amine. It does not react with Hinsberg reagent.

Ex.27 In which of the following sequence of reaction the end product does not exhibit tautomerism-

(A) $CH_3CH_2NH_2 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$ (B) $(CH_3)_2CHNH_2 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$

(C) $(CH_3)_3CNH_2 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$ (D) $CH_3CH(NH_2)C_2H_5 \xrightarrow{NOCl} \xrightarrow{AgNO_2}$

(Ans.C)

Sol. In the 3^{rd} reaction sequence the end product is a 3° nitro compound.

$(CH_3)_3CNO_2$ It does not have α-hydrogen as such tautomerism is not possible.

Ex.28 The acid used for the determination of molecular weights of amines is -

(A) H_2PtCl_6 (B) Picric acid (C) $HAuCl_4$ (D) H_2SO_4 **(Ans.A)**

Sol. The acid used is H_2PtCl_6. It is a solution of platinic chloride, Pt Cl_4 in con.HCl

$$2R\text{-}NH_2 + H_2\,[PtCl_6] \xrightarrow{\qquad} [R\,NH_3]_2^{+}\,[PtCl_6]^{-2}$$

alkylamine platinichloride

Chloroplatinates on ignition leave a residue of metallic Pt. This reaction is employed in determining molecular weight of amines.

Ex.29 Methyl amine on reaction with chlorine in the presence of NaOH gives-

(A) Chloroform

(B) Methyl chloride

(C) N-Methyl chloramine

(D) Chloramine **(Ans.C)**

Sol. Methyl amine reacts with Cl_2 in the presence of NaOH undergoes a substitution of a H-atom of amino group by a Cl group and N-methyl chloramine is formed.

$$CH_3NH_2 + Cl_2 \xrightarrow[\text{NaCl, } H_2O]{\text{NaOH}} \underset{\text{N-methyl chloramine}}{CH_3\text{–}NHCl}$$

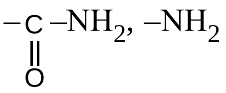
EXERCISE–I

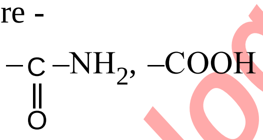
Q.1 Amide on heating with P_2O_5 gives –
(A) Alkane nitrile (B) Alkyl halide (C) Amine (D) None

Q.2 Mendius reaction involves the reduction of -
(A) Cyanoalkanes (B) Alkyl isocyanides (C) Oximes (D) Nitroalkanes

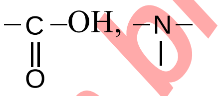
Q.3
$$\begin{tikzcd} CH_3CONH_2 \arrow[r, "PCl_5"] & A \arrow[r, "H_2O", "(partial)"'] \arrow[d, "reduction"] & B \\ & C & \end{tikzcd}$$

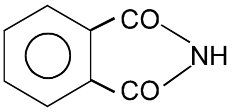
The functional groups of B and C respectively are -

(A) 
$-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$, $-NH_2$

(B) 
$-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$, $-COOH$

(C) –CN, –NH–

(D) 
$-\overset{\overset{\displaystyle O}{\|}}{C}-OH$, $-\underset{|}{N}-$

Q.4  $\xrightarrow{KOH} A \xrightarrow{CH_3Br} B \xrightarrow[H^+]{HOH} C + D$, C and D in the sequence are -
(A) Benzoic acid + aniline (B) Phthalic acid + ethylamine
(C) Phthalic acid + aniline (D) Benzoic acid + ethylamine

Q.5 Which of the following would undergo Hoffmann bromide reaction to form primary amine-
(A) $RCONHCH_3$ (B) $RCOONH_4$ (C) $RCONH_2$ (D) RCONHOH

Q.6 A reaction used in descending a homologous series would be -
(A) $RCONH_2 + Br_2 + KOH$ (B) $RCH_2Cl + KCN$
(C) $RNH_2 + CHCl_3 + KOH$ (D) None of the above

Q.7 In Hofmann degradation of amide the correct order of reagent is-
(A) Br_2, KOH, H_2O (B) KOH, Br_2, H_2O
(C) H_2O, KOH, Br_2 (D) None of the these

Q.8 Alkyl halide reacts with AgCN to form –
(A) Alcohol (B) Cyanide (C) Isocyanide (D) Both B & C

Q.9 In the reaction sequence identify the functional group present in A, B, C

$$A \xrightarrow{Sn/HCl} B \xrightarrow[0^oC]{HNO_2} C \xrightarrow{C_2H_5OH} C_6H_6 \text{ -}$$

(A) NO_2, NH_2, N=N (B) NO_2, NH_2, OH (C) –OH -NH_2, -NO_2 (D) –NH_2, -NO_2, –N=N

Q.10 $CH_3CH_2CONH_2 \xrightarrow[Br_2]{NaOH} A$

Aqueous solution of A :

(A) Turns blue litmus to red (B) Turns red litmus to blue

(C) Does not effect the litmus' (D) Decolourise the litmus

Q.11 Amines are basic in nature because-

(A) They produce OH^- ions when treated with water

(B) They have replaceable H atoms on N atoms

(C) They have lone pair of electron on N atom

(D) None of these

Q.12 Minimum boiling point would be of :

(A) Ethylmethyl amine (B) Ethyl.amine (C) n-Propyl amine (D) Trimethylamine

Q.13 A mixture of 1°, 2° and 3° amine is formed in the reaction-

(A) 1° Amide + caustic potash + bromine (B) Methyl halide and ammonia

(C) Cyclic imide + H_3O^+ (D) Alkyl isocyanide + H_2

Q.14 The presence of primary amines can be confirmed by-

(A) Reaction with HNO_2 (B) Reaction with $CHCl_3$ and alc. KOH

(C) Reaction with Grignard reagent (D) Reaction with acetyl chloride

Q.15 $C_2H_5NH_2$ cannot be prepared by the reduction of-

(A) $C_2H_5NO_2$ (B) $CH_3CH{=}NOH$ (C) C_2H_5NC (D) CH_3CN

Q.16 Tilden's reagent is-

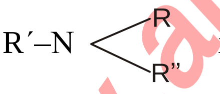
(A) $C_6H_5SO_2Cl$ (B) NOCl (C) $CINH_2$ (D) $(C_2H_5)_2$ Zn

Q.17 Acetonitrile has the structure :

(A) C_2H_5NC (B) C_2H_5CN (C) CH_3NC (D) CH_3CN

Q.18 The compound obtained by the reaction between primary amine and aldehyde is-

(A) An amide (B) Imine (C) Nitrite (D) Nitro

Q.19  is a-

$R'{-}N\begin{matrix}\diagup R\\ \diagdown R''\end{matrix}$

(A) Mixed 3° amine (B) Unsymmetrical amine

(C) Both 1st and 2nd (D) Quartenary salt

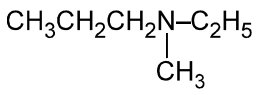
Q.20 The alkanenitriles are isomeric with-

(A) Primary alkanamines (B) Secondary alkanamines

(C) Alkyl isocyanides (D) Nitroalkanes

Q.21 Which of the following is obtained by reducing methyl cyanide with Na + C_2H_5OH -
(A) Methyl alcohol (B) Acetic acid (C) Ethyl amine (D) Methane

Q.22 Which of the following is optically active amine-
(A) CH_3NH_2 (B) CH_3NHCH_3
(C)



$CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{N}}-C_2H_5$

(D) Secondary butylamine

Q.23 Ethyl iodide on reaction with potassium nitrite gives –
(A) Ethyl nitrite (B) Nitro ethane (C) Amine (D) Acid

Q.24 Ethylamine can be prepared by the all except -
(A) Curtius reaction (B) Hoffmann reaction
(C) Mendius reaction (D) Reduction of formaldoxime

Q.25 Fast heating of urea yields :
(A) Cyanuric acid (B) Carbamic acid (C) Parabanic acid (D) Barbituric acid

Q.26 The basic character of amines can be explained-
(A) In terms of Lewis and Arrhenius concept
(B) In terms of Lowry and Bronsted concept
(C) In terms of Lewis and Lowry Bronsted concept
(D) Only by Lewis concept

Q.27 Which of the following diazonium salt is relatively stable of 0-5ºC -
(A) $CH_3–N\equiv N\}\ ^{\oplus}Cl^{-}$ (B) $CH_3–C(CH_3)–N\equiv N\}\ ^{\oplus}Cl^{-}$
(C) $C_6H_5–N\equiv N\}\ ^{\oplus}Cl^{-}$ (D) $(CH_3)_3C–N\equiv N\}\ ^{\oplus}Cl^{-}$

Q.28 Lowest boiling point will be of the compound-
(A) Ethylamine (B) Ethylmethylamine
(C) 1-Propaneamine (D) N,N-Dimethylmethanamine

Q.29 Which of the following compound gives the smell of mustard oil-
(A) Alkyl isocyanate (B) Alkyl isothiocyanate
(C) Alkyl isocyanide (D) Alkyl isonitrile

Q.30 The odour of alkyl cyanides is similar to –
(A) Bitter almonds (B) Acid (C) Fruity smell (D) None

EXERCISE–II

Q.1 Reaction :

Primary amine + $CHCl_3$ + KOH $\xrightarrow{\quad}$ product, here product will be - **[AIEEE-2002]**

(A) Cyanide (B) Isocyanide (C) Amine (D) Alcohol

Q.2 The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is - **[AIEEE-2004]**

(A) $Fe_4[Fe(CN)_6]_3$ (B) $Na_3[Fe(CN)_6]$ (C) $Fe(CN)_3$ (D) $Na_4[Fe(CN)_5NOS]$

Q.3 Which one of the following methods is neither meant for the synthesis nor for separation of amines ? **[AIEEE-2005]**

(A) Hofmann method (B) Hinsberg method (C) Curtius reaction (D) Wurtz reaction

Q.4 Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as – **[AIEEE-2005]**

(A) an enamine (B) a Schiff's base (C) an amine (D)an imine

Q.5 In the chemical reaction, $CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow (A) + (B) + 3H_2O$, the compounds (A) and (B) are respectively – **[AIEEE-2007]**

(A) C_2H_5CN and 3KCl (B) $CH_3CH_2CONH_2$ and 3KCl

(C) C_2H_5NC and K_2CO_3 (D) C_2H_5NC and 3KCl

Q.6 The reaction

$CH_3Br + NH_3(\text{excess}) \xrightarrow{\text{heat}} CH_3NH_2 + HBr$

is an example of a–

(A) bimolecular electrophilic substitution reaction

(B) unimolecular nucleophilic substitution reaction

(C) bimolecular nucleophilic substituion reaction

(D) bimolecular free radical substitution reaction

Q.7 A secondary amine is a compound which possesses–

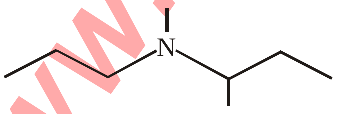
(A) two–NH_2 groups

(B) one–NH_2 group attached to a secondary carbon

(C) one–NH–group bonded to two alkyl or aryl groups

(D) one–NH_2 group attached to the second carbon of the main carbon chain

Q.8 The IUPAC name of the compound



is–

(A) N,3-dimethyl-N-propyl-3-propanamine (B) N-methyl-N-propyl-2-butanamine

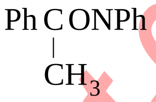
(C) s-butylmethyl-n-propylamine (D) N, 1-dimethyl-N-propyl-propanamine

Q.9 How many molecules of methyl bromide should react with ethylamine successively to convert the latter into a quaternary ammonium salt ?

(A) One (B) Two (C) Three (D) Four

Q.10 Which of the following compounds on hydrolysis yields a carboxylic acid and a secondary amine ?

(A) CH_3CH_2NC (B) $CH_3CONHCH_3$ (C) $PhNHCOCH_3$ (D)



$Ph\underset{\underset{CH_3}{|}}{C}ONPh$

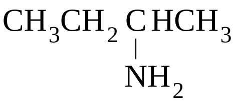
Q.11 The end product (B) formed in the reaction

$$CH_3CH_2Br \xrightarrow{AgCN} A \xrightarrow[H_3O^+]{1.\ NaOH,\ prolonged\ heat} B \text{ is–}$$

(A) $CH_3CH_2NHCH_3$ (B) $CH_3CH_2CH_2NH_2$ (C) $CH_3CH_2NH_2$ (D) CH_3CH_2NHCOH

Q.12 Which of the following compounds possesses a chiral nitrogen atom ?

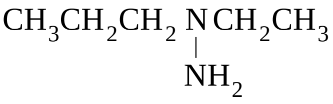
(A)



$CH_3CH_2\underset{\underset{NH_2}{|}}{C}HCH_3$

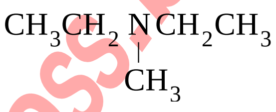
(B) $CH_3CH_2NHCH_2CH_3$

(C)



$CH_3CH_2CH_2\underset{\underset{NH_2}{|}}{N}CH_2CH_3$

(D)



$CH_3CH_2\underset{\underset{CH_3}{|}}{N}CH_2CH_3$

Q.13 An amine (X) on being heated with an excess of methyl bromide produces diethyldimethylammonium bromide. The amine (X) is–

(A) $C_2H_5NH_2$ (B) $(C_2H_5)_2NH$ (C) $C_2H_5NHCH_3$ (D) $C_2H_5N(CH_3)_2$

Q.14 Which one of the following compounds will produce a water-insoluble yellow oily liquid of nitrosamine on reaction with $NaNO_2$ and dilute HCl at 0ºC ?

(A) Ethylamine (B) Methylamine (C) Diethylamine (D) Triethylamine

Q.15 Which of the following compounds will liberate CO_2 from $NaHCO_3$?

(A) CH_3CONH_2 (B) $CH_3CH_2NH_2$ (C) $CH_3NH_3^+Cl^-$ (D) $(CH_3)_4N^+OH^-$

Q.16 The reaction of $RCONH_2$ with a mixture of Br_2 and aqueous KOH gives RNH_2 as the main product. The intermediate(s) involved in this reaction is(are)–

(A) RCONHBr (B) $RCO\overset{-}{N}BrK^+$ (C) R–N=C=O (D) All of these

Q.17 The end product (B) formed in the reaction

$$CH_2{=}CH_2 \xrightarrow[2.\ KCN\ (excess)]{1.\ Br_2\ CCl_4} A \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4} B$$

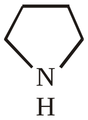
(A) $CH_2{=}CHCH_2NH_2$ (B) $H_2N(CH_2)_4NH_2$

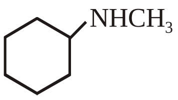
(C) $CH_3NH(CH_2)_2NHCH_3$ (D) $NC(CH_2)_2CN$

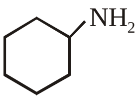
Q.18 In which of the following compounds are intermolecular hydrogen bonds not formed among its molecules ?

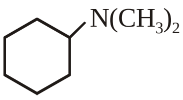
(A) $(C_2H_5)_2NH$ (B) C_2H_5OH (C) C_2H_5COOH (D) $(C_2H_5)_3N$

Q.19 Among the following compounds which one will produce a Schiff base on reaction with cyclohexanone?

(A) 

(B) 

(C) 

(D) 

Q.20 Which of the following reactions does not yield an amine ?

(A) $RX + NH_3 \rightarrow$

(B) $RCH{=}NOH \xrightarrow[C_2H_5OH]{Na}$

(C) $RCN + H_2O \xrightarrow{H^+}$

(D) $RCONH_2 \xrightarrow[2.\ H_2O]{1.\ LiAlH_4}$

Q.21 The product (A) and (B) of the reaction

$CH_3CH_2NH_2 + CH_3MgBr \rightarrow A + B$

are–

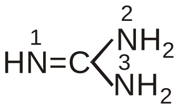
(A) $CH_3CH_2CH_3$ and NH_2MgBr

(B) $CH_3CH_2NHCH_3$ and $MgBr_2$

(C) $CH_3CH_2N(CH_3)_2$ and $MgBr_2$

(D) $CH_3CH_2NHMgBr$ and CH_4

Q.22 Which nitrogen is protonated readily in guanidine ?



(A) 1 (B) 2 (C) 3 (D) All of these

Q.23 Which of the following statements is not correct regarding ethylamine and aniline ?

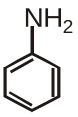
(A) Each has a $–NH_2$ group

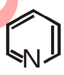
(B) Both dissolve in HCl

(C) Each reacts with a mixture of $CHCl_3$ and KOH to form a bad smelling compound

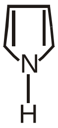
(D) Each reacts with HNO_2 to give a hydroxy compound

Q.24 Which of the following is most basic ?

(A) 

(B) 

(C) 

(D) 

Q.25 A compound (X) having the molecular formula C_3H_9N reacts with benzenesulphonyl chloride to form a solid that is insoluble in alkalis. The compound (X) is–

(A) $CH_3CH_2CH_2NH_2$

(B) $(CH_3)_2CHNH_2$

(C) $CH_3CH_2NHCH_3$

(D) $(CH_3)_3N$

Q.26 Which of the following may be prepared by Gabriel phthalimide synthesis ?

(A) Aliphatic amines (B) Aromatic amines (C) Aliphatic amides (D) Aromatic amides

Q.27 When an organic compound was treated with sodium nitrite and HCl in the ice-cold condition, nitrogen gas was evolved. The compound is :

(A) a nitro compound (B) a primary amine (C) a secondary amine (D) a tertiary amine

Q.28 Primary amines on being heated with CS_2 in the presence of $HgCl_2$ form alkyl/aryl isothiocyanates. The reaction is known as–

(A) Hofmann hypobromite reaction (B) Hofmann elimination reaction

(C) Hofmann-Martius reaction (D) Hofmann mustard oil reaction

Q.29 α-amino acids on heating with $Ba(OH)_2$ gives:

(A) Ba salt of acid (B) Amine (C) α-hydroxy acids (D) None of these

Q.30 $R–Cl + NH_3$ (excess) $\rightarrow$ (X) (major product), the major product (X) is a :

(A) 1° amine (B) 2° amine (C) 3° amine (D) 4° ammonium salt

ANSWER KEY

EXERCISE–I

Q.1	A	Q.2	A	Q.3	A	Q.4	B	Q.5	C	Q.6	A	Q.7	A
Q.8	D	Q.9	A	Q.10	B	Q.11	C	Q.12	D	Q.13	B	Q.14	B
Q.15	C	Q.16	B	Q.17	D	Q.18	B	Q.19	C	Q.20	C	Q.21	C
Q.22	C	Q.23	A	Q.24	A	Q.25	A	Q.26	C	Q.27	A	Q.28	A
Q.29	B	Q.30	A										

EXERCISE–II

Q.1	B	Q.2	A	Q.3	D	Q.4	A	Q.5	D	Q.6	C	Q.7	C
Q.8	B	Q.9	C	Q.10	D	Q.11	C	Q.12	C	Q.13	D	Q.14	C
Q.15	C	Q.16	D	Q.17	B	Q.18	D	Q.19	C	Q.20	C	Q.21	D
Q.22	A	Q.23	C	Q.24	C	Q.25	C	Q.26	C	Q.27	D	Q.28	D
Q.29	B	Q.30	A										

AROMATIC COMPOUNDS

Benzene

[i] Aromatic compounds contain high percentage of carbon. They burn with smoky flame,

[ii] Aromatic compounds have the cyclic system and contain $(4n + 2)\pi$ electrons [Huckel rule].
Where n = 0, 1, 2, 3, ...

Dipropylcyclopropenium perchlorate	$n = 0$	2π–electron
Benzene, pyridine, pyrrole, Furan, thiophen etc.	$n = 1$	6π–electron
Napthalene	$n = 2$	10π–electron
Anthracene	$n = 3$	14π–electron

Aromatic Compounds : Main Source

Bituminous coal when subjected to destructive distillation in the absence of air [1000º–1200ºC] the chief constituent obtained is coal tar.

Fractional distillation of coal tar : Different fractions are :

Fraction	Temperature	Main constituents
(a) Light oil	80 – 170ºC	Benzene, toluene, xylene etc.
(b) Middle oil (carbolic oil)	170º – 230ºC	Naphthalene, Phenol etc.
(c) Heavy oil	230º 270ºC	Cresols, naphthalene
(d) Green oil	270º – 360ºC	Anthracene

Benzene

[i] **Discoverer :** Michael Faraday

[ii] C–hybridisation : sp^2

[iii] Geometry – Hexagonal

[iv] Bond angle : 120º

[v] C–C Bond length : 1.39Å

[vi] C–H Bond length : 1.09 Å

Methods of Preparation of Benzene :

[1] Isolation From 'Light Oil Fraction – Industrial method :

[2] Decarboxylation of Sodium Benzoate – Laboratory Method :

Benzene is formed on dry distillation of sodium benzoate with soda lime.

$$C_6H_5COONa + NaOH \xrightarrow{\text{Dry distillation}} C_6H_6 + Na_2CO_3$$

[3] Reduction of Phenol : $C_6H_5OH + Zn \xrightarrow{\text{Dry distillation}} C_6H_6 + ZnO$

[4] Hydrolysis of Benzene sulphonic Acid : $C_6H_5SO_3H + H_2O\text{ (steam)} \xrightarrow[\text{dil.HCl}]{\Delta} C_6H_6 + H_2SO_4$

[5] Reduction of Benzenediazonium Chloride :

$$C_6H_5N_2Cl + C_2H_5OH \longrightarrow C_6H_6 + CH_3CHO + N_2 + HCl$$

Hypophoshorus acid (H_3PO_2) or sodium stannite ($SnCl_2$ + NaOH) or formic acid can also be used for reduction in place of ethanol.

$$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + H_3PO_3 + N_2 + HCl$$

$$C_6H_5N_2Cl + 2H \xrightarrow[NaOH]{SnCl_2} C_6H_6 + N_2 + HCl$$

$$C_6H_5N_2Cl + HCOOH \longrightarrow C_6H_6 + CO_2 + N_2 + HCl$$

[6] Hydrolysis of Phenylmagnesium bromide :

$$C_6H_5MgBr + H_2O \longrightarrow C_6H_6 + Mg(OH)Br$$

[7] Reduction of Chlorobenzene :

$$C_6H_5Cl + NaOH + 2H \xrightarrow{Ni/Al} C_6H_6 + NaCl + H_2O$$

[8] Trimerisation of Acetylene :

$$3C_2H_2 \xrightarrow[\text{In benzene}]{Ni(CO)_4+(C_6H_5)_3P} C_6H_6$$

[9] Hydroforming of n–Hexane :

$$CH_3(CH_2)_4CH_3 \xrightarrow[500^\circ]{\text{Heavy metal oxides}} C_6H_6 + 4H_2$$

Physical Properties :

Benzene is a colourless liquid (boiling point, 80º), having a characteristic smell. It forms a colourless crystaline solid (melting point, 5.4º) on cooling. It burns with smoky or sooty flame. It is lighter than water (relative density, 0.8790) and is immiscible with water. Being nonpolar in nature. It is miscible with many organic solvents, like alcohol ether, acetone, acetic acid, carbon tetrachloride, carbon disulphide, etc.

Reaction :

Benzene is a compound having very low reactivity, because it remains unaffected by many common reagents, like HCl, KOH, NaOH, $KMnO_4$, $K_2Cr_2O_7$, etc.

Benzene shows the following types of reactions :

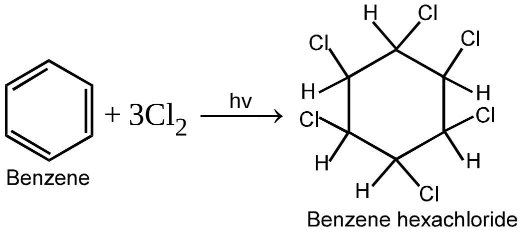
[a] Addition

[b] Electrophilic substitution

[c] Oxidation

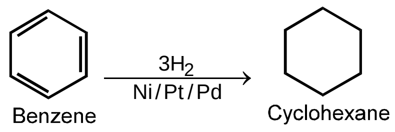
Addition Reaction :

1. Halogenation :

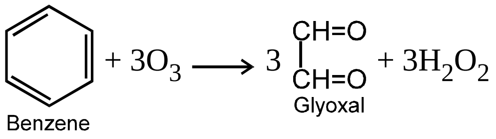


Benzene hexachloride is also known by many other names e.g., **B.H.C., gammaxene, gammane, lindane 666** (triple six) and **1,2,3,4,5,6–hexachlorocyclohexane.** It was found that the γ isomer is a very strong **insecticide** and **pesticide**, hence the names gammaxene and gammane.

2. Hydrogenation



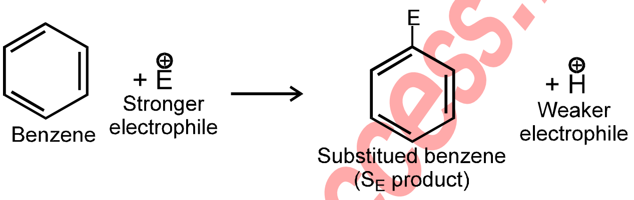
3. Ozonolysis :



$$3H_2O_2 + 3Zn \longrightarrow 3ZnO + 3H_2O$$

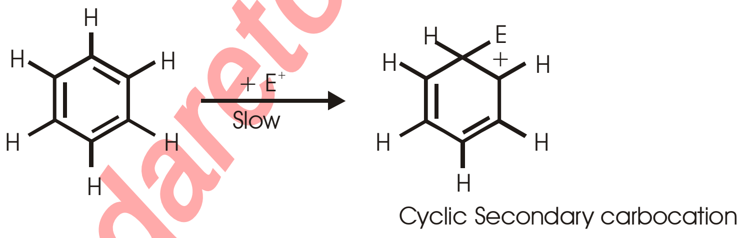
Electrophilic Substitution :

A continuous π cloud is spread above and below the benzene ring. Due to this, an electrophile is attracted towards the benzene ring. This electrophile removes proton (the weaker electrophile) and take its place in order to gain greater stability and forms an **electrophilic substitution product or SE product**. This process is called **aromatic electrophilic substitution**.

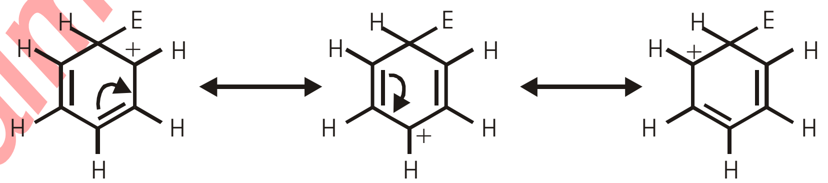


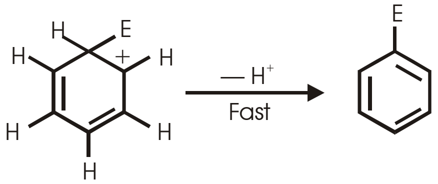
Nonaromatic intermediate carbocation formed in an aromatic electrophilic substitution reaction is known as **Wheland intermediate.**

Mechanism of Aromatic SE reaction :



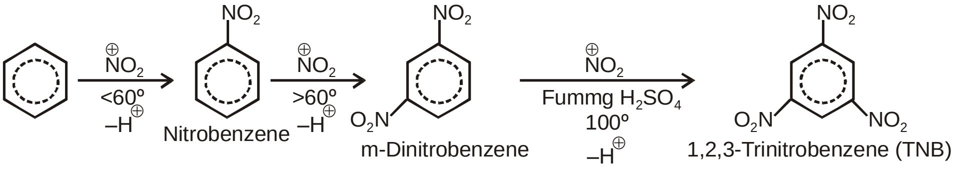
Cyclic secondary carboncation formed is established by resonance.





This is called as SE^2 mechanism i.e.; substitution electrophilic bimolecular reaction.

4. Nitration :



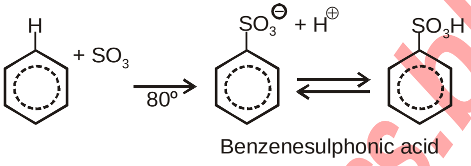
5. Halogenation :

$$\text{Cl–Cl} + \text{AlCl}_3 \longrightarrow \underset{\text{Chloronium ion}}{\overset{\oplus}{\text{Cl}}} + \text{Cl–}\overset{\ominus}{\text{AlCl}_3}$$

$$C_6H_5\text{–H} + \underset{\text{Electrophile}}{\overset{\oplus}{\text{Cl}}} \longrightarrow \underset{\text{Chlorobenzene}}{C_6H_5\text{–Cl}} + \overset{\oplus}{\text{H}}$$

6. Sulphonation :

$$\underset{\text{(Conc.)}}{H_2SO_4} \rightleftharpoons SO_3 + H_2O$$



7. Friedel–Crafts Reaction :

Friedel–Crafts reaction involves replacement of hydrogen atom of an aromatic ring by a carbocation species obtained from a compound in the presence of anhydrous aluminium chloride. Fridel–Crafts reaction is always carried out in nitrobenzene (boiling point. 211°) medium and in the presence of anhydrous $AlCl_3$.

[i] Friedel-Crafts Alkylation :

$$C_6H_6 + \underset{\text{Methyl chloride}}{CH_3 - Cl} \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\text{Toluene}}{C_6H_5 - CH_3} + HCl$$

$$C_6H_6 + C_2H_5 - Cl \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\text{Ethylbenzene}}{C_6H_5 - C_2H_5} + HCl$$

$$C_6H_6 + \underset{\text{n–Propyl chloride}}{CH_3CH_2CH_2 - Cl} \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\text{Cumene (67\%)}}{C_6H_5 - CH(CH_3)_2} + \underset{\text{n–Propylbenzene (33\%)}}{C_6H_6 - CH_2CH_2CH_3}$$

Note : A mixture of cumene and n–propylbenzene is also obtained on taking propylene in place of n–propyl chloride in the above reaction. because intermediate 1° carbocation rearrange to give 2° carbocation

$$2C_6H_6 + CH_2Cl_2 \xrightarrow[\text{AlCl}_3]{\text{Anhyd.}} \underset{\text{Diphenylmethane}}{C_6H_5 - CH_2 - C_6H_5} + 2HCl$$

$$3C_6H_6 + CHCl_3 \xrightarrow[\text{AlCl}_3]{\text{Anhyd.}} \underset{\text{Triphenylmethane}}{(C_6H_5)_3CH} + 3HCl$$

[ii] Friedel–Crafts Acylation : (reaction with acyl chloride)

[a] Acetylation :

$$C_6H_6 + \underset{\text{Acetyl chloride}}{ClCOCH_3} \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

$$C_6H_6 + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + CH_3COOH$$

[b] Benzoylation :

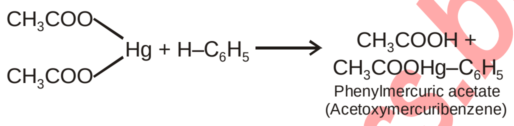
$$C_6H_6 + \underset{\text{Benzoyl chloride}}{ClCOC_6H_5} \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\text{benzophenone}}{C_6H_5COC_6H_5} + HCl$$

$$\underset{\substack{\text{Benzene}\\\text{(Excess)}}}{2C_6H_6} + \underset{\text{Phosgene}}{ClCOCl} \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + 2HCl$$

The above conversions can be carried out by taking many other compounds in place of anhydrous $AlCl_3$, e.g., $FeCl_3$, $FeBr_3$, $SnCl_2$, $ZnCl_2$, BF_3, etc.

8. Mercuration :

Benzene on heating with mercuric acetate forms **Acetoxymercuribenzene.**

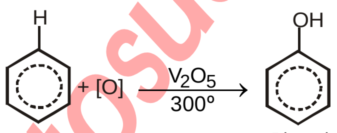


Oxidation :

9. Catalytic Air Oxidation :

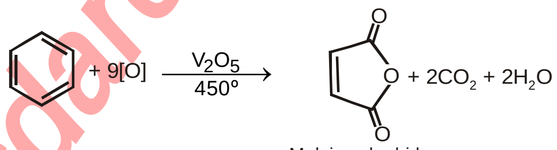
Oxidation of benzene by air in the presence of vanadium pentaoxide can be carried out as follows :

[i] At 300° – Phenol is obtained as the major product



Phenol

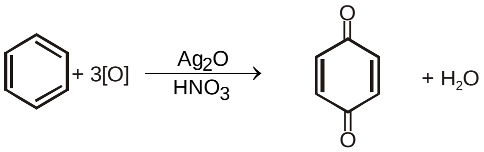
[ii] At 450° – Maleic anhydride is obtained as the major product.



Maleic anhydride

10. Silver Oxide Oxidation :

Mainly ***p*-benzoquinone** is formed when oxidation of benzene is carried out by silver oxide and HNO_3.



p-Benzoquinone

11. Combustion :

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

Catalytic Pyrolysis :

When the vapours of benzene are passed through red-hot copper or iron tube at 600º **biphenyl** is formed.

$$C_6H_5–H + H–C_6H_5 \longrightarrow C_6H_5–C_6H_5 + H_2$$

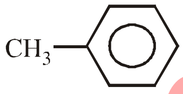
Uses of Benzene :

[1] As an industrial solvent.	[2] In dry cleaning.
[3] As a constituent of power alcohol.	[4] In the manufacture of an insecticide and pesticide.
[5] In the manufacture of an explosive.	[6] In the manufacture of dyes.
[7] In the manufacture of medicines.	[8] In the manufacture of perfumes.
[9] In the synthesis of many aromatic compounds.	[10] As a fuel.

TOLUENE

Toluene, $C_6H_5CH_3$

INTRODUCTION



(a) When a methyl group is directly attached with benzene ring, the compound is called Toluene.

(b) Toluene is a higher homologue of benzene.

(c) It can be obtained by the light oil obtained from distillation of 'Coal-tar'.

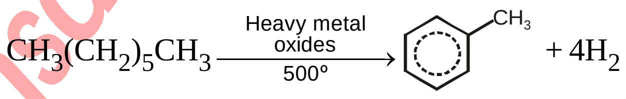
(d) Toluene is the compound, which is more reactive than benzene in chemical reactions.

Methods of Preparation

1. From 'Light Oil' Fraction – Industrial Method :

Toluene fraction can be collected by distillation at 110º after separation of benzene from 90% benzol.

2. By Hydroforming of *n*–Heptane :



3. By Dehydroxylation of Cresols :

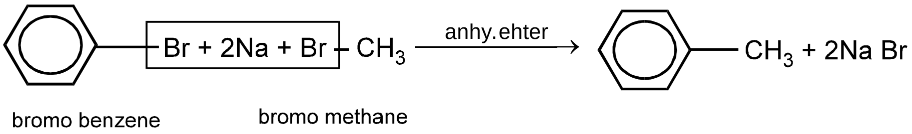
$$\underset{\text{Cresol (o, m or p)}}{CH_3 – C_6H_4 – OH} + Zn \xrightarrow{\text{Dry distillation}} CH_3–C_6H_5 + ZnO$$

4. By Friedel–Crafts Methylation of Benzene :

$$C_6H_5–H + Cl–CH_3 \xrightarrow{AlCl_3} C_6H_5–CH_3 + H–Cl$$

5. From Wurtz–Fitting reaction :–

A mixture of aryl & alkyl halide reacts in ether solution with sodium and forms toluene.



6. By Decarboxylation of Toluic Acids :

$$CH_3-C_6H_4-COONa + NaOH \xrightarrow[\text{Dry distillation}]{\text{CaO}} CH_3–C_6H_5 + Na_2CO_3$$

Sodium toluate
(o, m or p)

7 From Grignard's reagent :–

Phenyl magnesium iodide reacts with pure methyl iodide and forms toluene.

8. By Hydrolysis of Toluene Sulphonic Acids :

$$CH_3-C_6H_4-SO_3H + HOH \xrightarrow[\text{Conc. acid}]{\Delta} CH_3–C_6H_5 + H_2SO_4$$

Toluene sulphonic acids
(o, m or p)

9. By Reduction of Benzyl Chloride :

$$C_6H_5–CH_2Cl + 2H \longrightarrow C_6H_5–CH_3 + HCl$$

10. By Reduction of Toluenediazonium Chlorides :

$$CH_3-C_6H_4-N_2Cl + 2H \longrightarrow C_6H_5–CH_3 + N_2 + HCl$$

Toluenediazonium chlorides
(o, m or p)

Ethanol, hypophoshorous acid (H_3PO_2), sodium stannite ($SnCl_2$ + NaOH) or formic acid can be used as the reducing agents.

6.2 Physical Properties :

Toluene is a colourless liquid (boiling point 111°). It has benzene–like smell. It is lighter than water and immiscible with water. It is miscible with organic solvents, like alcohol, ether, benzene, etc. It also burns like benzene with smoky and sooty flame.

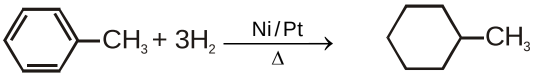
Chemical Propertes :

Toluene mainly gives four type of reactions :–

1. Addition reactions
2. Ring substitution reactions
3. Side chain substitution reaction
4. Oxidation reactions

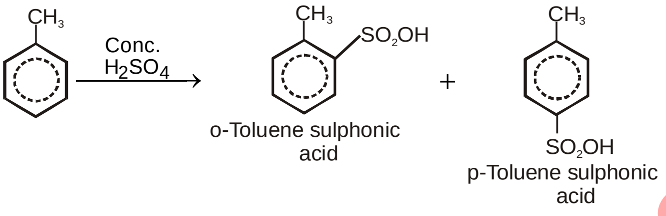
Addition reaction (Reactions Due to Benzene Nucleus):

1. Catalytic Hydrogenation :



Methylecyclohexane

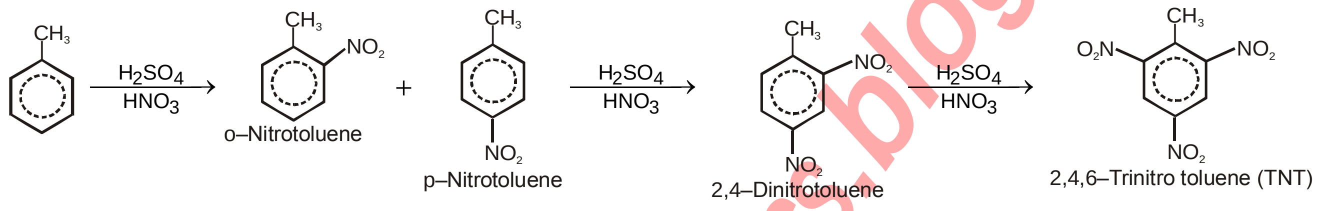
2. Sulphonation :



o-Toluene sulphonic acid

p-Toluene sulphonic acid

3. Nitration :



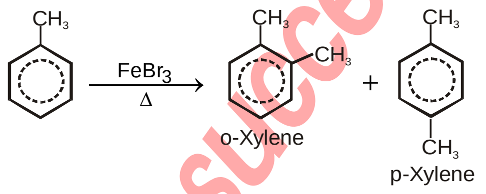
o–Nitrotoluene

p–Nitrotoluene

2,4–Dinitrotoluene

2,4,6–Trinitro toluene (TNT)

4. Alkylation :



o-Xylene

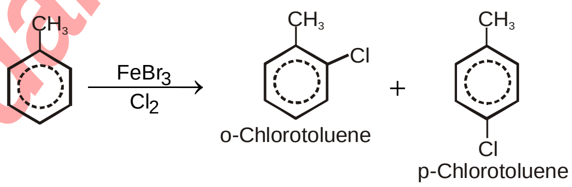
p-Xylene

5. Free Radical Nuclear Additive Chlorination :

$$C_6H_5CH_3 + 3Cl_2 \xrightarrow{hv} C_6H_5CH_3Cl_6$$

Toluene hexachloride

6. Nuclear Electrophilic Substitutive Chlorination :



o-Chlorotoluene

p-Chlorotoluene

Reactions Due to Methyl Side Chain :

7. Free Radical Side Chain Substitutive Chlorination :

$$C_6H_5{-}CH_3 \xrightarrow[110^\circ]{Cl_2} C_6H_5-CH_2Cl \xrightarrow[110^\circ]{Cl_2} C_6H_5-CHCl_2 \xrightarrow[110^\circ]{Cl_2} C_6H_5-CCl_3$$

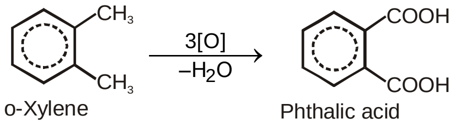
Benzyl chloride, Benzal chloride, Benzotrichloride

8. Oxidation :

Benzoic acid is obtained on oxidation of toluene by **alkaline permanganate** or **acidified dichromate** or **dilute nitric acid**.

$$C_6H_5{-}CH_3 \_ 3[O] \longrightarrow C_6H_5{-}COOH + H_2O$$

If more than one side chain is present, then the same number of COOH groups will be formed for example, phthalic acid is formed from o-xylene.



Reaction due to Whole Molecule :

9. Combustion :

$$C_6H_5–CH_3 + 9O_2 \longrightarrow 7CO_2 + 4H_2O$$

Uses :

[1] As a constituent of aviation gasoline.

[2] As a solvent.

[3] In the manufacutre of explosive.

[4] In the manufacture of dyes.

[5] In the manufacture of medicines.

[6] In the manufacture of perfumes.

[7] In the synthesis of many aromatic compounds.

PHENOL (C_6H_5OH)

Phenol is also known as carbolic acid or Benzenol or hydroxy benzene.

In phenol –OH group is attached to sp^2 – hybridised carbon

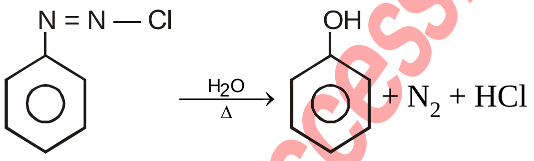
It was discovered by Runge in the middle oil fraction of coaltar distillation and named it carbolic acid (carbo = coal; oleum = oil)

It is also present in traces in human urine.

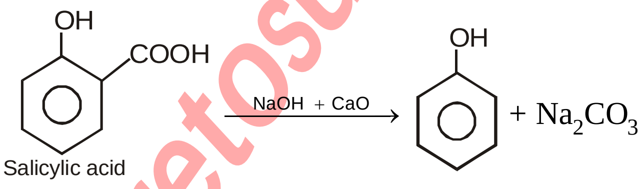
Methods of preparation :

[1] From Benzene sulphonic acid :
When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.
$C_6H_5SO_3Na + NaOH \rightarrow C_6H_5OH + Na_2SO_3$

[2] From benzene diazonium chloride :
When benzene diazonium chloride solution is warmed phenol is obtained with evolution of nitrogen.



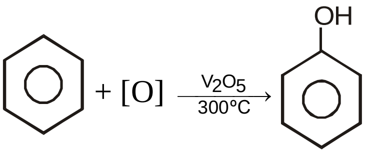
[3] By distilling a phenolic acid : with sodalime (decarboxylation) :



[4] From Gignard reagent : The grignard reagent on reaction with oxygen and subsequent hydrolysis by acid yields phenol

$C_6H_5MgBr \xrightarrow{[O]} C_6H_5OMgBr \xrightarrow{H_2O} C_6H_5OH + MgBrOH$

[5] From bezene :

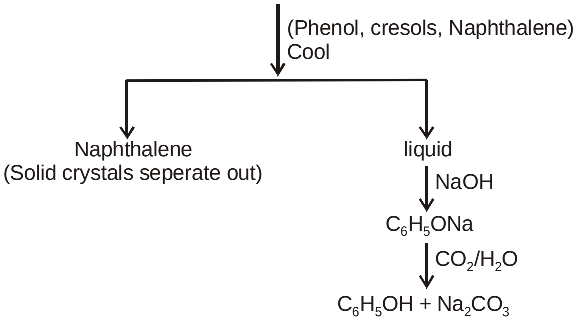


[6] Industrial preparation of phenol : Phenol can be prepared commercially by :

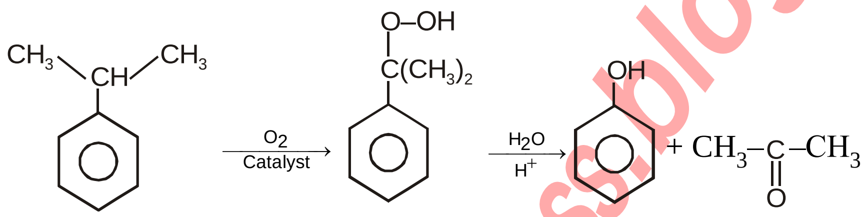
[a] Middle oil fraction of coaltar distillation
[b] Raschig process
[c] Dow's process
[d] Cumene

[a] Middle oil fraction of coaltar :

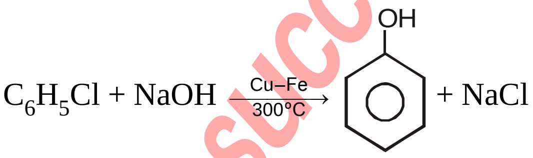
$$\text{Coaltar} \xrightarrow[\text{distillation}]{\text{Fractional}} \text{Middle oil } (172\text{–}230^\circ\text{ C})$$



[b] From cumene : (Isopropyl benzene) : Curmene is oxidised with oxygen in to cumene hydro peroxide in presence of a catalyst. This is decomposed by dil. H_2SO_4 in to phenol and acetone.

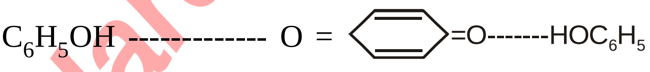


[c] Dow process : This process involves alkaline hydrolysis of chloro benzene



2. Physical Properties :

- Phenol is a colourless, hydroscopic crystalline solid.
- It attains pink colour on exposure to air and light.



Phenoquinone (Pink colour)

- It is poisonous in nature but acts as antiseptic and disinectant.
- Phenol is silghtly soluble in water, readily soluble in organic solvents.
- Solubility of phenol in water is much lower than alcohols because of larger hydrcarbon part in the molecule.
- Due to intermolecular H–Bonding, phenol has relatively high B.P. than the corresponding hydrocarbons, aryl halides etc.

3. Chemical properties : Chemical properties of phenol are classified in the following four categories.

1 Reactions of —H atom of —OH group.
2 Reactions of —OH group of phenol.
3 Reactions of Benzene ring.
4 Other Reactions.

1. **Reactions of —H atom of —OH group**

2. **Acidic Nature :** Phenol is a weak acid. The acidic nature of phenol due to formation of stable phenoxide ion in solution.

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H^+{}_3O$$

The phenoxide ion is stable due to resonance.

- The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion.
- Electron with drawing groups ($-NO_2$, –Cl) increase the acidity of phenol while electron releasing groups ($-CH_3$ etc.) decrease the acidity of phenol.
- Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.

The acidic nature of phenol is observed in the following :

[i] Phenol changes blue litmus to red.

[ii] Highly electron positive metals react with phenol.

$$2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$$

[iii] Phenol reacts with strong alkalies to form phenoxides

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

[vi] However phenol does not decompose Na_2CO_3 or $NaHCO_3$ because phenol is weaker acid than carbonic acid.

$$C_6H_5OH + Na_2CO_3 \text{ or } NaHCO_3 \rightarrow \text{No reaction}$$

Reaction due to –OH group :

[1] **Reaction with PCl_5 :** Phenol reacts with PCl_5 to form chloro benzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.

$$C_6H_5OH + PCl_5 \rightarrow C_6H_5Cl + POCl_3 + HCl$$

$$3C_6H_5OH + POCl_3 \rightarrow (C_6H_5)_3PO_4 \ \ 2HCl$$

[2] **Reaction with Zn dust :** When phenol is distilled with zinc dust benzene is obtained.

$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$$

[3] **Reaction with NH_3 :** Phenol reacts with NH_3 in presence of anhydrous $ZnCl_2$ to form aniline.

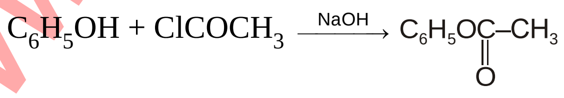
$$C_6H_5OH + NH_3 \xrightarrow{ZnCl_2} C_6H_5NH_2 + H_2O$$

[4] **Reaction with $FeCl_3$:** Phenol gives violet colouration with $FeCl_3$ solution (netural) due to formation of a complex.

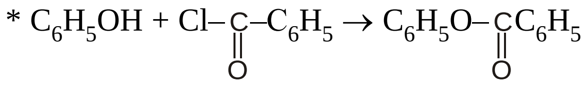
$$C_6H_5OH + FeCl_3 \rightarrow \text{Voilet colour}$$

* This reaction is used to differentiate phenol from alcohols.

[5] **Acetylation :** Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.



$$C_6H_5OH + ClCOCH_3 \xrightarrow{NaOH} C_6H_5O\overset{}{\underset{\underset{O}{\|}}{C}}-CH_3$$



$$* \; C_6H_5OH + Cl-\underset{\underset{O}{\|}}{C}-C_6H_5 \rightarrow C_6H_5O-\underset{\underset{O}{\|}}{C}C_6H_5$$

This reaction is called **Schotten–Baumann reaction.**

[6] **Ether Formation :** Phenol reacts with alkyl halides in alkali solution to form phenyl ethers.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa \xrightarrow[-NaX]{RX} C_6H_5OR$$

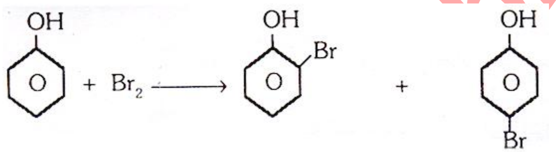
$$* \;\; C_6H_5OH + CH_2N_2 \longrightarrow C_6H_5OCH_3 + N_2\uparrow$$

[7] **Reaction with P_2S_5 :**

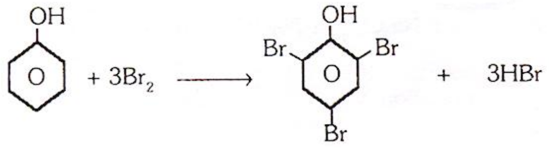
$$5C_6H_5OH + P_2S_5 \longrightarrow 5C_6H_5SH + P_2O_5$$

Reaction of Benzne Ring : The –OH group is ortho and para directing. It activates the benzene nucleus.

[1] **Halogenation :** Phenol reacts with bromine in CCl_4 to form mixture of o–and p–bromo phenol.

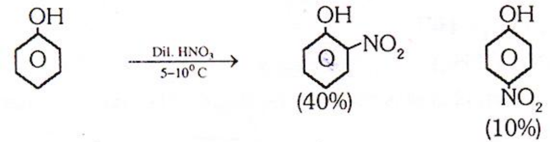


*Phenol reacts with bromine water to from a white ppt. of 2, 4, 6 tribromo phenol.

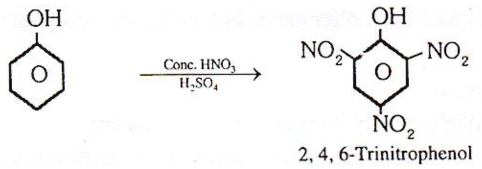


[2] **Nitration :**

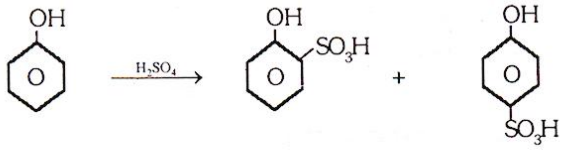
[a] Phenol reacts with dil. HNO_3 at 5–10ºC to form o– and p– nitro phenols.



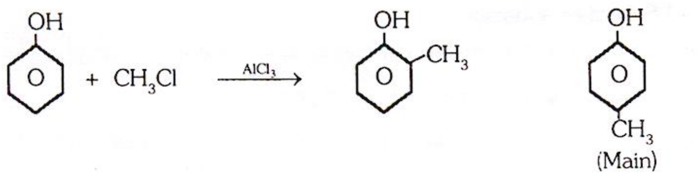
[b] When phenol is treated wtih conc. HNO_3 in presence of conc. H_2SO_4 2,4,6–trinitro phenol (picric acid) is formed.

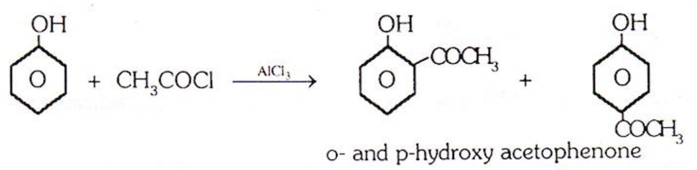


[3] **Sulphonation :** Phenol reacts with conc. H_2SO_4 to form mixture of o– and p– hydroxy benzene sulphonic acid.



[4] **Friedel–Craft's reaction :** Phenol when treated with methyl chloride in presence of anhydrous $AlCl_3$ p–cresol is main product.

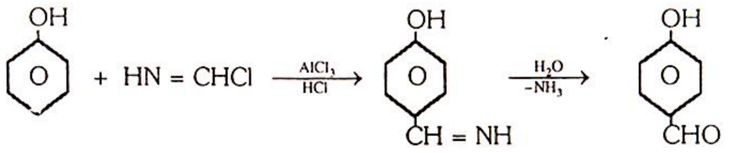




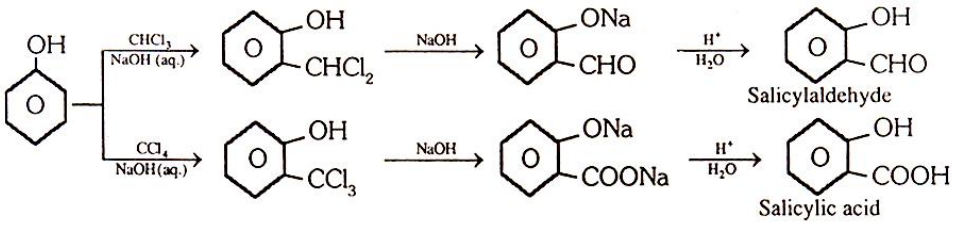
o- and p-hydroxy acetophenone

[5] **Gattermann aldehyde synthesis :** When phenol is treated with liquid HCN and HCl gas in presence of anhydrous $AlCl_3$ yields mainly p–hydroxy benzaldehyde.

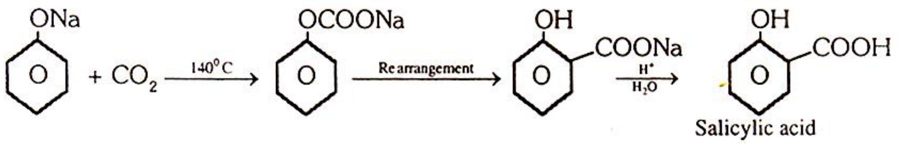
$$HCl + HCN \xrightarrow{AlCl_3} HN = CHCl$$



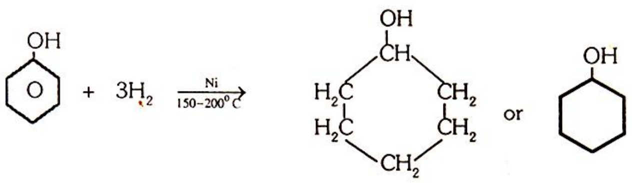
[6] **Reimer–Tiemann reaction :** Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o–hydroxy benzaldehyde. When CCl_4 is used salicylic acid is formed.



[7] **Kolbe's Schmidt reaction :** This involves the reaction of C_6H_5ONa with CO_2 at 140°C followed by acid hydrolysis salicylic acid is formed.

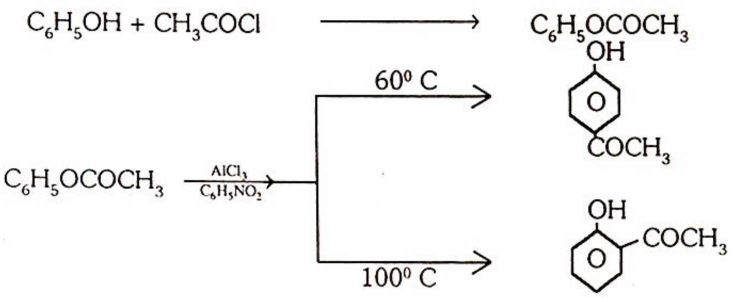


[8] **Hydrogenation :** Phenol when hydrogenated in presence of Ni at 150–200° C forms cyclohexanol.



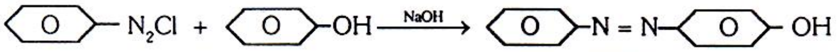
[9] Fries rearrangement reaction :

When phenyl ester is heated in nitrobenzene solution, in the presence of anhy. $AlCl_3$ then rearrangement takes place in which acyl group is transferred at o - & p-positions of phenolic group. Up to 60ºC, para product is obtained mainly and above 160ºC ortho products are obtained as major product.



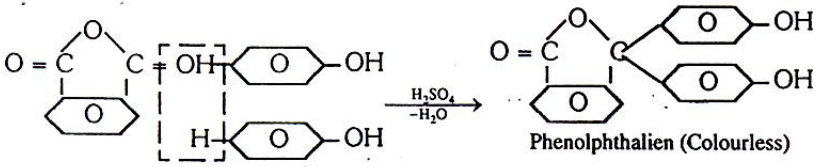
[10] Coupling reactions :

[a] Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye(p–hydroxy azobenzene)



p-hydroxy azobenzene (Orange dye)

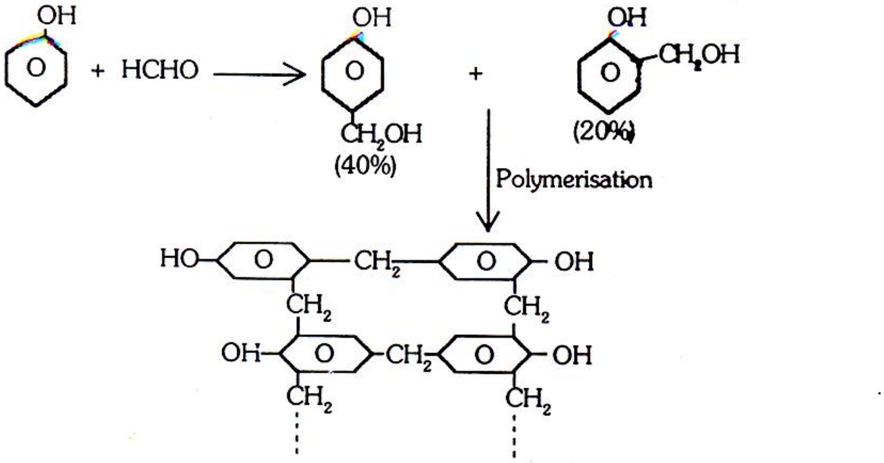
[b] Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form a dye (phenolphthalien)



Phenolphthalien (Colourless)

[11] Condensation with formaldehyde :

Condensation with formaldehyde : Phenol condenses with HCHO (excess) in presence of NaOH to form a polymer known as bakelite.

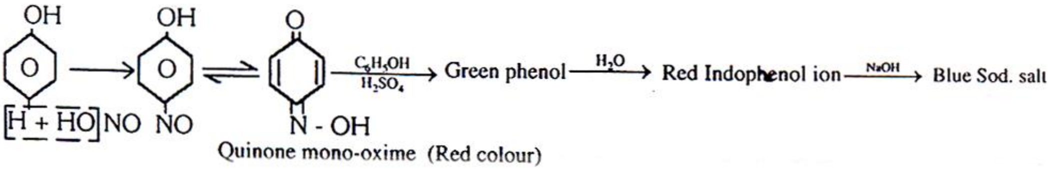


Polymer bakelite (Phenol formaldehyde resin)

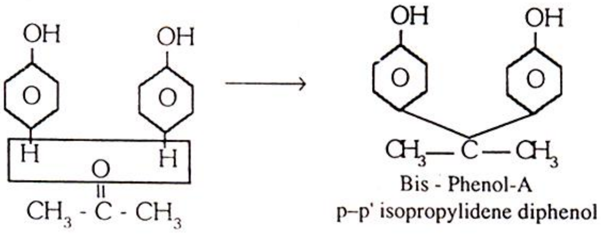
[12] **Liberman's nitroso reaction :** When phenol is reacted with $NaNO_2$ and conc. H_2SO_4 it gives a deep green or blue colour which changes to red on dilution with water. When made alkaline with NaOH original green or blue colour is restored.

The reaction is used as a test of phenol.

$$2NaNO_2 + H_2SO_4 \longrightarrow 2HNO_2 + Na_2SO_4$$

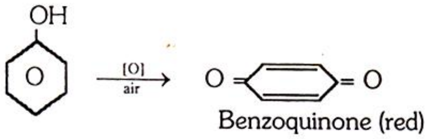


[13] **Reaction with acetone :**

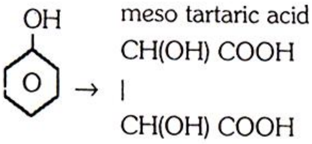


[14] **Oxidation :**

[1] In presence of air :



[2] $KMnO_4$:



Test of Phenol :

[1] Phenol turns blue litmus to red.

[2] Aqueous solution of phenol gives a violet colour with a drop of ferric chloride.

[3] Phenol gives Lieber mann's nitroso test.

$$\text{Phenol in conc. } H_2SO_4 \xrightarrow[\text{excess of water}]{NaNO_2} \text{Red colour} \xrightarrow{\text{NaOH excess}} \text{Blue colour}$$

[4] Aqueous solution of phenol gives a white ppt. of 2,4,6 tribromophenol with bromine water.

[5] Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali.

[6] With ammonia and sodium hypochlorite, phenol gives blue colour.

Differences between phenol and alcohol (C_2H_5OH) :

[1] Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.

[2] Phenol gives violet colour with $FeCl_3$ while aliphatic alcohol does not give.

[3] Phenol gives triphenyl phosphate with PCl_5 while aliphatic alcohol gives alkyl chloride.

[4] Phenol has phenolic odour whereas alcohol has pleasent odour.

[5] Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

Uses of Phenol :

Phenol is used :

[1] As an antiseptic in soaps and lotions.

[2] In manufacutre of azodyes, phenolphthalein, picirc acid (explosive), cyclohexanol (Solvent for rubber), plastic (bakelite) etc.

[3] In manufacture of drugs like aspirin salol, phenacetin etc.

[4] As preservation for ink.

	Test/ Reaction	**Alcohol**	**Phenol**
1	Litmus test	No reaction	Blue litmus red
2	$FeCl_3$ solution	No reaction	Violet colour
3	Benzene diazonium salt	No reaction	Yellow or orange azo dye
4	Br_2 water	No reaction	2,4, 6 -tribromophenol

BENZALDEHYDE

Benzaldehyde, C_6H_5CHO, Oil of bitter Almonds

Benzaldehyde is present in the form of glucoside called amygdalin in bitter almonds. One molecule of amygdalin is composed of one molecule of benzaldehyde, two molecules of glucose and one cyano groups bonded to one another. Banzaldehyde is obtained on hydrolysis of amygdalin by dilute acid or by an enzyme emulase.

Method of Preparation

[1] **By Oxidation of Benzyl Alcohol :** Benzaldehyde is obtained on oxidation of benzyl aclohol by dilutre nitric acid

$$C_6H_5CH_2OH + [O] \xrightarrow{\text{Dil. } HNO_3} C_6H_5CHO + H_2O$$

[2] **By Catalytic Dehydrogenation of Benzyl Alcohol :** Benzaldehyde is obtained on passing benzyl alcohol vapour over copper catalyst or zinc oxide heated to 300°.

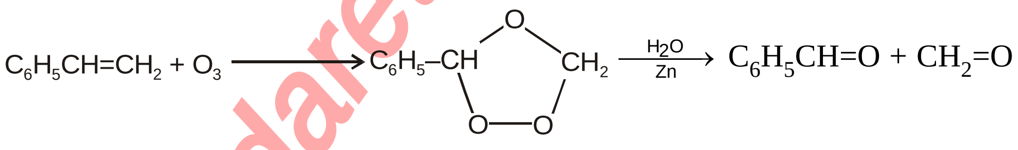
$$C_6H_5CH_2OH \xrightarrow[300°]{\text{Cu or ZnO}} C_6H_5CHO + H_2$$

[3] **By Alkaline Hydrolysis of Benzal Chloride :** Benzaldehyde is obtained by hydrolysis of benzal chloride, i.e., benzylidine chloride using dilute alkali.

$$C_6H_5CHCl_2 + 2KOH \longrightarrow \underset{\text{Unstable}}{[C_6H_5CH(OH)_2]} + 2KCl$$

$$[C_6H_5CH(OH)_2] \longrightarrow C_6H_5CHO + H_2O$$

[4] **By Ozonolysis of Styrene :** A mixture of benzaldehyde and formaldehyde is obtained on ozonolysis of styrene.



Styrene ozonide

[5] **By Dry Distillation of Calcium Salts of Acids :** Benzaldehyde can be obtained by dry distillation of a mixture of calcium benzoate and calcium formate taken in equimolar ratio.

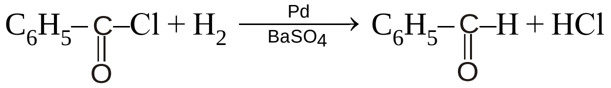
$$(C_6H_5COO)_2Ca + (HCOO)_2Ca \longrightarrow 2C_6H_5CHO + 2CaCO_3$$

Barium salts can also be used in place of calcium salts of carboxylic acids.

[6] **By Grignard's Reagent :** Banzaldehyde is formed by the reaction of phenylmagnesium bromide with ethyl formate :

$$C_6H_5\text{–}MgBr + EtO\text{–}\underset{\underset{O}{\|}}{C}\text{–}H \longrightarrow C_6H_5\text{–}\underset{\underset{O}{\|}}{C}\text{–}H + EtO\text{–}MgBr$$

[7] By Rosenmund's Reaction : Benzaldehyde is formed by the reduction of benzoyl chloride in the presence of palladised barium sulphate.



$$C_6H_5-\underset{\underset{O}{\|}}{C}-Cl + H_2 \xrightarrow[BaSO_4]{Pd} C_6H_5-\underset{\underset{O}{\|}}{C}-H + HCl$$

[8] By Stephen's Reaction : Benzaldehyde is obtained on reduction of benzaldimine, which is formed on reduction of benzonitrile (cyanobenzene) by stannous chloride and conc. HCl in ethereal solution.

$$C_6H_5-C\equiv N + 2H \longrightarrow \underset{\text{Benzaldimine}}{C_6H_5-CH=NH} \longrightarrow C_6H_5-CH=O$$

[9] By Oxidation of Benzyl Chloride : Slow oxidation of benzyl chloride takes place on passing a stream of carbon dioxide through the aqueous solution of copper nitrate or lead nitrate and benzaldehyde is formed.

$$C_6H_5CH_2Cl \xrightarrow[CO_2]{H_2O} C_6H_5CH_2OH \xrightarrow[\text{or } Pb(NO_3)_2]{Cu(NO_3)_2} C_6H_5CHO$$

[10] By Sommelet Reaction of Benzyl Chloride : Benzyl chloride is refluxed with urotropine in aqueous alcoholic solution, when a product is formed. This product is subjected to hydrolysis by steam–distillation after adding small amount of an acid, when benzaldehyde is obtained.

$$C_6H_5CH_2Cl + (CH_2)_6N_4 \xrightarrow[EtOH]{H_2O} \{C_6H_5CH_2(CH_2)_6N_4\}^+ \; Cl^- \xrightarrow{H^+} [C_6H_5CH_2-N=CH_2] \longrightarrow$$

$$C_6H_5CH=N-CH_3(\text{N–Methylbenzaldimine}) \xrightarrow[\text{Distillation}]{H_3O^+} C_6H_5CH=O$$

[11] By Gattermann Aldehyde Synthesis : Benzaldehyde can also be obtained by heating benzene, HCN and HCl in the presence of anhydrous $AlCl_3$.

$$C_6H_5H + [HCN + HCl] \longrightarrow C_6H_5CH=NH + HCl$$

$$C_6H_5CH=NH \xrightarrow{H_2O} C_6H_5CH=O$$

Physical Properties

Benzaldehyde is a colourless, volatile oily liquid (boiling point 179°) having characteristic odour of bitter almonds. It is miscible with organic liquids, like alcohol, ether, *etc.*, and immiscible with water. Its solubility in water is very low. It is poisonous and volatile in steam.

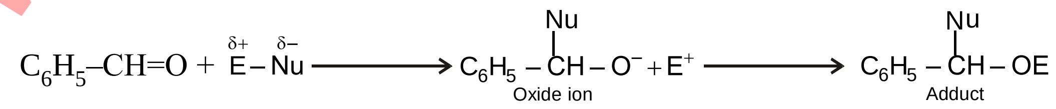
Reaction : Benzaldehyde gives the following two types of reactions.

[A] Reactions due to aldehyde group

[B] Reactions due to benzene ring

[A] Necleophilic Addition on Aldehyde group :

Nucleophilic addition on -CHO group in benzaldehyde takes place as follows.



$$C_6H_5-CH=O + \overset{\delta+}{E}-\overset{\delta-}{Nu} \longrightarrow \underset{\text{Oxide ion}}{C_6H_5-\overset{\overset{Nu}{|}}{C}H-O^-} + E^+ \longrightarrow \underset{\text{Adduct}}{C_6H_5-\overset{\overset{Nu}{|}}{C}H-OE}$$

[B] Electrophilic Substitution Reactions Due to Benzene Ring :

Aldehyde group bonded to the benzene ring is deactivating and meta-directing group due to strong negative mesomeric effect (-M effect). Therefore, the attack of an electrophile on aromatic ring of benzaldehyde takes Place at slower rate as compared to unsubstituted benzene. and *m*- S_E substitution product is formed under strong conditions, *i.e.*, not easily.

[A] Reaction Due to Aldehyde Group :

[1] **Reduction :** Benzyl alcohol is formed on reuction of benzaldehyde by sodium amalgam + HCl or Zn + HCl.

$$C_6H_5CHO + 2H \longrightarrow C_6H_5CH_2OH$$

[2] **Oxidation :** Benzoic acid is formed by slow auto-oxidation of benzaldehyde in the presence of air and light. Other oxidants bring about oxidation very fast.

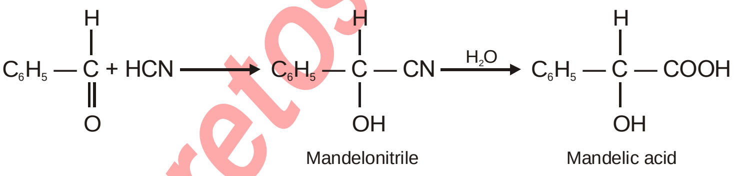
$$C_6H_5CHO + [O] \longrightarrow C_6H_5COOH$$

Due to its easy oxidation, benzaldehyde behaves a s reducing agent. However. It is weaker reducing agent as compared to aliphatic aldehydes. It restores pink colour of Schiff's reagent, gives white precipitate turning grey with mercuric chloride solution, and it reduces silver ions of Tollen reagent, i.e., ammoniacal silver nitrate solution to metallic silver. But it does not give red precipitate of cuprous oxide with Fehling's solution and Benedict's solution due to strong steric hindrance of benzene ring.

[3] **With Sodium Bisulphite :** The reaction of sodium bisulphite with benzaldehyde gives benzaldehyde-sodium bisulphite adduct, which is a white crystalline solid.

$$C_6H_5CHO + NaHSO_3 \longrightarrow C_6H_5CH(OH)SO_3Na$$

[4] **With Hydrogen Cyanide :** Mandelic acid is obtained on hydrolysis of mandelonitrile i.e., benzaldehyde cyanohydrin, formed by addition of hydrogen cyanide on benzaldehyde.



[5] **With Alcohols :** An aromatic acetal is obtained on heating a mixture of benzaldehyde and alcohol in the presence of dry HCl gas.

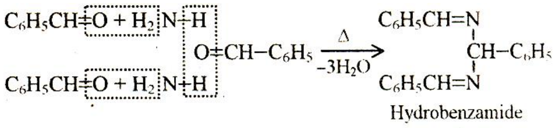
$$C_6H_5CHO + 2HOC_2H_5 \xrightarrow{\text{Dry HCl gas}} C_6H_5CH(OC_2H_5)_2 + H_2O$$

The above aromatic acetal obtained from benzaldehyde and ethanol is called phenytal.

[6] **With Thiols :** Aromatic thioacetals are formed by reacting benzaldehyde and thioalcohols in the presence of dry HCl gas.

$$C_6H_5CHO + 2HSC_2H_5 \xrightarrow{\text{Dry HCl gas}} C_6H_5CH(SC_2H_5)_2 + H_2O$$

[7] **With Ammonia :** On heating benzaldehyde with ammonia a complex compound called hydrobenzamide is formed.



[8] With Primary Amines : Schifff's bases are formed on heating benzaldehyde with primary amines. The reaction of benzaldehyde and aniline gives a Schiff's base, named benzlideneaniline or benzalaniline of N–phenylbenzaldimine.

$$C_6H_5\text{–}CH{=}O + H_2N\text{–}C_6H_5 \xrightarrow{\Delta} \underset{\text{benzylideneaniline}}{C_6H_5-CH=N-C_6H_5} + H_2O$$

[9] With Hydroxylamine : Benzaldoxime is formed by the reaction of benzaldehyde and NH_2OH.

$$C_6H_5\text{–}CH{=}O + H_2N\text{–}OH \longrightarrow \underset{\text{Benzaldoxime}}{C_6H_5-CH=N-OH} + H_2O$$

[10] With Hydrazine : Benzladehydehydrazone is formed by the reaction of benaldehyde and NH_2NH_2.

$$C_6H_5\text{–}CH{=}O + H_2N\text{–}NH_2 \longrightarrow \underset{\text{Benzaldehydehydrazone}}{C_6H_5-CH=N-NH_2} + H_2O$$

[11] With Phenylhydrazine : The reaction of benzladehyde and $C_6H_5NHNH_2$ gives benzaldehydephenylhydrazone.

$$C_6H_5CH{=}O + H_2N\text{–}NHC_6H_5 \longrightarrow \underset{\text{benzaldehydephenylhydrazone}}{C_6H_5CH=N-NHC_6H_5} + H_2O$$

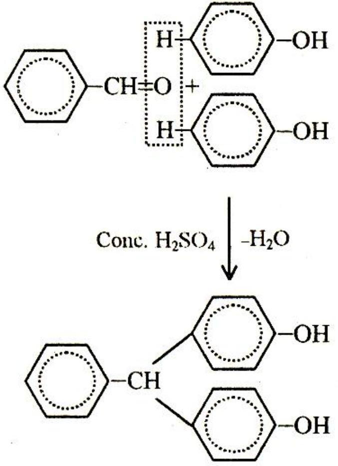
[12] With Semicarbazide : The reaction of benzaldehyde and semicarbazide gives benzaldehyde semicarbazone.

$$C_6H_5\text{–}CH{=}O + H_2N\text{–}NH\text{–}CO\text{–}NH_2 \longrightarrow \underset{\text{Benaldehyde semicarbzaone}}{C_6H_5-CH=N-NH-CO-NH_2} + H_2O$$

[13] With Phosphorus Pentachloride : Benzaldehyde reacts with PCl_5 to form benzal chloride, which is also called benzylidene dichloride.

$$C_6H_5\text{–}CH{=}O + PCl_5 \longrightarrow C_6H_5\text{–}CHCl_2 + POCl_3$$

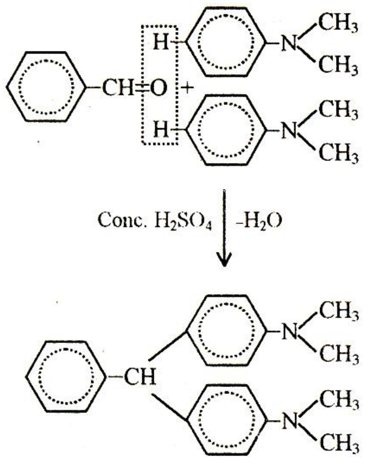
[14] With Phenol :



p.p'–Dihydroxytriphenylmethane

The above product is a triphenylmethan dye :

[15] **With N,N–Dimethylaniline :** If the reaction of benzldehyde and N,N–dimethylaniline is carried out in the presence of a few drops of conc. H_2SO_4 or anhydrous $ZnCl_2$, then a green coloured triphenylmethyl dye, called Malachite green is obtained.

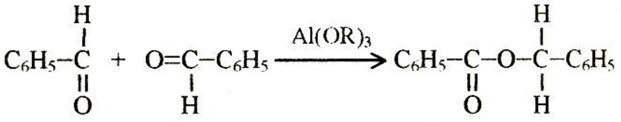


Malachite green
(p.p'–Bis–[dimethylamino]triphenylmethane)

[16] **Cannizzaro's Reaction :** Due to absece of α hydrogen atom in benzaldehyde, oxidation of one molecule to benzoate ion and reduction of the second molecule to benzyl alcohol takes place on adding strong solution of caustic alkali at room temperature

$$2C_6H_5CHO + OH^- \longrightarrow C_6H_5COO^- + C_6H_5CH_2OH$$

[17] **Tischenko Reaction :** When benzaldehyde is heated in the presence of an aluminium alkoxide (ethoxide, isopropoxide, etc.) taken in an inert solvent (CCl_4, xylene, etc.), benzyl benzoate is formed by bimolecular addition.



$$C_6H_5-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{\|}}{C}} + O=\underset{\underset{\displaystyle H}{|}}{C}-C_6H_5 \xrightarrow{Al(OR)_3} C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C_6H_5$$

Benzyl benzoate

[18] **Benzoin Condensation :** When benzaldehyde is heated with aqueous alcoholic KCN solution, a ketonic secondary alcohol, benzoin is formed by bimolecular condensation.

$$C_6H_5CHO + C_6H_5CHO \xrightarrow[H_2O,\,EtOH,\,\Delta]{KCN} C_6H_5COCH(OH)C_6H_5$$

On Oxidation of benzoin with conc. nitric acid, the secondary alcohol group is converted to a ketone group and a diketone, called benzil is formed.

$$C_6H_5COCHOHC_6H_5 + [O] \xrightarrow{\text{Conc.}HNO_3} C_6H_5COCOC_6H_5\ (\text{Benzil}) + H_2O$$

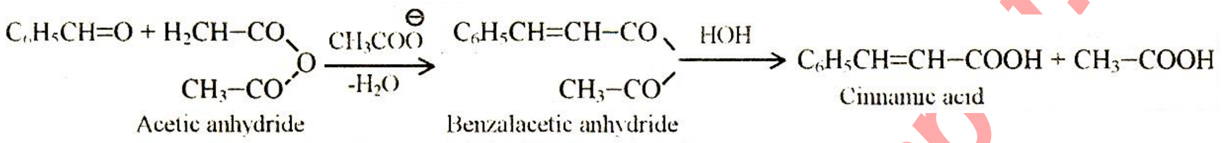
[19] **Claisen Reaction :** An α, β–unsaturated aldehyde (or ketone) is formed on the condensation of benzaldehyde with an aldehyde (or a ketone) having at least two α hydrogen atoms, in the presence of dilute alkali cinnamaldehyde is obtained on the condensation of benzaldehyde with acetaldehyde.

$$C_6H_5CH=O + H_2CH–CHO \longrightarrow \underset{\text{Cinnamaldehyde}}{C_6H_5CH=CH-CHO} + H_2O$$

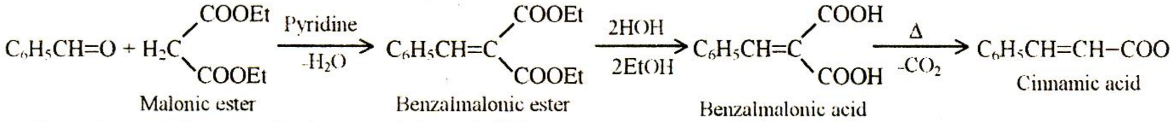
Benzalacetone, i.e. benzlideneacetone is obtained on condensation of benzaldehyde with acetone.

$$C_6H_5CH{=}O + H_2CHCOCH_3 \xrightarrow{\text{Dil. alkali}} \underset{\text{Benzalacetone}}{C_6H_5CH = CHCOCH_3} + H_2O$$

[20] Perkin's Reaction : When benzaldehyde is heated at 180° with an anhydride and the sodium salt of a carboxylic acid, then an unsaturated carboxylic acid is formed. For example, Cinnamic acid is obtained on the reaction of acetic anhydride and sodium acetate on benzaldehyde.

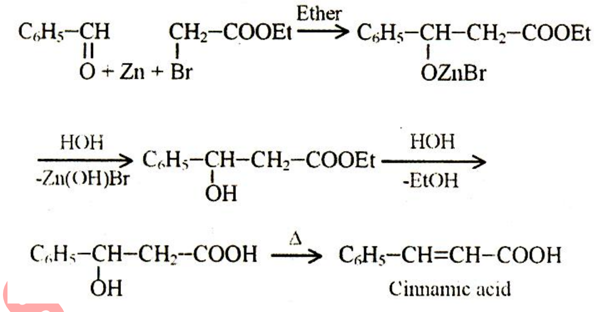


[21] Knoevenagel Reaction : When benzaldehyde is heated with malonic ester in the presence of pyridine. then cinnamic acid is formed in the following steps.



Malonic ester contains one reactive methylene group. whose two reactive hydrogen atoms take away the oxygen atom from benzaldehyde to form a water molecule. A reactive methylene group is present between two strongly electronattracting groups (like CO. CN. *etc.*), due to which the hydrogen atoms of methylene group acquire a tendency of getting released in the form of protons.

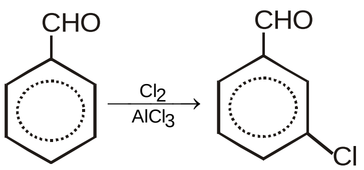
[22] Reformatsky Reaction : When benzaldehyde is reacted with bromoacetic ester in the presence of zinc in dry ether. then cinnamic acid is obtained in the following steps.



[B] Reactions Due to Benzene Ring :

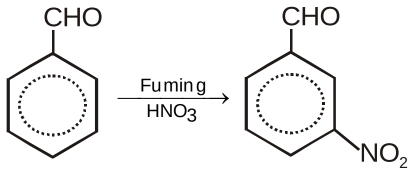
Benzaldehyde gives the following S_E reactions.

[23] Halogenation : m–Chlorobenzaldehyde (or m–Bromobenzaldehyde) is formed on heating benzaldehyde with chlorine (or bromine) in the presence of $AlCl_3$.

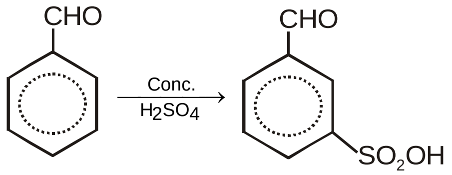


[24] Nitration :

m–Nitrobenzaldehyde is formed on nitration of benzaldehyde by fuming nitric acid.



[25] Sulphonation : Benzaldehyde undergoes sulphonation on heating with conc. sulphuric acid to form m–formylbenzensulphonic acid.



[26] Friedel–Crafts Reaction : It should be noted that due to strong deactivation of benzene ring in benzaldehyde. Friedel–Crafts reaction does not take place.

USES : Benzaldehyde is used

[1] As a deodorant.

[2] In the manufacture of synthetic dyes, and

[3] In the synthesis of many aromatic compounds.

Some Important Point :

Uses :

S.No.	Formaldehyde	Acetaldehyde	Acetone
1	Disinfectant and preservative for biological specimens. (formalin)	In the preparation of dyes polish, varnishes	Solvent for cellulose,
2	Urotropine, a urinary antiseptic	In the manufacture of ethanol, acetic acid, synthetic rubber etc.	In the preparation of sulphonals (hypotic)
3	Formamint, for throat treatment (formalin + lactose)	For the preparation of metaldehyde (a solid fuel)	In the preparation of chlororform, iodoform

Distinction between Aldehydes and Ketones :

Test	Aldehyde	Ketone
Schiff's reagent	Pink colour	X
Tollen's reagent	Silver mirror	X
Fehling Solution	Red ppt.	X
NaOH solution	Brown resin	X
Mercuric chloride	Black ppt.	X

NITRO BENZENE

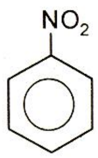
1 Introduction :

[a] Aromatic nitro compounds are obtained when hydrogen atom or atoms are of aromatic compound replaced by $-NO_2$ (nitro) group.

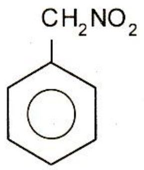
[b] Aromatic nitro compound are of two types.

[i] Those compounds in which nitro group is attached directly to the benzene ring eg. nitrobenzene.

[ii] Those compounds, in which nitro group is attached to a side chain which is directly attached to the benzne ring.



I
(nitro benzene)



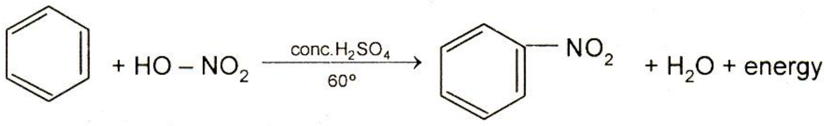
II
(phenyl nitromethane)

[c] Nitrobenzene is also called as 'oil of mirbane' or 'artifical oil of bitter almond's.

[d] If has a smell similar to benzaldehyde.

2. Methods of Preparation :

From Benzene (Nitration) :



vap. phase

Note :

[i] The reaction species is $^+NO_2$ (nitronium ion)

[ii] The above reaction is lab method of nitrobenzene preparation.

3. Physical Properties :

[a] It is yellowish, oily liquid, insoluble in water and soluble in organic solvents.

[b] It has odour like bitter almonds.

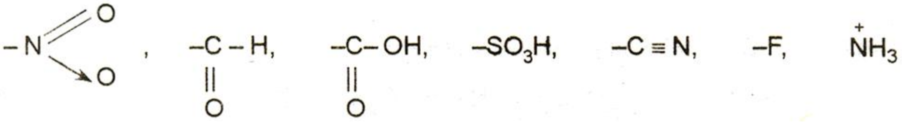
[c] It is steam volatile and poisonous in nature.

[d] Its boiling point is 211°C.

4. Resonance in nitrobenzene :

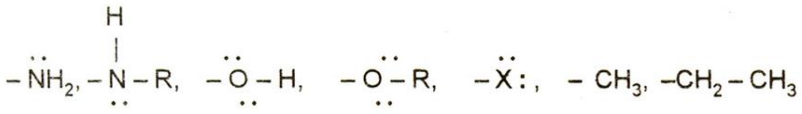
[a] The groups which can attract the electron from benzene ring or deactivate the benzene ring or make electron dificient to the benzene ring or shows –I effect or shows –M effect or –R effect are called as meta directing groups. They do not show Friedel Craft reaction.

eg.



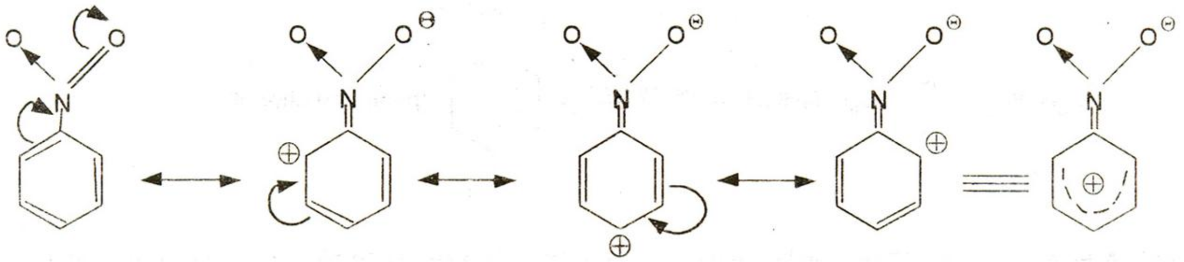
$-N\overset{O}{\underset{O}{\lessgtr}}$, $-\underset{\underset{O}{\|}}{C}-H$, $-\underset{\underset{O}{\|}}{C}-OH$, $-SO_3H$, $-C\equiv N$, $-F$, $\overset{+}{N}H_3$

[b] The group which can donate the electron to the benzene ring or activate the benzene ring or make electron efficient to the benzene ring or shows + I effect of + M or +R effect are always ortho and para directing groups.

eg.  etc.

$-\ddot{N}H_2, -\overset{H}{\overset{|}{\ddot{N}}}-R, -\ddot{O}-H, -\ddot{O}-R, -\ddot{X}:, -CH_3, -CH_2-CH_3$ etc.

[c] Resonating structures of nitrobenzene.



It is evident from the above structures that ortho and para positions are electron deficient and attacking electrophilie is also electron deficient, so it does not attack on ortho and para positions but attacks at meta position.

5. **Chemical Reactions :** Chemical reaction of nitrobenzene are classified in three groups as follows :

1. Reaction of $-NO_2$ group
2. Reaction of Benzene ring
3. Other reactions

1 **Reaction of $-NO_2$ group :**

Readuction :

[a] **Acidic medium :**

Reagents : Sn/HCl or $SnCl_2$/HCl or Zn/CH_3COOH etc.

$$C_6H_5NO_2 \xrightarrow{+6H} C_6H_5NH_2 + 2H_2O$$

aniline

Propbale intermediate steps :

$$C_6H_5{-}NO_2 \xrightarrow[-H_2O]{+2H} C_6H_5NO \xrightarrow{+2H} C_6H_5NHOH \xrightarrow[-H_2O]{+2H} C_6H_5NH_2$$

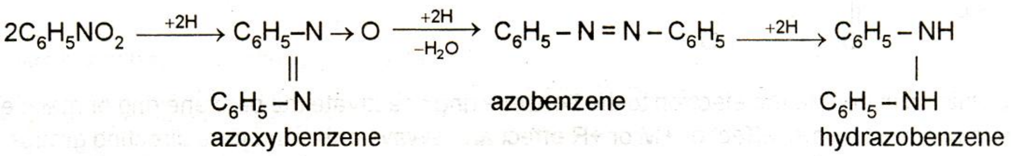
nitrosobenzene phenyl hydroxylamine aniline

[b] Neutral Medium : Reagents : Zn/NH_4Cl or Zn/$CaCl_2$ or Al–Hg/NH_4Cl etc.

$$C_6H_5NO_2 \xrightarrow{+4H} C_6H_5NHOH + H_2O$$

Phenyl hydroxylamine

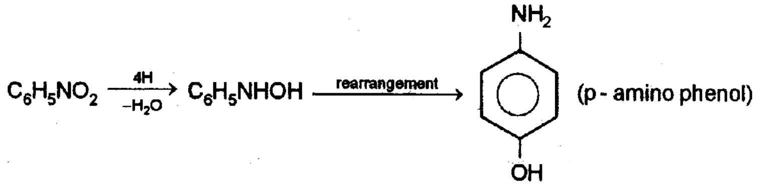
[c] Alkaline Medium : Reagents : Zn/NaOH or $SnCl_2$/NaOH, or Glucose/NaOH etc.



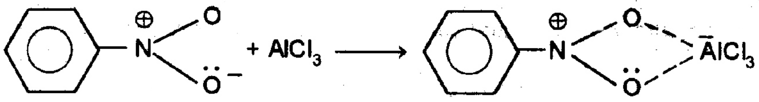
$$2C_6H_5NO_2 \xrightarrow{+2H} \underset{\substack{\| \\ C_6H_5-N}}{C_6H_5-N\rightarrow O} \xrightarrow[-H_2O]{+2H} C_6H_5-N=N-C_6H_5 \xrightarrow{+2H} \underset{\substack{| \\ C_6H_5-NH}}{C_6H_5-NH}$$

azoxy benzene — azobenzene — hydrazobenzene

[d] Electrolytic reduction : [Medium : conc, H_2SO_4]

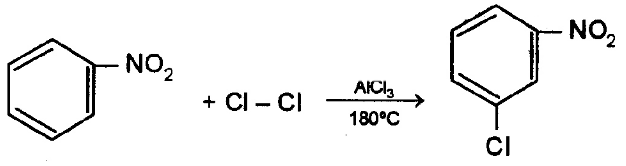


Reaction with $AlCl_3$: Nitrobenzene behaves as weak base and makes a complex compound with aluminium chloride.



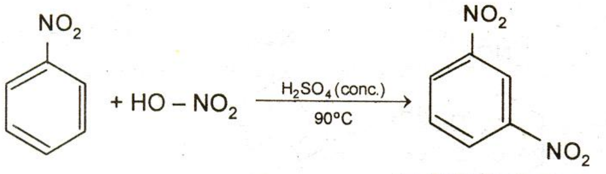
2. **Reaction of Benzene ring :**

Halogenation :

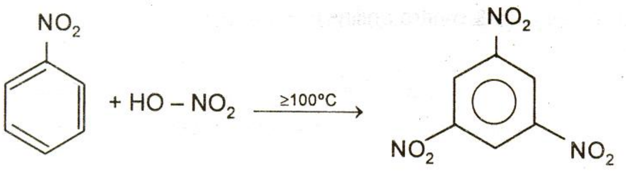


m-chloro nitrobenzene

Nitration :

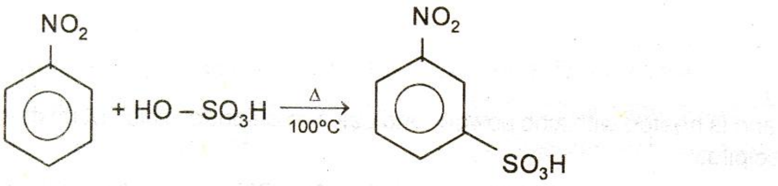


m-dinitrobenzene
(yellow crystalline solid)



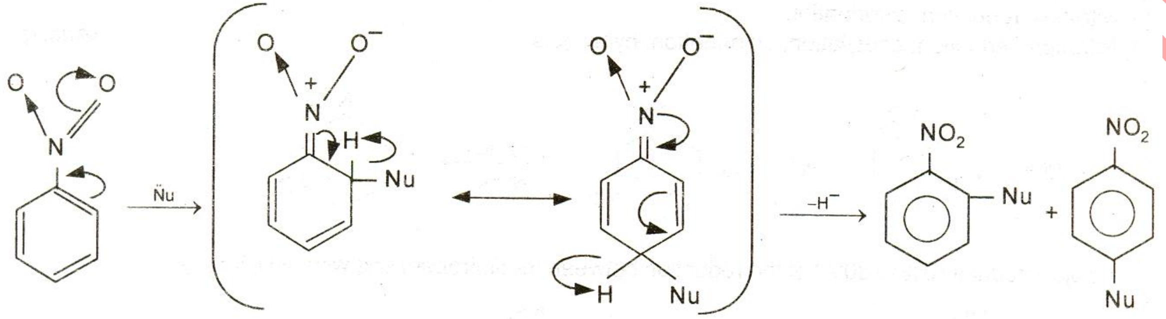
T.N.B (explosive in nature)

Sulphonation :

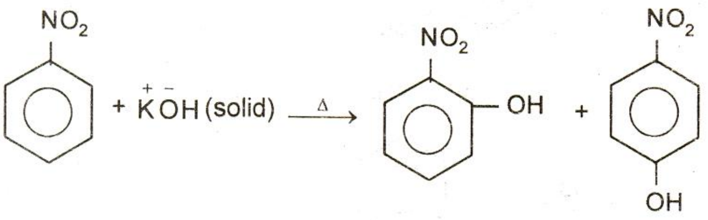


fuming — m-nitrobenzene sulphonic acid

3. **Other Reactions :** Nitrobenzene shows nucleophilic substitution reaction also. It is accomplishes in the following way. **Mechanism of nucleophilic substitution reaction** – In nitrobenzene nucleophile attackes at o– & p– positions as these are the electron deficient centres.

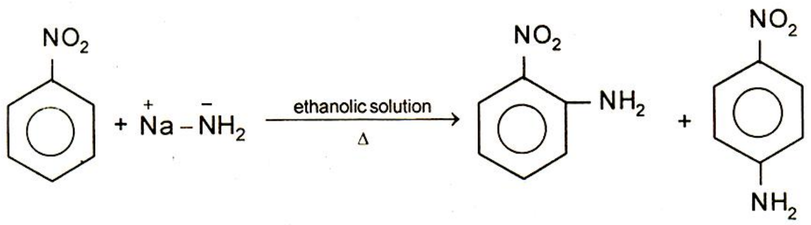


Reaction with Solid KOH :



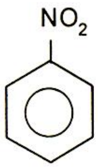
(o- & p-nitrophenol)

Reaction with Sodamide :



(o & p-nitro aniline)

Reaction with Ethanol :



$+ C_2H_5OH \longrightarrow$ o– and p–nitro phenetole

Test for Nitrobenzene :

[Mulliken and Barker's method]

The alcoholic solution of nitrobenzene is heated with zinc powder and calcium chloride. This hot mixture on filtration in Tollen's reagent gives a black precipitate.

$C_6H_5NO_2$ (alcoholic) + Zn + $CaCl_2 \xrightarrow{\Delta}$ [C_6H_5NHOH] filter in $AgNO_3 + NH_4OH \longrightarrow 2Ag\downarrow$
Black precipitate

ANILINE

1 Introduction :

[a] Aniline is called phenyl derivative of ammonia.

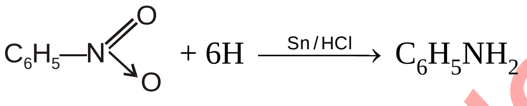
[b] It was initially obtained by the scientist 'Unverdorben'.

[c] Aniline is also called amino derivative of benzene because when a hydrogen atom is replaced by NH_2 group, aniline is obtained.

2. Method of Preparation :

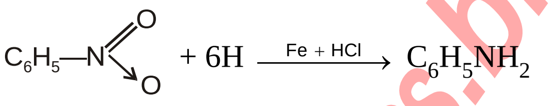
From Nitrobenzene (Reduction in acidic medium) :

[a] Lab method :



$$C_6H_5-N\overset{O}{\underset{O}{\lessgtr}} + 6H \xrightarrow{Sn/HCl} C_6H_5NH_2$$

[b] Industrial method :



$$C_6H_5-N\overset{O}{\underset{O}{\lessgtr}} + 6H \xrightarrow{Fe\ +\ HCl} C_6H_5NH_2$$

From Benzamide :

$$C_6H_5-\underset{\underset{O}{\|}}{C}-NH_2 + Br_2 + KOH\ (alc.) \longrightarrow C_6H_5NH_2 + K_2CO_3 + KBr + H_2O$$

Note : The above reaction is called as **'Hofmann hypobromite reaction'.**

From Chlorobenzene :

[a] With NH_3 :

$$C_6H_5\boxed{Cl + H}NH_2 \xrightarrow[200°C]{Cu_2O} C_6H_5\ NH_2 + HCl$$

Note : We use Cu_2O to neutralize the formed HCl otherwise HCl forms additional salt with aniline.

$$Cu_2O + 2HCl \longrightarrow Cu_2Cl_2 + H_2O$$

[b] With sodamide :

$$C_6H_5\boxed{Cl + Na}NH_2 \xrightarrow[200°C]{\Delta} C_6H_5NH_2 + NaCl$$

From Phenol :

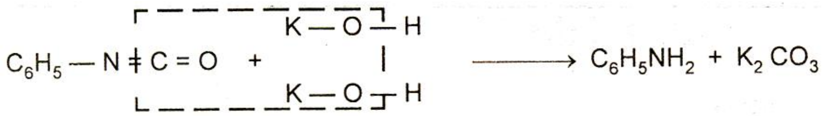
$$C_6H_5\boxed{OH + H}NH_2 \xrightarrow[300°C]{anhy.\ ZnCl_2} C_6H_5-NH_2 + H_2O$$

From Grignard reagent :

$$C_6H_5\boxed{MgCl + Cl}NH_2 \longrightarrow C_6H_5NH_2 + MgCl_2$$

chloramine

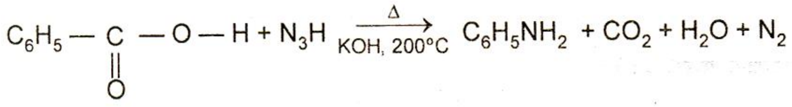
From phenyl isocyanate (By alkaline hydrolysis) :



$$C_6H_5-N\neq C=O + \begin{matrix}K-O-H\\ |\\ K-O-H\end{matrix} \longrightarrow C_6H_5NH_2 + K_2CO_3$$

Note : The above method is called as **'wurtz method'**.

From Benzoic acid (Schimdt reaction) :



$$C_6H_5-\underset{\underset{O}{\|}}{C}-O-H + N_3H \xrightarrow[KOH,\ 200^\circ C]{\Delta} C_6H_5NH_2 + CO_2 + H_2O + N_2$$

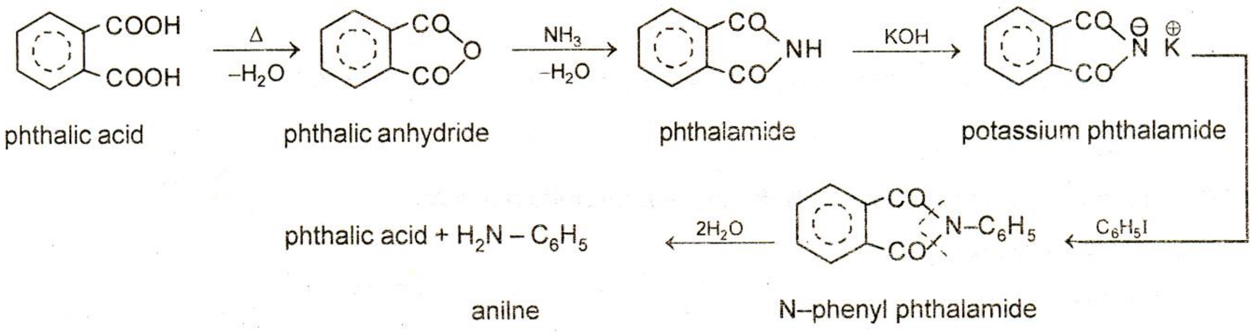
By reudction of azo and hydrazo compounds with sodium dithionite :

$$C_6H_5-N=N-C_6H_5 + 2\,Na_2S_2O_4 + 4H_2O \longrightarrow 2\,C_6H_5NH_2 + 4\,NaHSO_3$$

By curtius reaction :

$$C_6H_5COCl + NaN_3 \longrightarrow C_6H_5CON_3 + NaCl$$
$$C_6H_5CON_3 + H_2O \longrightarrow C_6H_5NH_2 + CO_2 + N_2$$

By Gabriel Phthalimide reaction :



3. Physical properties :

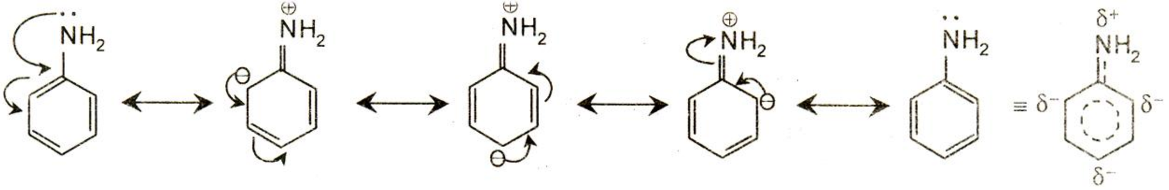
[a] Aniline is soluble in organic solvents as well as in water.

[b] Solubility in water is due to hydrogen bonding.

[c] It is colourless and poisonous liquid.

4. Resonance in Aniline :

Aniline is less basic than ammonia and primary amine because it possess resonance



It is evident from the above sturcutres that I.p. on N atom is delocalised and aniline behaves as a weak base. In these resonating structure, its ortho and para positions are electron richer (due to presence of negative charge) so electrophile attacks on these positions only. That's why we can say it is ortho & para directing.

5. Chemical Reaction :

Chemical reactions of aniline are broadly classified in the following two ways :

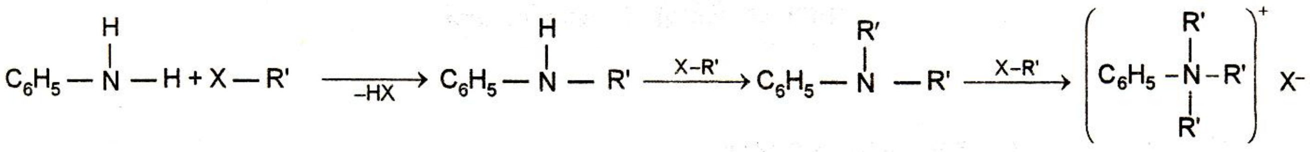
5.1 Reaction of $-NH_2$ group

5.2 Reactions of benzene ring

5.3 Other reactions

5.1 Reactions of $-NH_2$ group :

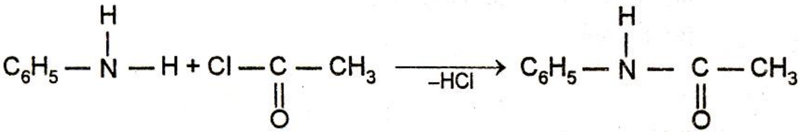
Alkylation :



$$C_6H_5-\overset{H}{N}-H+X-R' \xrightarrow[-HX]{} C_6H_5-\overset{H}{N}-R' \xrightarrow{X-R'} C_6H_5-\overset{R'}{N}-R' \xrightarrow{X-R'} \left(C_6H_5-\underset{R'}{\overset{R'}{N}}-R'\right)^+ X^-$$

quaternary salt

Acetylation :

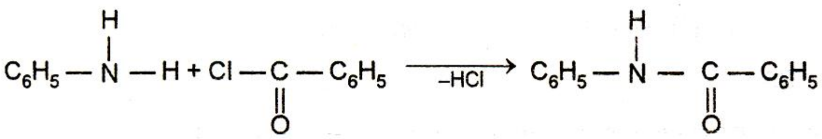


$$C_6H_5-\overset{H}{N}-H+Cl-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow[-HCl]{} C_6H_5-\overset{H}{N}-\underset{O}{\underset{\|}{C}}-CH_3$$

N-phenyl acetamide Or acetanilide

Note : The product formed is important because it is used in preservation of $-NH_2$ group in aniline.

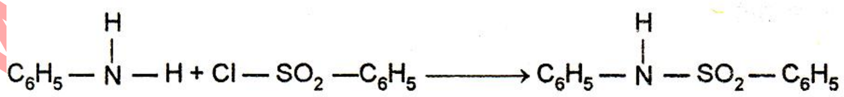
Schotten–baumann reaction :



$$C_6H_5-\overset{H}{N}-H+Cl-\underset{O}{\underset{\|}{C}}-C_6H_5 \xrightarrow[-HCl]{} C_6H_5-\overset{H}{N}-\underset{O}{\underset{\|}{C}}-C_6H_5$$

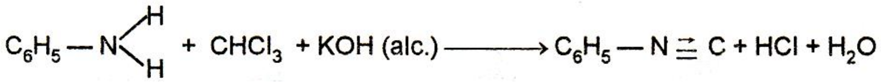
N–phenyl benzamide or benzanilide

Reaction with Hinsberg reagent :



$$C_6H_5-\overset{H}{N}-H+Cl-SO_2-C_6H_5 \longrightarrow C_6H_5-\overset{H}{N}-SO_2-C_6H_5$$

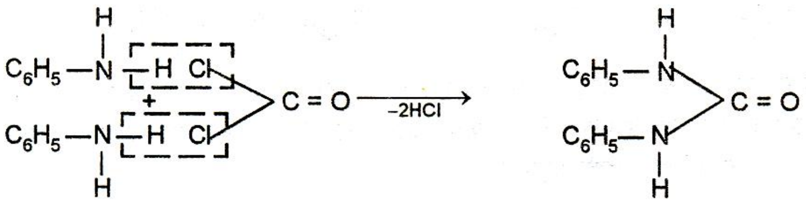
Hoffmann Carbylamine reaction (Isocyanide test) :



$$C_6H_5-NH_2 + CHCl_3 + KOH\,(alc.) \longrightarrow C_6H_5-N \overset{\rightarrow}{=} C + HCl + H_2O$$

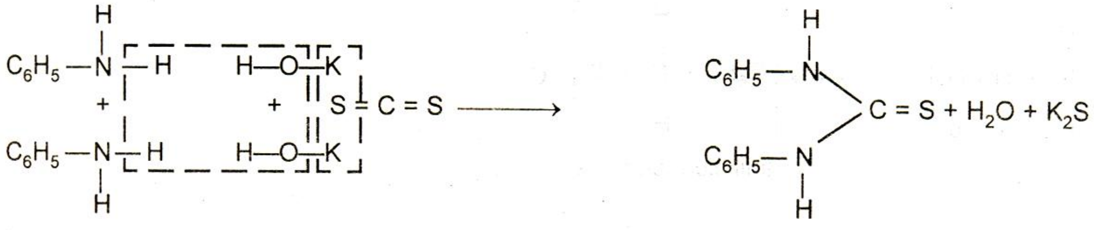
There isocyanides has very offensive smell. Reaction is used for testing of primary amines.

Reaction with Phosgene :



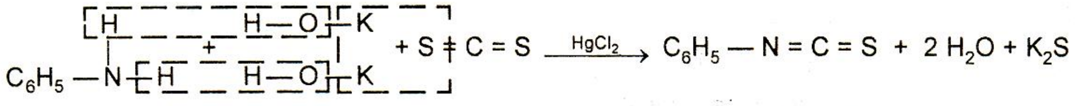
Reaction with Carbondisulphide :

[a] When aniline is in excess :



N, N' – diphenyl thio urea

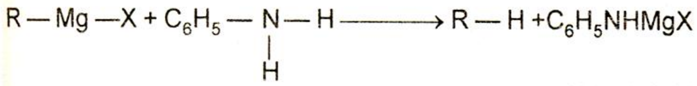
[b] When aniline is in lesser quantity :



phenyl iso thio cyanate

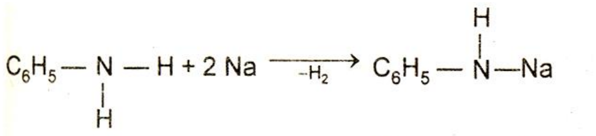
Note : There isothiocyanate has odour like mustard oil so reaction is called '**Hoffmann–mustard oil reaction.**

Reaction with Grignard reagent :



$$R-Mg-X + C_6H_5-\underset{H}{\underset{|}{N}}-H \longrightarrow R-H + C_6H_5NHMgX$$

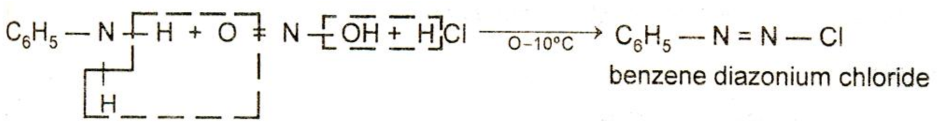
Reaction with Sodium metal :



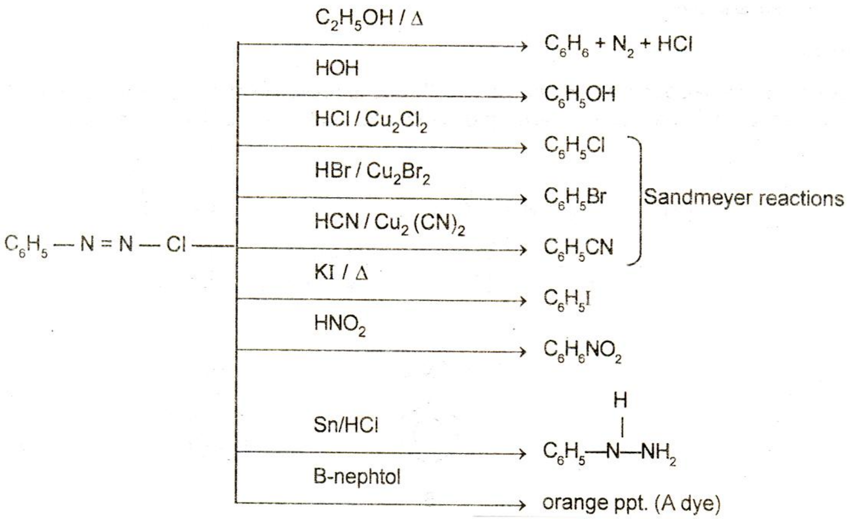
$$C_6H_5-\underset{H}{\underset{|}{N}}-H + 2\,Na \xrightarrow[-H_2]{} C_6H_5-\overset{H}{\overset{|}{N}}-Na$$

N- phenyl sodamide

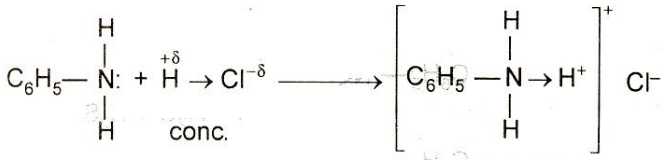
Reaction with HNO_2 and HCl (Diazotisation) :



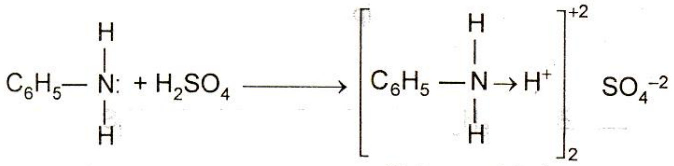
Note : It is an important compound because we can obtain a number of aromatic compounds from benzene diazonium chloride like.



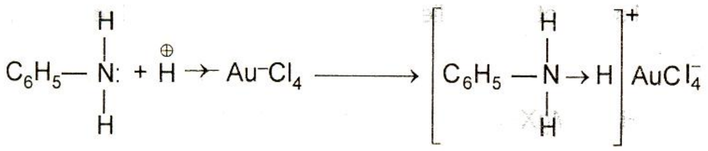
Salt formation :



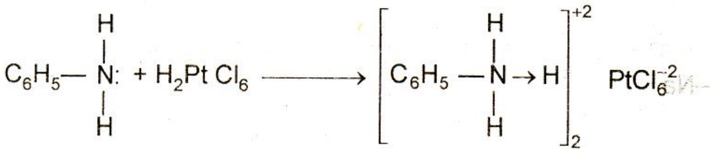
anilinium chloride



anilinium sulphate



anilinium chloraurate



anilinium chloroplatinate

Note : By the help of this salt we can calculate the mol. wt. of primary amine.

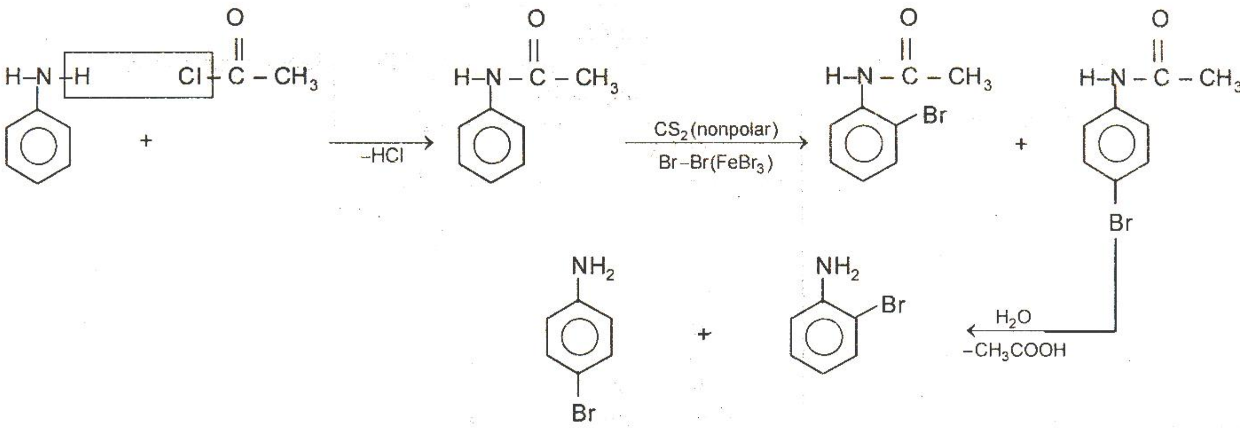
Reaction with Benzaldehyde :

$$C_6H_5NH_2 + C_6H_5CHO \longrightarrow \underset{\text{(schiff base or anil)}}{C_6H_5\text{–}CH\text{=}N\text{–}C_6H_5}$$

5.2 Reaction of benzene ring :

Halogenation :

Aniline does not show halogenation or nitration directly due to presence of active hydrogen on $-NH_2$ group so for nitration, halogenations first we preserve $-NH_2$ group with acetyl chloride or by the formation of acetanilide.



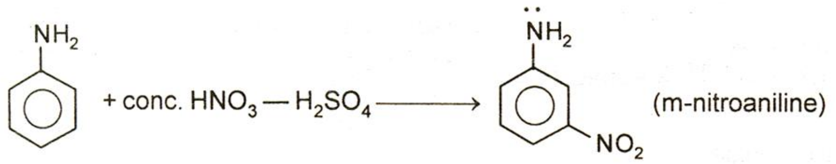
Note :

[i] Para product always yield more :

[ii] If reaction occurs in the presence of polar medium like bromine water, then product will be white ppt. of 2, 4, 6 tribromo aniline.

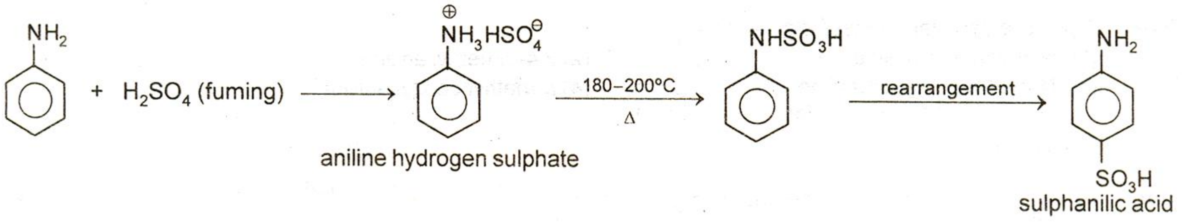
[iii] Aniline on iodination gives para–iodo product only.

Nitration :



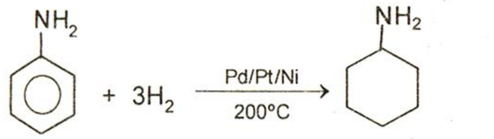
Note : [i] Meta products is formed because intermediate anilinium ion is formed which is meta directing.
[ii] If nitration occurs with conc. HNO_3 then product will be yellow ppt. of 2, 4, 6–trinitroaniline.

Sulponation :



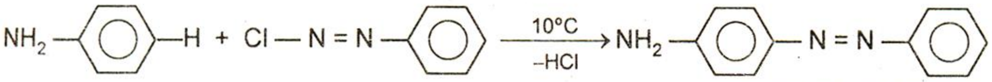
Note : Sulphanilic acid is used as hypnotic drug.

Reduction :



cyclo hexyl amine

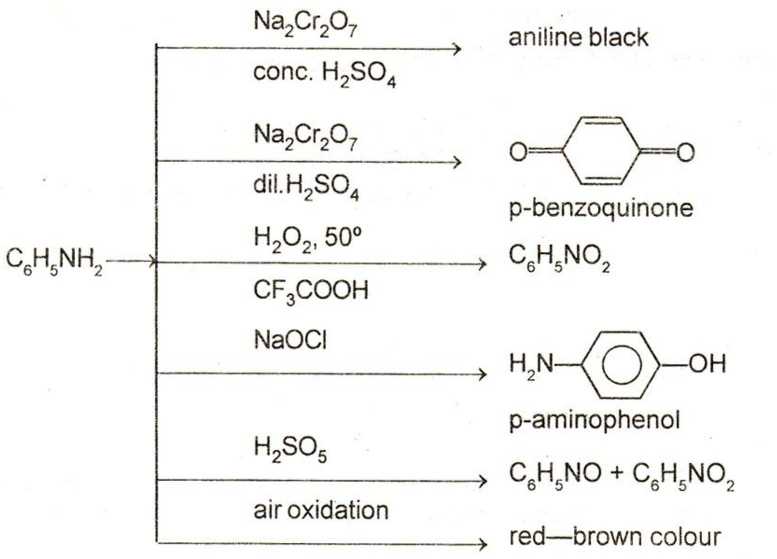
Reaction with benzene diazonium chloride :



p-amino azobenzene

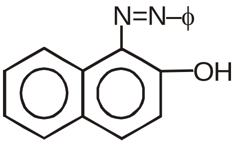
5.3 Other reactions :

Oxidation : Aniline forms different compounds on oxidation as follows :



Test for Aniline :

[a] Aniline $\xrightarrow[HCl(0-5^\circ)]{NaNO_2}$ $C_6H_5N_2Cl$ $\xrightarrow[+\beta-\text{naphthol}]{10\%\ NaOH}$



α-phenyl azo β–naphthol (orange–red dye)

[b] Aniline + NaOCl → p–Aminophenol $\xrightarrow{\text{light}}$ Purple–colour

[c] Aniline $\xrightarrow[KOH]{CHCl_3}$ Phenyl isocyanide
(most unpleasant smell)

SOLVED EXAMPLE

Ex.1 Which of the following is not correctly matched-

(A) Hydrolysis of phenyl magnesium iodide – benzene

(B) γ–Isomer of BHC– lindane

(C) (2n + 4) π Rule– aromaticity

(D) Trimerisation of propyne– mesitylene **Ans.(C)**

Sol. The Huckel rule to account for aromaticity is closed ring of (4n + 2) π electrons.

Ex.2 Benzene can be directly obtained from-

(A) Acetylene (B) Ethene and butadiene

(C) Chlorobenzene (D) All the above **Ans.(A)**

Sol. See Text.

Ex.3 Ozonolysis of benzene yields -

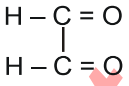
(A) Glyoxal (B) Glycerine (C) Glycol (D) Glycerol **(Ans.A)**

Sol. Ozonolysis of benzene yields glyoxal. Benzene adds three molecules of ozone and forms benzene triozonide which on decomposition with water gives three molecules of glyoxal

$$C_6H_6 + 3O_3 \longrightarrow C_6H_6O_9$$

benzene ozone benzene triozonide

$C_6H_6O_9 \xrightarrow{+H_2O} 3$



$$\begin{matrix} H-C=O \\ | \\ H-C=O \end{matrix}$$

benzene triozonide glyoxal

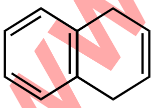
Ex.4 An aromatic compound contains .... π electrons

(A) 4n (B) 4n + 1 (C) 4n + 2 (D) 4n + 3 **(Ans.C)**

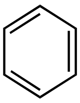
Sol. An aromatic compound contains (4n + 2) π electrons. It is according to Huckel's rule, which represents the aromaticity of the molecules. Aromatic compounds possess a sweet smell which is characteristic and different from other fragments.

The term aromatic compounds is now used for benzene and the compounds structurally related to benzene, even if they do not possess a sweet smell.

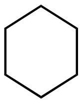
Ex.5 Which of the following will show aromatic character -



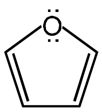
I



II



III

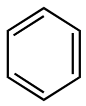


IV

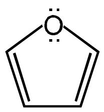
(A) I, II and III (B) II and III (C) II and IV (D) All the four

(Ans.C)

Sol. Benzene has 6π electrons (2 from each double bond) present in cyclic continous form.



benzene



furan

Furan also has 6π electrons present in continous cyclic cloud, note that one of the pair of electrons present in sp^2 orbital does not involve in overlapping of the sextet; while the unused pair of electrons present in p orbital is involved in overlapping forming sextet.

Ex.6 Which of the following is not a friedel craft's reaction –

(A) $C_6\,H_5 - OH + Cl - COCH_3 \longrightarrow C_6H_5OCOCH_3$

(B) $C_6\,H_6 + ClCOCH_3 \xrightarrow{AlCl_3} C_6H_5\text{–}COCH_3$

(C) $C_6\,H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6\,H_5 - CH_3$

(D) $C_6\,H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5 - C_2H_5$ **[Ans. A]**

Sol. Friedel craft reaction occurs in the presence of lewis acid. Note that carbon directly links with benzene ring in friedel crafts reaction.

Ex.7 Toluene may be prepared by :–

(A) Toluic acid (B) Cresol

(C) Toluene sulphonic acid (D) All the above **[Ans. D]**

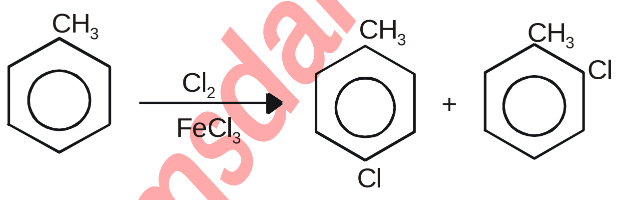
Sol. Toluene may be prepared by all the above compounds described earlier.

Ex.8 The chlorination of toluene in presence of ferric chloride gives predominantly–

(A) Benzyl chloride (B) m–Chlorotoluene

(C) Benzal chloride (D) *o*– and *p*– Chlorotoluene **[Ans. D]**

Sol.



In presence of halogen carrier, substitution occurs in benzene nucleus.

Ex.9 Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives –

(A) o – Cresol (B) p – Cresol

(C) 2,4–Dihydroxytoluene (D) Benzyl alcohol **[Ans. D]**

Sol. $C_6H_5CH_3 + Cl_2 \xrightarrow{\text{light, heat}} C_6H_5CH_2Cl \xrightarrow{\text{aq.NaOH}} C_6H_5CH_2OH$

Ex.10 $\phi\text{–}CH_3 \xrightarrow{CrO_2Cl_2} A \xrightarrow{H_2O} B$

[Where $\phi = C_6H_5$]

The functional group present in B and name of the reaction would be –

(A) –CHO, Gattermann aldehyde synthesis (B) –CHO, Etard reaction

(C) $–COCH_3$, Friedel Crafts reaction (D) –CHO, Oxo reaction **[Ans. B]**

Sol. The compound ' B ' is benzaldehyde and the reaction is called Etard reaction.

Ex.11 The correct order of reactivity towards electrophilic substitution is -

(A) Phenol > Benzene > Chlorobenzene > Benzoic acid

(B) Benzoic acid > Chlorobenzene > Benzene > Phenol

(C) Phenol > Chlorobenzene > Benzene > Benzoic acid

(D) Benzoic acid > Phenol > Benzene > Chlorobenzene **(Ans.A)**

Sol. Presence of o-, p- directing groups in benzene nucleus activates ring for SE reaction. Presence of m-directing group deactivates ring for SE reactions. Also halogens are deactivating gp. due to — IE. inspite of o-and p-directing nature.

Ex.12 Which among the following is the strongest o-, p-directing group in benzene is -

(A) –OH (B) –Cl (C) $–OCH_3$ (D) $–CH_3$ **(Ans.A)**

Sol. –OH gp. posses the maximum tendency to throw electron pair towards benzene nucleus.

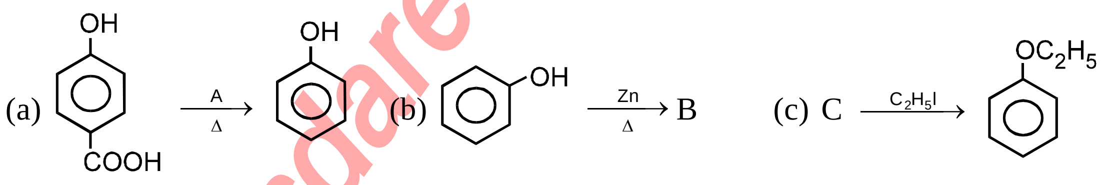
Ex.13 The compound represented by the molecular formula C_7H_8O are -

(A) Only alcohol (B) Only ether

(C) Only phenolic compound (D) All the three types of compounds **(Ans.D)**

Sol. Benzyl alcohol, anisole and o —, m—, p— cresols can be written by the molecular formula C_7H_8O.

Ex.14 Indenify A, B, and C in the following reactions–



(A) Sodalime, benzene, potassium phenoxide

(B) Zn, benzene, sodium ethoxide

(C) Zn, cyclohexanone, sodium ethoxide

(D) None of the above **(Ans.A)**

Sol. Sodalime, benzene, potassium phenoxide are the A, B and C compounds respectively.

Ex.15 Rate of substitution reaction in phenol is -

(A) Slower than the rate of benzene (B) Faster than the rate of benzene

(C) Equal to the rate of benzene (D) None **(Ans.B)**

Sol. – OH group is activating group towards electrophilic substitution reactions.

Ex.16 Which is least soluble in water -

(A) Phenol (B) Ethanol (C) Benzoic acid (D) Benzene **(Ans.D)**

Sol. Benzene can not form H-bonding thus, it is least soluble.

Ex.17 Which of the following reagen (s) cannot be used to distinguish between phenol and benzyl alcohol-

(A) NaOH (B) $NaHCO_3$ (C) Br_2/CCl_4 (D) $FeCl_3$ **(Ans.C)**

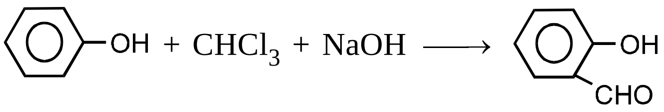
Sol. Only phenol reacts with NaOH, $NaHCO_3$ and $FeCl_3$ none of the two compounds react with Br_2/CCl_4.

Ex.18 Phenol condenses with formaldehyde to form-

(A) Bakelite (B) Asbestos (C) Polyacrylaldehyde (D) Polyester **(Ans.A)**

Sol. When phenol and formaldehyde react in presence of dilute alkali, p-hydroxybenzyl alcohol is obtained as a major product on further heating for some time, a cross-linked polymer, called phenol- formaldehyde resin or bakelite is formed.

Ex.19



The above reaction is called -

(A) Gattermann Kosch aldehyde synthesis

(B) Gattermann aldehyde synthesis

(C) Reimer Tiemann reaction

(D) Ledrer Mannase reaction **(Ans.C)**

Sol. The above reaction is Reimer Tiemann reaction.

Ex.20 In Etard's reaction toluene is oxidised to benzaldehyde using –

(A) H_2O_2 (B) Cl_2

(C) Chromium trioxide or CrO_2Cl_2 (D) $KMnO_4$ **(Ans. C)**

Sol. CrO_3 or CrO_2Cl_2 and a mixture of $K_2Cr_2O_7 + H_2SO_4 + NaCl$ can also be used.

Ex.21 In Perkin reaction –

(A) Benzaldehyde reacts with acetic anhydride in the presence of sodium acetate forming cinnamic acid.

(B) Benzaldehyde reacts with acetaldehyde in the presence of sodium hydroxide to give cinnamaldehyde.

(C) Calcium salt of benzoic acid on dry distillation gives benzophenone.

(D) None of these **(Ans.A)**

Sol. Perkin reaction can be shown as –

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH = CH - COOH + CH_3COOH$$

Ex.22 Benzaldehyde and formaldehyde differ from acetaldehyde in their reaction with –

(A) NaOH (B) HCN

(C) 2,4-Dinitrophenyl hydrazine (D) Semi carbazide **(Ans.A)**

Sol. Benzaldehyde (C_6H_5 – CHO) and formaldehyde do not have α-hydrogen atoms so they give disproportionation reaction with NaOH but CH_3CHO does not give it.

Ex.23 When an aldehyde was heated with alkali, part of it was converted into an alcohol and part of it into an acid. The aldehyde is –

(A) An aliphatic aldehyde other than formaldehyde

(B) An aliphatic aldehyde or salicylaldehyde

(C) An aromatic aldehyde other than salicylaldehyde

(D) An aromatic aldehyde or formaldehyde **(Ans.D)**

Sol. The aldehydes which do not have α-hydrogen atoms show disproportionation reaction. These aldehyde may be aliphatic aldehyde (formaldehyde) or aromatic aldehyde.

Ex.24 Product obtained on the addition of an aqueous alkali to benzaldehyde followed by acid hydrolysis is –

(A) Benzoic acid (B) Benzyl alcohol (C) Benzyl benzoate (D) All of the above

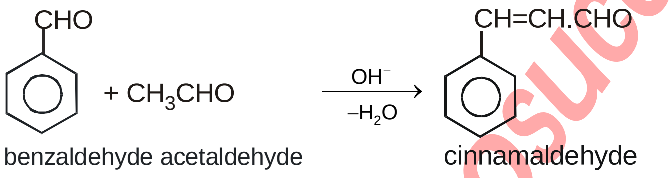
(Ans.D)

Ex.25 Benzaldehyde reacts with acetaldehyde in the presence of a base to give –

(A) Crotonaldehyde (B) Cinnamaldehyde (C) Crotonic acid (D) Cinnamic acid

(Ans.B)

Sol. Benzaldehyde reacts with acetaldehyde in the presence of a base to give cinnamaldehyde. It is called crossed Aldol condensation or Claisen's condensation



Ex.26 In the reaction between benzaldehyde and formaldehyde, point out the wrong statement

(A) Benzaldehyde is reduced to benzyl alcohol

(B) Formaldehyde is oxidised to formic acid

(C) Benzyl formate is formed

(D) The reaction is known as crossed aldol condensation

(Ans.D)

Sol. In the reaction between benzaldehyde and formaldehyde the wrong statement is that the reaction is known as crossed aldol condensation. Actually the reaction is called Crossed Cannizaro's reaction.

$$C_6H_5CHO + HCHO \xrightarrow[(2)HCl]{(1)OH^-}$$

benzaldehyde formaldehyde

$$C_6H_5CH_2OH + HCOOH$$

benzylalcohol formic acid

Ex.27 Which of the following will undergo aldol condensation –

Acetaldehyde (1) Propanaldehyde (2)

Benzaldehyde (3) rideuterosacetaldehyde (4)

(A) 1 (B) 1, 4 (C) 1, 2, 4 (D) All of them **(Ans.C)**

Sol. CH_3CHO (1) CH_3CH_2CHO (2)

C_6H_5CHO (3) CD_3CHO (4)

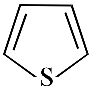
Benzaldehyde has no α-hydrogen atom, remember that CH_3CHO and CD_3CHO both behave similarly in chemical properties.

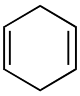
EXERCISE I

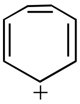
Q.1 Solvent used in the, Friedel Craft's reaction is :

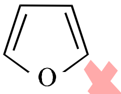
(A) Nitrosobenzene (B) Nitrobenzene (C) Benzene (D) Toluene

Q.2 Which of the following is not an aromatic compound:

(A) 

(B) 

(C) 

(D) 

Q.3 Benzene is obtained when phenol is distilled with -

(A) Copper turnings (B) Aluminium dust (C) Zinc dust (D) Pumice stone

Q.4 Which one of the following is the most basic compound :

(A) $C_6H_5–NH_2$ (B) $C_6H_5–NHCH_3$ (C) $C_6H_5–N(CH_3)_2$ (D) $C_6H_5N(C_2H_5)_2$

Q.5 Friedel–Crafts' reaction does not occur in case of –

(A) Toluene (B) Benzene (C) Naphthalene (D) Pyridine

Q.6 Toluene may be prepared by -

(A) Friedel craft's reaction (B) Wurtz–fitting reaction

(C) Grignard reagent (D) All of the above

Q.7 The main product of the reduction of benzaldehyde with Zn-Hg/conc. HCl is -

(A) Benzyl alcohol (B) Cyclohexyl methanol

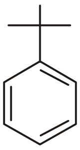
(C) Toluene (D) None of these

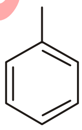
Q.8 $C_6H_6 \xrightarrow[AlCl_3]{CH_3COCl} A \xrightarrow[HCl]{Zn–Hg} B$

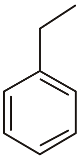
The end product in the above sequence is:

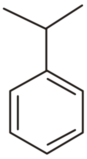
(A) Toluene (B) Ethyl benzene (C) Both the above (D) None

Q.9 Which of the following will undergo sulphonation at fastest rate ?

(A) 

(B) 

(C) 

(D) 

Q.10 Ozonolysis of toluene gives -

(A) Two molecule of glyoxale

(B) Three molecule of glyoxale

(C) Two molecule of glyoxale and one molecule of methyl glyoxale

(D) Two molecule of methyl glyoxale and one molecule of glyoxale

Q.11 m-Bromotoluene is prepared by:
(A) Bromination of toluene
(B) Friedel Craft's reaction of bromobenzene with CH_3Cl
(C) Bromination of nitrobenzene and subsequent replacement of $-NO_2$ group with methyl group
(D) Bromination of aceto-p-toluidine followed by hydrolysis and deamination

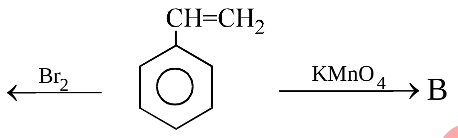
Q.12 Phenol reacts with conc. HNO_3 in the presence of conc. H_2SO_4 to give –
(A) Meta nitrophenol (B) Ortho nitrophenol
(C) Ortho and para nitrophenol (D) Picric acid

Q.13 In the Liebermann's nitroso reaction changes in the colour of phenol occurs as:
(A) Brown or red-greenish red-deep blue (B) red-deep blue-green
(C) red-green-white (D) white-red-green

Q.14 Reimer Tiemann reaction involves -
(A) Carbanion intermediate (B) A carbene intermediate
(C) Carbonium ion intermediate (D) Free redical intermediate

Q.15 Methyl group attached to benzene can be oxidised to carboxyl group by reacting with:
(A) Fe_2O_3 (B) $AgNO_3$ (C) $KMnO_4$ (D) CrO_3

Q.16 The formylating agent in 'Gattermann Koch' synthesis is -
(A) CO + HCl (B) CO + H_2 (C) HCl + HCN (D) $CHCl_3$ + alc.KOH

Q.17


Compound A and B respectively are:
(A) o-Bromostyrene, benzoic acid (B) p-Bromostyrene, benzaldehyde
(C) m-Bromostyrene, benzaldehyde (D) Styrene dibromide, benzoic acid

Q.18 Benzaldehyde is oxidised and reduced simultaneously in the presence of –
(A) $NaHCO_3$ (B) NaOH (C) Na_2CO_3 (D) HCl

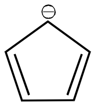
Q.19 Benzaldehyde can be converted to benzyl alcohol by –
(A) HCl (B) NaOH (C) $LiAlH_4$ (D) B and C are correct

Q.20 Benzaldehyde condenses with acetic anhydride to give cinnamic acid in presence of –
(A) Sodium acetate (B) Sodium chloride (C) Sodium benzoate (D) Sodium metal

Q.21 HCHO and C_6H_5CHO can be distinguished by –
(A) Fehling solution (B) Tollen's reagent (C) $KMnO_4$ (D) All of these

Q.22 Nitrobenzene has a smell similar to that of :
(A) Benzaldehyde (B) Formaldehyde (C) Acetaldehyde (D) Salisylaldehyde

Q.23 How many π electron are there in the following species :



(A) 2 (B) 4 (C) 6 (D) 8

Q.24 Benzene is a resonance hybrid mainly of two Kekule structures. Hence:
(A) Half of the molecules correspond to one structure, and half of the second structure
(B) At low temperatures benzene can be separated into two structures
(C) Two structures make equal contribution to resonance hybrid
(D) An individual benzene molecule changes back and forth between two structures

Q.25 Which of the following group is divalent:
(A) Benzoyl (B) Benzyl (C) Benzal (D) p-Tolyl

Q.26 Which of the following is not the property of benzene:
(A) Characteristic smell (B) Inflammable
(C) Addition reactions (D) Colourless

Q.27 The intermediate formed in the reaction of benzene with an electrophile is –
(A) Wheland intermediate (B) σ– complex
(C) Benzenium cation (D) All the above

Q.28 Anhydrous $AlCl_3$ is used in the Friedel – Craft's reaction because it is -
(A) Electron rich
(B) Soluble in ether
(C) Ionisable to chloride and aluminium ions
(D) Electron deficient

Q.29 Acetylene on polymerisation gives -
(A) Mesitylene (B) Benzene (C) Ethyl benzene (D) Propyle benzene

Q.30 Nitration of toluene takes place at -
(A) o – Position (B) m –Position
(C) p – Position (D) Both o– and p – positions

EXERCISE–II

Q.1 Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment?

(A) B was C_6H_5I (B) Addition of HNO_3 was unnecessary

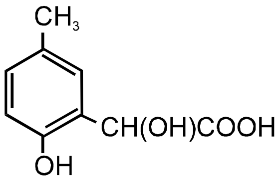
(C) A was C_6H_5I (D) A was $C_6H_5CH_2I$ **[AIEEE-2003]**

Q.2 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ? **[AIEEE-2004]**

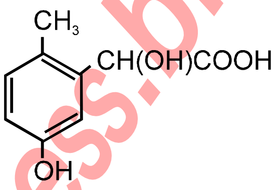
(A) Phenol (B) Benzaldehyde (C) Butanal (D) Benzoic acid

Q.3 p–cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound. B The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is - **[AIEEE-2005]**

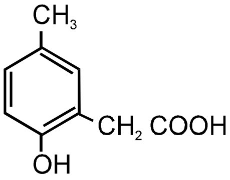
(A)



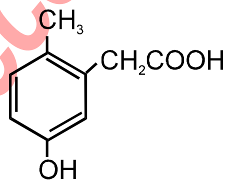
(B)



(C)



(D)



Q.4 Fluorobenzene (C_6H_5F) can be synthesized in the laboratory - **[AIEEE 2006]**

(A) from aniline by diazotisation followed by heating the diazonium salt with HBF_4

(B) by direct fluorination of benzene with F_2 gas

(C) by reacting bromobenzene with NaF solution

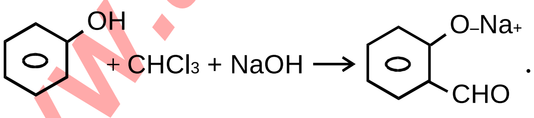
(D) by heating phenol with HF and KF

Q.5 Phenyl magnesium bromide reacts with methanol to give - **[AIEEE 2006]**

(A) a mixture of benzene and Mg(OMe) Br (B) a mixture of toluene and Mg(OH)Br

(C) a mixture of phenol and Mg(Me)Br (D) a mixture of anisole and Mg(OH) Br

Q.6



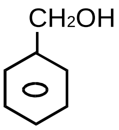
The electrophile involved in the above reaction is - **[AIEEE 2006]**

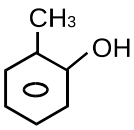
(A) dichlorocarbene (:CCl_2) (B) trichloromethyl anion ($\overset{\ominus}{C}Cl_3$)

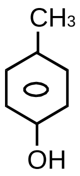
(C) formyl cation ($\overset{\oplus}{C}HO$) (D) dichloromethyl cation ($\overset{\oplus}{C}HCl_2$)

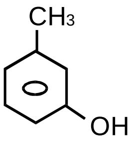
Q.7 The structure of the compound that gives a tribromo derivative on treatment with bromine water is -

[AIEEE 2006]

(A) 

(B) 

(C) 

(D) 

Q.8 The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives predominantly- **[AIEEE 2007]**

(A) benzoyl chloride (B) benzyl chloride

(C) o-and p-chlorotoluene (D) m-chlorotoluene

Q.9 Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives- **[AIEEE 2008]**

(A) o-nitrophenol (B) p-nitrophenol (C) nitrobenzene (D) 2,4,6-trinitrobenzene

Q.10 Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains- **[AIEEE 2008]**

(A) mixture of o– and p-dibromobenzenes (B) mixture of o- and p-bromoanilines

(C) mixture of o- and m-bromotoluenes (D) mixture of o- and p-bromotoluenes

Q.11 The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is - **[AIEEE 2009]**

(A) salicylaldehyde (B) salicyclic acid (C) phthalic acid (D) benzoic acid

Q.12 Which of the following are classified as aromatic?

(A) 1, 2, 3-Triphenylcyclopropenium cation (B) Cyclooctatetraenyl dianion

(C) Azulene (D) Annulene

Q.13 $C_6H_5NO_2 \xrightarrow{SnCl_2\,/\,HCl} A \xrightarrow[0^o]{NaNO_2\,/\,HCl} B \rightarrow$ Benzene, In the above sequence B $\rightarrow$ Benzene is suitably obtained by using :

(A) Ethanol (B) H_3PO_2 (C) Both the above (D) Methanol

Q.14 Which of the following reactions of benzene proves the presence of three carbon–carbon double bonds in it:

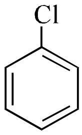
(A) Formation of a triozonide with ozone

(B) Hydrogenation of benzene to cyclohexane

(C) Formation of $C_6H_6Cl_6$ by addition of chlorine

(D) Formation of nitrobenzene on heating benzene with a mixture of concentrated nitric acid and sulphuric acid

Q.15 Which of the following can be used in Friedel Crafts reaction to generate electrophile?

(A) 

(B) $CH_2=CH–Cl$ (C) CH_3CH_2Cl (D) $CH_2=CH–CH_2–Cl$

Q.16 Aniline is purified by :
(A) Azeotropic distillation (B) Steam distillation
(C) distillation in presence of magnesium (D) Fractional crystallisation

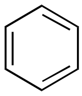
Q.17 The replacement of a hydrogen atom in benzene by alkyl group can be brought about with the following reagents:
(A) Alkyl chloride and $AlCl_3$ (B) Alkene and $AlCl_3$
(C) Alkanol and alkali (D) Alkanol and acid

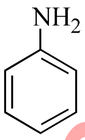
Q.18 $C_6H_5NH_2$, $CHCl_3$ and KOH give the main product :
(A) Phenyl cyanide (B) Benzyl cyanide (C) Benzyl carbylamine (D) Phenyl isonitrile

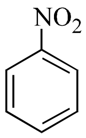
Q.19 Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ to give predominantly:
(A) n-Propylbenzene (B) Isopropylbenzene
(C) 3-Propyl-1-chlorobenzene (D) Cumene

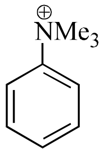
Q.20 Aniline on direct nitration produces :
(A) o-Nitroaniline (B) m-Nitroaniline (C) p-Nitroaniline (D) 1 & 3 are correct

Q.21 Which of the following does not gives Friedel-Crafts reaction?

(A) 

(B) 

(C) 

(D) 

Q.22 Which one of the following is not an azo compound :-
(A) Methyl orange (B) Benzenediazonium chloride
(C) Phenolphthalein (D) p-hydroxyazobenzene

Q.23 The good method for converting benzene into propyl benzene is:
(A) $C_6H_6 + CH_3CH_2CH_2Cl$ + Anhyd. $AlCl_3$
(B) $C_6H_6 + CH_3CH_2COCl$ + Anhyd. $AlCl_3$ and then treatment with Zn/Hg/HCl
(C) $C_6H_6 + CH_3CH_2COCl$ + Anhyd. $AlCl_3$ and then treatment with H_2 Ni
(D)C_6H_6 + Anhyd. $AlCl_3$ + cyclopropane

Q.24 Which of the following statements is incorrect for electrophilic substitution.
(A) Ortho-and para-directing groups increase electron density at ortho-and para-positions
(B) Meta-directing groups increase electron density at meta-position
(C) Meta-directing groups decrease electron density at meta-position
(D) Ortho-and para-directing groups decrease electron density at meta-position

Q.25 Nitration of aniline is carried out after acylation, because :
(A) Oxidation can be avoided
(B) Reaction becomes manageable
(C) o and p-nitroanilines are obtained in good amount
(D) All the above .

Q.26 Which of the following statements is/are not true?
(A) All ortho-para directing groups activates the ring
(B) All ortho-para directing groups except halogens activate the ring
(C) All meta-directing groups have π-bond on the atom directly attached to the ring
(D) All meta directing groups are deactivating.

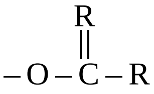
Q.27 Nitration of aniline comes under :

(A) $\overset{\ominus}{N}$u-addition (B) $\overset{\ominus}{N}$u-substitution (C) $\overset{\oplus}{E}$-addition (D) $\overset{\oplus}{E}$-substitution

Q.28 False statement is / are :
(A) Although benzene contains three double bonds, normally it does not undergo addition reaction.
(B) m-chlorobromobenzene is an isomer of m-bromochlorobenzene.
(C) In benzene, carbon uses all the three p orbitals for hybridization.
(D) An electron donating substitutent in benzene orients the incoming electrophilic group to the meta position.

Q.29 Urethanes are esters of –
(A) Carbamic acid (B) Citric acid (C) Malonic acid (D) Succinic acid

Q.30 Amongst the following, the moderately activating group is

(A) —NHR (B) —NHCOCH$_3$ (C) 
$-O-\overset{\overset{R}{||}}{C}-R$ (D) —CH$_3$

ANSWER KEY

EXERCISE I

Q.1	B	Q.2	B	Q.3	C	Q.4	D	Q.5	D	Q.6	D	Q.7	C
Q.8	B	Q.9	B	Q.10	C	Q.11	D	Q.12	D	Q.13	A	Q.14	B
Q.15	C	Q.16	A	Q.17	D	Q.18	B	Q.19	D	Q.20	A	Q.21	A
Q.22	A	Q.23	C	Q.24	C	Q.25	C	Q.26	C	Q.27	D	Q.28	D
Q.29	B	Q.30	D										

EXERCISE–II

Q.1	C	Q.2	B	Q.3	A	Q.4	A	Q.5	A	Q.6	A	Q.7	D
Q.8	C	Q.9	A	Q.10	D	Q.11	B	Q.12	ABC	Q.13	C	Q.14	ABC
Q.15	CD	Q.16	B	Q.17	ABD	Q.18	D	Q.19	BD	Q.20	B	Q.21	BCD
Q.22	C	Q.23	BD	Q.24	BCD	Q.25	A	Q.26	ABC	Q.27	D	Q.28	BCD
Q.29	A	Q.30	BC										

BIOMOLECULES

I. Introduction :

(a) All common activities of a living organism (bioactivity) involve reactions of certain organic compounds (mostly organic). Such compounds are called 'biomolecule'

(b) The synthesis of a biomolecules inside the body is known as anabolism while its degradation to simple products is known as 'catabolism' and two process collectively are called metabolism.

(c) Nowadays, carbohydrates are defined as the optically active polyhydroxy aldehydes or ketones or Substances which yield these on hydrolysis.

II. Carbohydrates :

(a) In these compounds H : O = 2 : 1 (same as water).

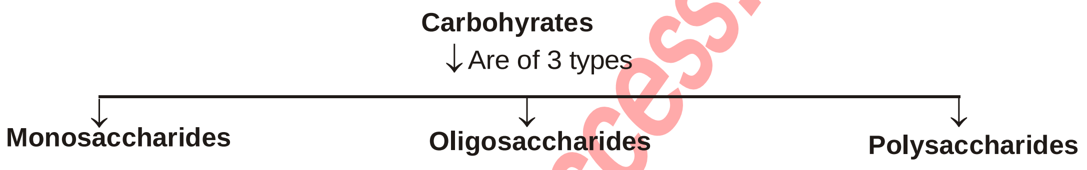
(b) Animal cell – Glucose, Glycogen. (forms of carbohydrates).

(c) Plant cell – cellulose, starch form (In plant cells carbohydrates are stored in form of starch).

(d) It's formula is : $C_n(H_2O)_m$.

(e) These are called hydrates of carbon.

Classification



1. Monosoccharides :

(a) In it n = m

(b) There naming is of following type –

S.No.	Formula	Group	Aldolase	Ketose
1	$C_3H_6O_3$	Triosase	Gylceraldehyde	Dihydroxy acetone
2	$C_4H_8O_4$	Tetrosase	Eryithrose	Erythrulose
3	$C_5H_{10}O_5$	Pentosase	Ribose	Ribulose
4	$C_6H_{12}O_6$	Hexosase	Glucose	Fructose.

Because in monosaccharides - CHO (Aldehyde) group is present so it keep reducing nature. They are reduced by Fehling (Cu_2O), Benedict solution.

(c) In aldolase aldehyde group is present and all central molecules are asymmetrical (chiral).

(d) In ketose ketone group is present and except 2nd carbon all molecules are asymmetrical.

(e) These are found in two isomeric forms L–form and D–form

(f) Simplest sugar → Glyceraldehyde

(g) Monosaccharides are of two types

(h) Cyclic compound are of 2 types :

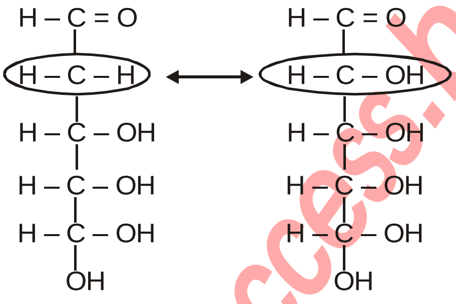
Pyranosase – Ring made up of 6 members

Furanosase – Ring made up of 5 members

(i) Pyranosase and furanosase name was Coined by Howorth on basis of thermodynamics.
(j) Body sugar is called as glucose.
(k) Fructose, Mannose and galactose are hexoses.
(l) Water hydrolysis of monosaccharides cannot take place.
(m) Main isomeric form in it is α–isomers, α, β isomers → Anomeres.

(i) Derivatives of Monosaccharides : Following are derivatives of monosaccharrides.

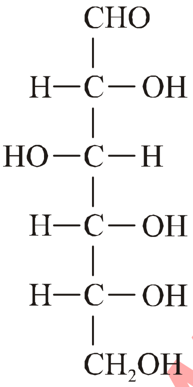
(a) Deoxy suger : If 1 hydrogen occupies the position of one – OH or one – OH is replaced by one -H than deoxy sugar is formed.

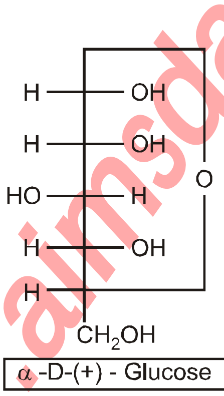


Deoxyribose **Ribose**

(b) Amino sugar : –OH group of Aldolase is replaced by $-NH_2$ group than it is called as amino sugar.
Eg. D–glucosamine, D–galactosamine

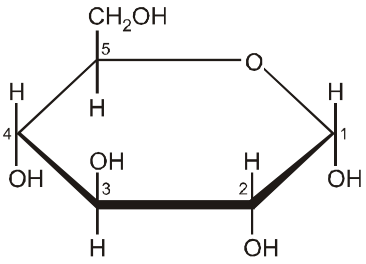
(ii) Structure of Glucose & Fructose Glucose is adohexose it is a monomer of larger carbohydrate. structure:





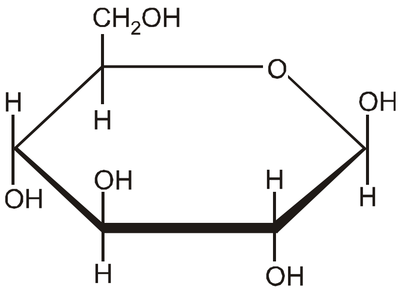
α -D-(+) - Glucose

(Fischer formula)



α -D- Glucopyranose

(Haworth structure)



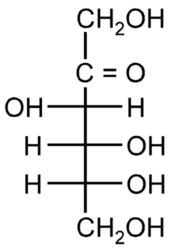
β -D- Glucopyranose

FRUCTOSE (LAEVULOSE), $C_6H_{12}O_6$

Fructose is a ketohexose. It is obtained along with glucose by the hydrolysis of sucrose..

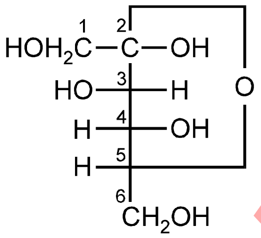
Structure of Fructose

Fructose has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at C—2 and six carbon atoms in straight chain as in case of glucose. It belongs to D-series and is a laevorotatory compound. Therefore, fructose is correctly named as D-(–)-fructose. Its open chain structure may be written as:

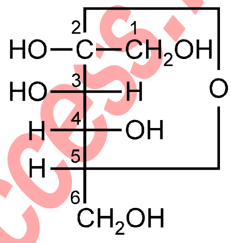


D-(–)Fructose

Fructose also exists in two cyclic forms which are obtained by the addition of –OH at C–5 to the ($>$C = O) group. The ring thus formed is a five membered ring and is named as furanose with analogy to the compound furan.

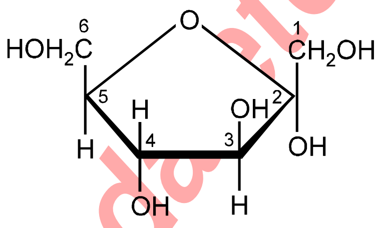


α-D-(–)-Fructofuranose

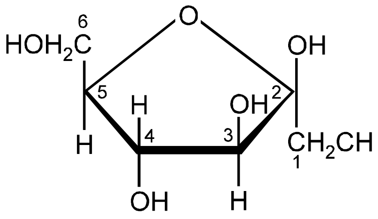


β-D-(–)-Fructofuranose

The cyclic structures of two anomers of fructose are represented by Haworth structures as given



α-D-(–)-Fructofuranose



β-D-(–)-Fructofuranose

2 Oligo saccharides :

It is formed by combination of 2 to 9 mono saccharide units.

(i) Disaccharides :

(a) The disaccharides are sugars composed of two molecule of same or different monosaccharides.

(b) Generally one molecule of water is reduced in forming disaccharides.

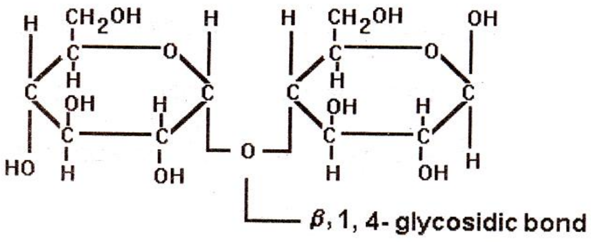
(c) Reaction is called as dehydrogenation

(d) General Formula = $C_n(H_2O)_{n-1}$

(e) Monosaccharides attach called as monomers.

(f) Bond present in between them is called as **glycosidic bond**.

Some Important Disaccharides :



Maltose

(i) **Maltose** → $\boxed{\text{Glucose + Glucose = Maltose}}$

(ii) **Lactose** → $\boxed{\text{Galactose + Glucose = Lactose}}$

- ➢ 5% in milk (only mammals)

(iii) **Sucrose** → $\boxed{\text{Glucose + Fructose = Sucrose}}$

- ➢ It is a commercial or kitchen sugar.
- ➢ It is called invert sugar or (cane sugar)
- ➢ Hydrolysis *of* sugar is called as inversion *of* sucrose
- ➢ Equimolar mixture of glucose and fructose called as invert sugar.

(iv) **Trehalose**

- ➢ It is the major sugar *of* insect haemolymph. Among plants,.it is found in fungi and yeasts.

(ii) **Trisaccharides : (Three monomers)**

(a) Manotriose = 2 Galactose + 1 Glucose

(b) Raffinose = 1 Glucose + 1 Galactose + 1 Fructose

- ➢ It is found in cotton seed.

(c) Melanoxylose = 1 Fructose + 2 Glucose

(iii) **Tetrasaccharides (Four monomers)**

- ➢ Stachyose = 1 Glucose + 1 Fructose + 2 galactose

3 **Polysaccharides**

(a) Polysaccharides yield more than 9 molecules *of* monosaccharides on hydrolysis.

(b) General Formula = $(C_6H_{10}O_5)_n$.

(c) These are linear polymers and also highly branched

(d) These are not called as sugar. because are not sweet in taste.

Excep. - Inulin is sweet.

(e) Glycosidic bond is present between monomers

(f) Suffix - 'an' is present in last part of there names.

Polysaccharides
↓ two types

Homopolysaccharide | **Heteropolysaccharides**

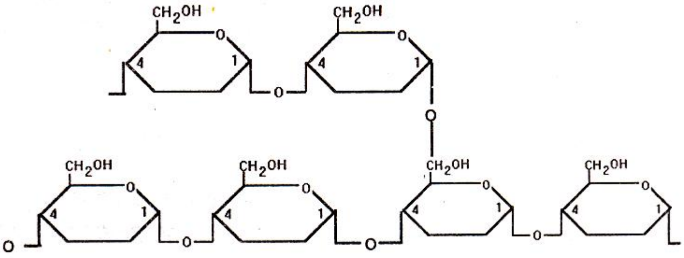
(i) **Homopolysaccharides :**

(a) There monomers are of one type of monosaccharides.

(b) These are simple type polysaccharides.

(c) Physiologically important homopolysaccharides.

(A) **Starch**



Formula of Starch

- **Stored food of plant**
- It is most improtant food source
- It is found in normal amount in all types of food source It is insoluble in water.
- It gives blue colour with iodine
- Its monomer is a α–D glucose.
- It is mixture of two compounds.

Amylose **Amylopectin**

(a) **Amylose :**

- They give blue colour with I_2.
- It is 15% to 20% in starch.

(b) **Amylopectin :**

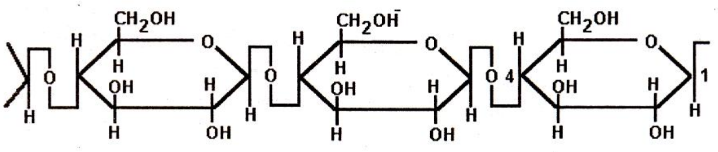
- Branch of 24–30 glucose monomers.
- Give Purple colour with I_2.
- It is 80–85%.

(B) **Glycogen :**

- Stored food of animals.
- Called as animal starch.
- Give red colour with I_2.

(C) **Cellulose ;**

- It is mainly found in plant cells.
- It is main constituent of cell wall.



Structure. of Cellulose

Preparation of Glucose

1. By Hydrolysis of Cane-sugar

In laboratory glucose can be prepared by hydrolysis of cane-sugar in the prsence of alcohol using dilute hydrochloric acid. Glucose and fructose are formed in equal amounts. Glucose, being less soluble in ethyl alcohol than fructose, crystallizes out.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

2. By Hydrolysis of Starch

Glucose is obtained, **on commercial scale**, by hydrolysis of starch by boiling it with dilute sulphuric acid at 393 K under a pressure of 2–3 bar.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393K,2-3bar]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Evidences that support the linear structure of Glucose

1. Reduction

$$HOH_2C\,.\,(CHOH)_4\,.\,CHO + H_2 \xrightarrow{Ni} \underset{\text{Sorbitol}}{HOCH_2.(CHOH)_4\,.\,CH_2OH}$$

2. Reaction with Hydrogen Iodide

$$HOCH_2-(CHOH)_4-CHO \xrightarrow{HI} H_3C-CH_2-CH_2-CH_2-CH_2-CH_3$$

n-Hexane

3. Oxidation

$$HOH_2C\ .\ (CHOH)_4\ .\ CHO + [O] \xrightarrow{Br_2/H_2O} HOCH_2\ .(CHOH)_4\ .\ COOH$$

Gluconic acid

IV PROTEINS

(a) Proteins are polymers of amino acids.

(b) Protein is 3/4 part of dry weight of tissues.

(c) Protein forms structure of body.

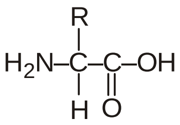
(d) C, H, O, N are necessary present in proteins.

(e) In some proteins P, S, Fe, Cu, I, also may be present. They are called trace elements.

(f) 70 types of Amino acids are known. But in proteins about 20 types of amino acids are used. other amino acids are called non-proteinious amino acid for e.g. citruline, ornithine

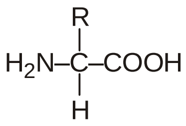
1 Chemical Structure :

(a) Amino acids can be given by the general formula.



$H_2N-\underset{H}{\overset{R}{C}}-\underset{\overset{\|}{O}}{C}-OH$

or



$H_2N-\underset{H}{\overset{R}{C}}-COOH$

R = Alkyl group.

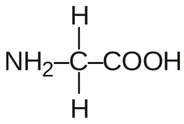
(b) If 'R' Changes amino acids formed also changes.

e.g. If R = H → Glycine (Simplest A. Acid)

If $R = CH_3$ → Alanine

If $R = CH_2OH$ → Serine.

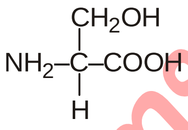
'R' group attach with the carbon than that carbon is called α - carbon.



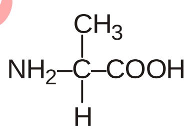
$NH_2-\underset{H}{\overset{H}{C}}-COOH$

or NH_2-CH_2-COOH

Glycine



$NH_2-\underset{H}{\overset{CH_2OH}{C}}-COOH$



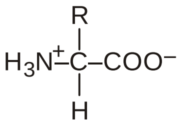
$NH_2-\underset{H}{\overset{CH_3}{C}}-COOH$

Serine Alanine

(c) Amino acids have also NH_2 group. Which is basic and also COOH group. Which is acidic. So Nature of Aminoacid is Acidic + Basic

(d) Amino Acids are amphoteric in nature. So for it a special term is coined called **Zwitter ion**.

(e) They have following structure in solution



$H_3\overset{+}{N}-\underset{H}{\overset{R}{C}}-COO^-$

[Zwitter Ion]

[Net charge on it is zero]

2 Classification of Amino Acids :

(A) According to synthesis amino acid is of two types-

(i) Essential amino Acids :

⇒ These are taken by food. Not synthesized in the body.

⇒ These are as follows

(1) Leucine
(2) Isoleucine
(3) Lysine
(4) Methionine
(5) Phyenyl alanine
(6) Threonine
(7) Tryptophan
(8) Valine

Arginine and Histidine are **semiessential** amino acids ie. they are bartly synthesized in tissues.

(ii) Non - Essential Amino Acid :

(a) These are synthesized in body.

(b) These are not required in food.

(c) These are as follows

(1) Alanine
(2) Aspargine
(3) Aspartic acid
(4) Cistine
(5) Glutamic acid
(6) Glutamine
(7) Hydroxy proline
(8) Glycine
(9) Proline
(10) Serine
(11) Tyrosine

(d) Except glycine all Amino Acid has 2 optical image (1 and 2)

(e) Optical isomerism are those which has a simmilar common formula but there images opposes to each other.

(f) For it chiral carbon atom is necessary. Chiral carbon atom is that carbon atom whose four valency are not satisfied by same group or atoms.

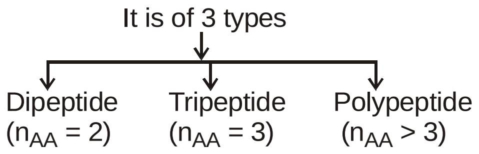
(g) In Glycine chiral carbon atom is absent. It is optically inactive.

(h) L-form synthesize protein.

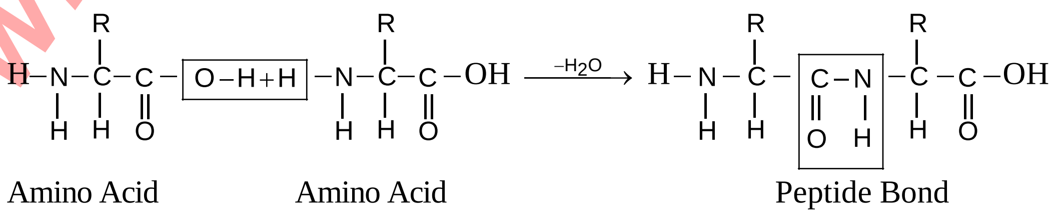
3 Peptide bond :

(a) Two or more than two amino acid linked and form a peptide.

(b) The bond present in between peptides is called peptide bond.



(c) A peptide bond is bond between -NH_3 of one Amino acid and -COOH of another amino acid.



Formation of Peptide Bond

4 Configuration of proteins :

(a) Biological nature or function of protein was confirmed by its conformation.

(b) This conformation is of 4 types

Primary Secondary Tertiary Quaternary

(A) Primary Structure :

⇒ This type of structure was given by **Friedrich Sanger** in 1953 in Insulin (of one chain)

⇒ Primary structure is conformed by a single polypeptide chain in a linear manner.

⇒ All amino acid are attached in a straight chain by peptide bond.

⇒ No biological importance & soon changed to other forms.

(B) Secondary Structure :

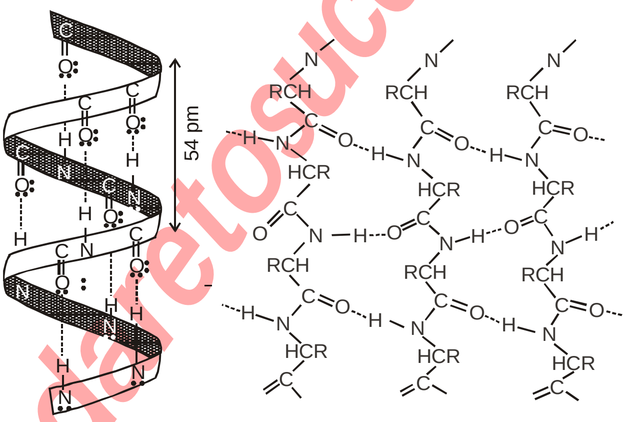
⇒ In it structure of straight chain from irregular changes to form coils.

⇒ H-bond + peptide bond present in secondary. structure.

⇒ This H bond is present between hydrogen of Amino group and oxygen atom carboxylic acid group.

⇒ This structure is of two types

α-helix β- pleated sheet



(i) α - helix

⇒ Chain is spiral

⇒ 3.7 atoms in one coiling

⇒ Right handed circular.

Eg. → Myosin, Keratin etc.

(ii) β-pleated sheet

⇒ Structure of protein is not arranged in a sequence.

⇒ Polypeptide chain are parallel to each other

⇒ H - bond form by near chains **Eg.** Silk fibres.

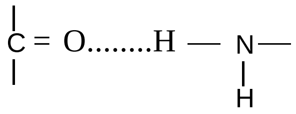
(C) Tertiary structure :

⇒ In this structure of protein atoms are highly coiled and form a spherical form

Ex. Albumin

⇒ This structure is formed by 4 regular hydrogen bonds which makes a regularity in it

(i) Hydrogen bond :



$$\underset{|}{\overset{|}{C}}=O........H-\underset{\underset{H}{|}}{N}-$$

Hydrogen bond

⇒ They are formed between oxygen of acidic amino acid and H of basic amino acid.

(ii) Hydrophobic bond -

⇒ Non - polar side chains of neutral amino acid tends to be closely associated with one another in proteins.

⇒ Present in between the amino Acid.

⇒ These are not true bonds.

(iii) Ionic bond :

$$-COO^{-}.....H_3{}^{+}N-$$

Ionic bond

⇒ These are salt bonds formed between oppositely charged groups in side chains of Amino acids

Eg. Aspartic acid

Glutamic acid

(iv) Disulphide bonds :

| ------ S - S ---- |

⇒ Relatively stable bond and thus is not broken readily under usual conditions of denaturation.

⇒ Formed between the -SH group of Amino acid Ex. Cystine and Methionine.

(D) Quaternary structure :

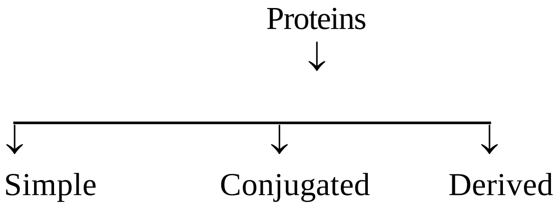
⇒ When 2 or more polypeptide chains united by forces other than covalent bonds (i.e. not peptide and disulphide bonds) are called Quaternary structure.

⇒ It is most stable structure.

Ex. Haemoglobin

5 Types of proteins

⇒ Classification of protein is based upon three general properties shape, Solubility and Chemical composition.



(i) Simple proteins

⇒ It is formed of only Amino Acids

⇒ Types

Fibrous　　Globular

(A) Fibrous :

⇒ It is insoluble

⇒ It is of elongated shape.

⇒ It is highly resistant to digestion by proteolytic enzymes.

⇒ Their main function - Protection.

Ex. Collagen, Keratin etc

(B) Globular :

⇒ These are spherical and oval in shape. Chains are highly coiled

⇒ These are soluble.

Ex. Albumin

(ii) Conjugated Proteins

⇒ These are complex proteins in which protein molecule is combined with characteristic non-amino acid substance.

⇒ Non-amino acid or Non - Protein part is called as prosthetic group

Ex. Nucleoproteins
(Protein + Nucleic acid),
Phosphoproteins (Protein + $(PO_3)^{2-}$)
Eg. → Casein of milk., Vitelline of egg - yolk

(iii) Derived proteins :

(a) These are obtained as a result of partial hydrolysis of natural proteins.
Eg. → Proteose, Metaproteins, Peptones

(b) **Denaturation of Proteins**

When a protein in its native form, is subjected to a physical change like change in temperature, or a chemical change like change in pH, the native conformation of the molecule is disrupted and proteins so formed are called denaturated proteins.

The denaturation may be reversible or irreversible. The coagulation of egg on boiling is an example of irreversible protein denaturation.

However, it has been shown now that in some cases, the process is actually reversible. The reverse process is called **renaturation**.

6 Test of Protein :

(a) With conc. HNO_3 on heating give yellow ppt. Which on more heating give solution On adding NH_4OH Red colour appears. It is **Xanthoprotic test**.

(b) (NH_4OH) + dil. $CuSO_4$ protein give Blue violet colour. It is a **biurete test**.

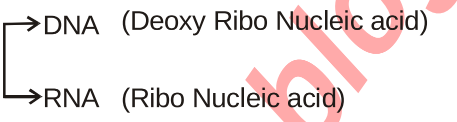
7 **Biological Importance of protein :**

(a) Component of plasma membrane.
(b) All enzymes are protein.
(c) Many hormones are protien.
(d) Antigen and antibody are protein.
(e) Actin and myosin protein are important in muscle contraction.
(f) Proteins are important in growth, regeneration and repairing.
(g) Calorific value 4.0 kcal.

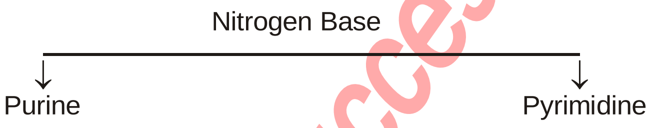
8 **Nucleic Acid :**

(a) These are special type of acids which are present in nucleus & cytoplasm.
(b) Control help in metabolic activity of cell
(c) They are also found in Mitochondria, centriole and chloroplast.

Types → These are of 2 types



(d) It is discovery by First of all in pus cells of WBC in 1869 by Friedrich Meischer.
(e) Fischer discovered Nitrogen bases in 1888

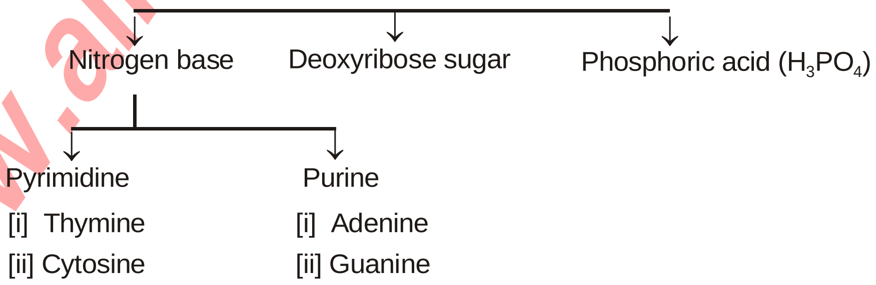


(f) Levan found sugar

(g) Altman coined the term "nucleic acid"

9 **DEOXY RIBONUCLIC ACID (D.N.A.) :**

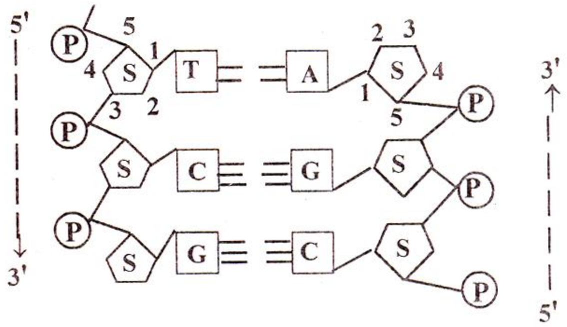
(a) It is found in Nucleus
(b) Double helical structure of DNA was given by Watson Crick. (a)
(c) Chargaff told that ratio of $\underbrace{A \text{ or } T}$ and $\underbrace{G \text{ or } C} = 1$
(d) DNA made up of 3 units



(e) Nucleoside

When nitrogen base combined with deoxyribose sugar it constitute a nucleoside.

Deoxyadenosine → It is a part of Nucleotide.



(f) Nucleotide
(g) Nitrogen base + Sugar + Phosphate → Nucleotide
(h) It is a unit of DNA
(i) All nucleotides combined and form a chain called polynucleotides by which RNA and DNA formed.

(A) Function of DNA :

(i) Self–Replication or self–Duplication
(ii) Protein Synthesis
(iii) Mutation →

(B) Replication of DNA :

(a) The synthesis of new DNA molecules from preexisting DNA is called replication.
(b) It occurs in mitosis and meiosis I in S phase of interphase.
(c) DNA replication is semiconservative proposed by Watson and Crick.

(C) Significance of DNA :

Chromosomes are mainly composed of DNA, RNA and histone protein.
Among these molecules, DNA is the main hereditary material.

10. Ribonuclic Acid (RNA) :

Found in cytoplasm as well as in nucleus.

Cytoplasm → In the ribosome (heigher amount)
Occourence
Nucelus → Nucleus

(A) Types of RNA and their Functions :

There are 3 main types of RNA molecules
(i) Messenger RNA (mRNA)
(ii) Transfer RNA (tRNA)
(iii) Ribosomal RNA (rRNA)

(i) Messenger RNA (mRNA)

Discovered by Astrachan, Huxley.

11. Enzymes :

Proteins which are used as a catalyst in biochemical reaction is known as biocatalysts.

(A) Structure of enzyme

(a) They are globular proteins.
(b) With having tertiary structure it can be collected as crystals.
(c) In the presence of enzymes biochemical reactions is completed with body temperature, normal pressure and normal pH 7 in the body.

(B) Specific cheracteristics :

Enzymes have following two specific cheracter as :

(i) Specificity (ii) Efficiency

(C) Specificity of enzymes

(a) Generaly one enzyme can catalyze only one biochemical reaction.
(b) It can increases rate of reaction upto 10^{20} times.
(c) In some cases one enzyme can catalyzes more than one reaction and one reaction can be catalyzes more than one enzyme also.
eg. Enzyme present in Yeast (Zymase) can fermant both glucose and fructose into .alcohol and also cane-sugar can be hydrolyses by invertase and sucrase enzymes.

(D) Efficiency of enzymes

(a) One molecule of enzyme can convert millions of substrate molecules into product per second.
eg. Carbonic anhydrase enzyme present in red blood carpcells can convert 6 lac molecules of carbonic acid into carbondioxide and water per second.
(b) With having tertiary structure it can be collected as crystals.
(c) Enzyme can be stored at low temperature.

(E) Importance of enzymes

In the thousands of enzymes presents in body if even a single enzyme would be absent or damaged than complex disease in results.

eg. Scacity of Phenylalaine hydroxylase enzyme in human body is result in phenylketonuria disease.

11. VITAMINS

It has been observed that certain organic compounds are required in small amounts in our diet but their deficiency causes specific diseases. These compounds are called vitamins.

Classification of Vitamins

Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) Fat soluble vitamins:

Vitamins which are soluble in fat and oils. But insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

(ii) Water soluble vitamins:

B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and can not be stored (except vitamin B_{12}) in our body.

Some important vitamins, their sources and diseases caused by their deficiency are listed in table.

[redacted]

POLYMERS

1. INTRODUCTION :

A polymer is a compound of high molecular mass formed by the combination of large number of small molecules and process is called polymerisation. The small molecules which constitute the repeating units in a polymer are called monomer units. These large molecule have relative molecular masses in the range 10^4 - 10^6.

eg.

$$\underset{\text{ethene}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{polythene.}}{[-CH_2-CH_2-]_n.}$$

Where n is as high as 10^5. The number of monomers units in a polymer is called the degree of polymerisation.

2. CLASSIFICATION OF POLYMERS

Polymers are classified on the following basis -

2.1 Classification based on monomers :

(a) **Homopolymer :** The polymer formed from one kind of monomer is called homopolymer.
eg. Polyethylene

(b) **Copolymer or mixed polymer :** Polymer formed from more than one kind of monomer units is called copolymer.
eg. Buna - S

2.2 Classification based upon origin or source :

There are of two types based on source

(a) **Natural polymers** whose source is animal and plants are called natural polymers
eg. starch,cellulose, protein etc.

(b) **Synthetic polymers** :- These are man made polymers synthesised in the laboratory from low molecular weight compounds.
eg. Nylon, dacron, bakelite, synthetic rubber, polystyrene etc.

2.3 Classification bassed on structure :

These are of three types based on structure –

(i) Linear polymers
(ii) Branched chain polymers
(iii) Cross linked polymers

(i) Linear polymers : In which monomer units are linked together to form long straight chains. The polymeric chains are stacked over one another to give a well packed structure. Such polymers have high densities, high tensile strength and high melting points.
eg. : Polythene, Nylon and polyesters

(ii) Branched chain polymers : In this type of polymers, the monomeric units are linked to constitute long chains (called main chain). There are side chains of different lengths which constitute branches. Branched chain polymers are irregularly packed and they have lower tensile strength and lower melting points as compared to linear polymers.
eg. : Amylopectin (Component of starch)

(iii) **Cross linked polymers :** The monomeric units are linked together to constitute a three dimensional network. Cross linked polymers are hard , rigid and brittle because of their network structure.
eg. : Bakelite, Formaldehyde resin etc.

2.4 Classification based on synthesis :

These are of two types based on synthesis -

(a) **Condensation polymerisation**: In this the monomer (same or different) units link with each other by the elimination of a small molecule (e.g. water, methyl alcohol) as a by-product. The polymer formed is known as condensation polymer. Nylon and terylene are the most common examples.
Since the condensation polymerisation proceeds by a stepwise intermolecular condensation, it is also known as step polymersation and the polymer formed is known as step growth polymer.

(b) **Addition polymerisation** : This involves the self addition of several unsaturated molecules of one or two monomers without loss of any small mulecule to form a single giant molecule. The polymer formed is known as addition polymer. Polythene is the most common example.

Differences between Addition and Condensation Polymers

S.N.	Addition polymers	Condensation polymers
1.	Formed by addition reaction.	Formed by condensation process with elimination of small molecules like H_2O.
2.	Molecular mass is a whole number multiple of the monomer.	Molecular mass is not whole number multiple of the monomer units.
3.	Generally involve one monomer unit.	Generally involve more than one monomer unit.
4.	Monomers are unsaturated molecules.	Monomer units must have two active functional groups.
5.	They are generally chain growth polymers.	They are generally step growth polymers.

2.5 Classification based on intermolecular forces :

(a) **Elastomers :** These are the polymers having elastic character. The polymer chains in such type of polymers are held together by weakest intermolecular forces. These forces permit the polymer to be stretched under stress but they regain their former shape when the stress is relieved. The elasticity of such polymers can be further modified by introducing few cross links between the chains.
eg. : Natural rubber

(b) **Fibres :** These are the polymers which have quite strong interparticle forces such as H-bonds.
eg. : Nylon , Dacron etc.

(c) **Thermoplastics :** These are the polymers which can be easily moulded into desired shapes by heating and subsequent cooling to room temperature. The intermolecular forces in thermoplastic polymers are intermediate to those of elastomers and fibres. Thermoplastic polymers soften on heating and become fluids but on cooling they become hard.
eg. : Polyethene, Polystyrene

(d) **Thermosetting polymers :** These are the polymers which become hard and infusible on heating. Heating results in excessive cross linking between the chains forming three dimensional network of bonds.
eg. : Bakelite, Melamine

3. METHOD OF POLYMERISATION

(a) Addition Polymers :

(i) A polymer formed by direct addition of repeated monomer's without the elimination of any byproduct molecules.

(ii) In this type, the monomers are unsaturated compounds and are generally derivative of ethene.

(iii) The addition polymers have same empirical formula as their monomers.

Ex. Nylon 6, 6, Terylene, bakelite etc.

Chain growth polymerization :

(i) There is a series of reaction each of which consume a reactive particle and produce another, similar particle, each individual reaction thus depend upon the previous one.

(ii) The reactive particle can be free radical, cations or anions.

(iii) The polymerization start when a molecule of monomers react with an initiator to form an active intermediate.

(iv) This active intermediate is added to another monomer forming another intermediate. In this way chain propagation continue and ultimately a polymer is formed.

(a) Peroxide $\longrightarrow$ Rad$^\bullet$ $\longrightarrow$ Chain initiating step

(b) $CH_2 \longrightarrow Rad - CH_2 - CH_2^\bullet$

Chain Propagating step

(c) $Rad - CH_2 \longrightarrow Rad - CH_2 - CH_2 - CH_2 - CH_2^\bullet$

Chain Propagating step

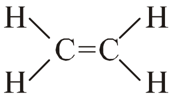
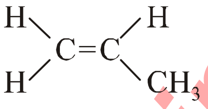
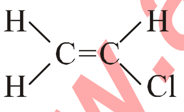
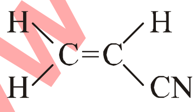
(d) $Rad - CH_2 - CH_2 - CH_2 - CH_2^\bullet \longrightarrow$

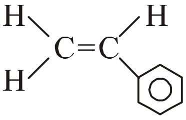
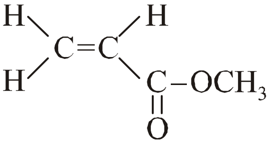
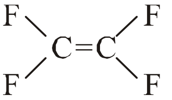
$[-CH_2 - CH_2-]_n + Rad^\bullet \longrightarrow$

Chain terminating step

Example :

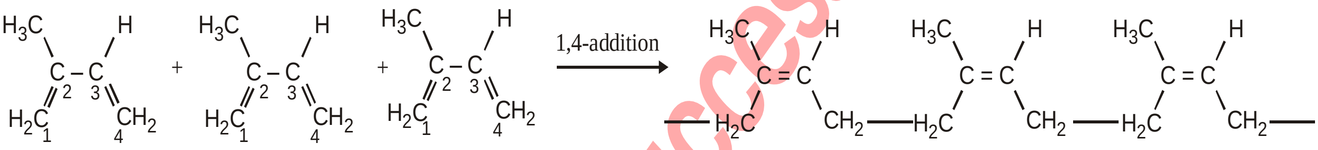
Polyethylene, Polypropylene, PVC, teflon, etc.

Monomer	**Polymer**	**Uses**
 Ethylene	Polythene	Bags, toys etc.
 Propylene	Polypropylene	Beakers, mill cartons etc.
 Vinyl chloride	Polyvinyl chloride (PVC)	Rain Coats, pipes, tiles etc.
 Acrylonitrile	Poly acrylonitrile, (PAN) Orlon	Carpets etc.

 Styrene	Polystyrene	Thermocole, insulating, material etc.
 Methyl methacrylate	Plexiglass	Transparent objects lenses etc.
 Tetrafluoro ethylene	Teflon (PTFE)	Chemical equipment Non stick cookware

4 NATURAL RUBBER

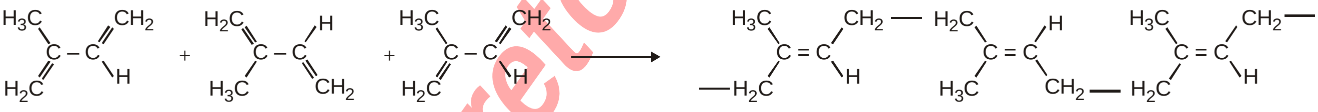
(a) It is cis Polyisoprene



Isoprene

cis -polyisoprene (natural rubber)

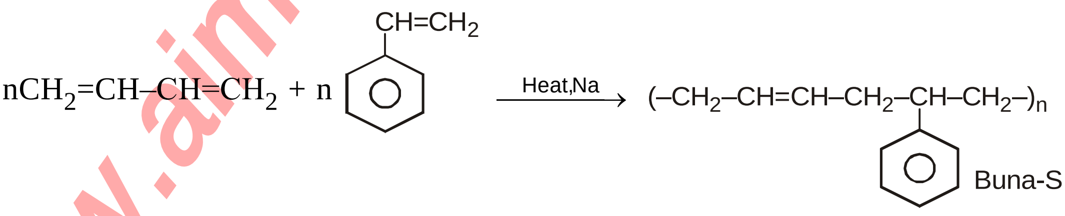
(b) Gutta percha:



trans - polyisoprene (gutta percha)

5. SYNTHETIC RUBBER

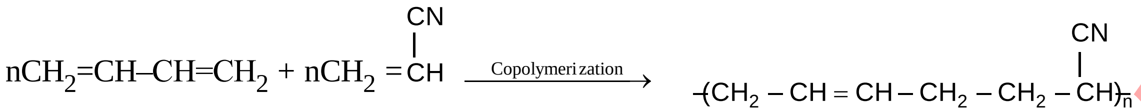
(i) **Buna S :** It is copolymer of 1, 3 butadiene and styrene. It is obtained by the polymerisation of butadiene and styrene in the ratio of 3 : 1 in the presence of sodium



Butadiene styrene

Uses : Buna - S is also vulcanised and used in making tyres for the vehicles. It is also used as rubber soles and in making water proof shoes.

(ii) Buna-N :

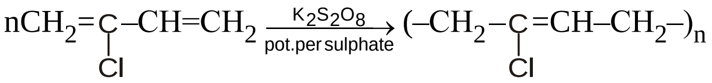


$$nCH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}\overset{\overset{CN}{|}}{CH} \xrightarrow{\text{Copolymerization}} {-}\!\left(CH_2-CH=CH-CH_2-CH_2-\overset{\overset{CN}{|}}{CH}\right)\!{-}_n$$

1,3-Butadiene Acrylonitrile Buna-N

⇒ It is used in making oil seals, tank lining, etc.

(iii) Neoprene

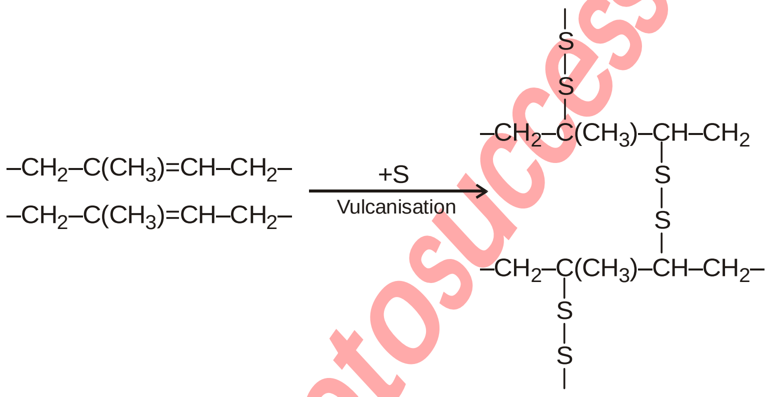


$$nCH_2{=}\underset{\underset{Cl}{|}}{C}{-}CH{=}CH_2 \xrightarrow[\text{pot.per sulphate}]{K_2S_2O_8} (-CH_2-\underset{\underset{Cl}{|}}{C}{=}CH{-}CH_2-)_n$$

Chloroprene Neoprene

Vulcanisation :

In vulcanisation rubber is heated (3 hrs) it with sulphur (3-10%) at a temperature of 125-140^{0}C. Rubber hydrocarbon combines with the sulphur atoms to form the sulphur bridges. The resulting product is tough, non-elastic and resistance to heat. It becomes non-abrasive and not affected by chemicals.

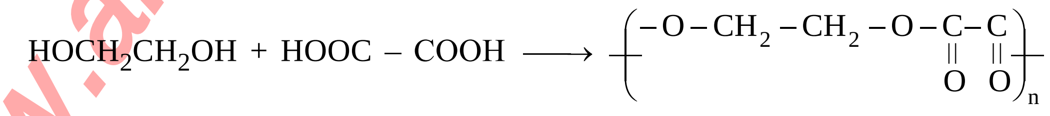


6. STEP GROWTH POLYMERISATION

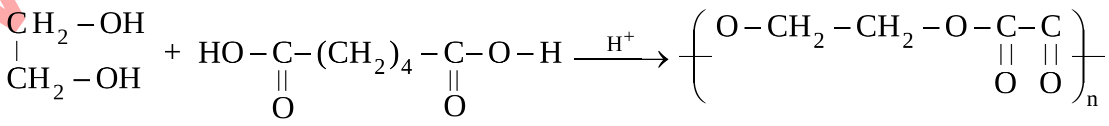
(i) This type of polymerization involve a series of reaction each of which is essentially independent of the proceeding one.

(ii) A polymer is formed simply because the monomer happen to undergo reaction at more than one functional group.

(iii) In the case of polyester, a diol for example, react with a dicarboxylic acid to form an ester but each moiety of the simple ester contain a group that can react to generate another ester linkage and hence a large molecule, which itself can react further, and so on



$$HOCH_2CH_2OH + HOOC-COOH \longrightarrow {-}\!\left(-O-CH_2-CH_2-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}\right)\!{-}_n$$



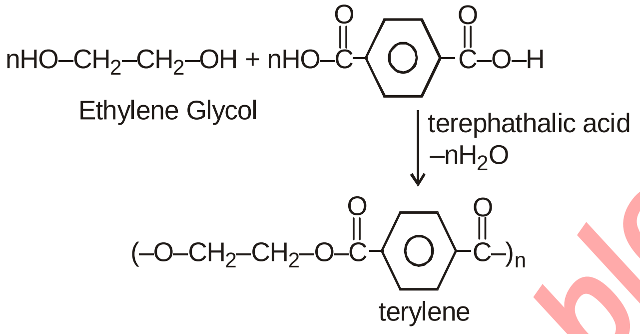
$$\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix} + HO-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-O-H \xrightarrow{H^+} {-}\!\left(O-CH_2-CH_2-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}\right)\!{-}_n$$

6.1 Condensation polymers :

(i) A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecule like -
H_2O / NH_3 etc..

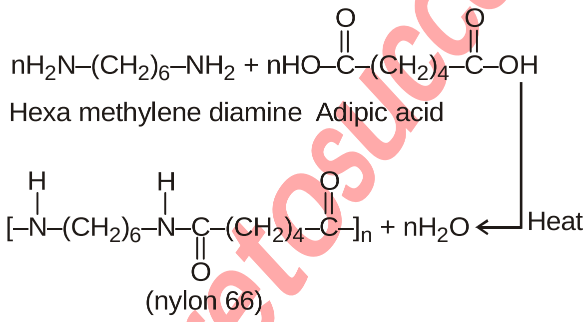
(ii) In this type, each monomer generally contain two functional group. Ex.Nylon 6, 6, Terylene, bakeliteete

(a) Polysters : These are the polymers having ester linkage ($-\overset{O}{\overset{||}{C}}-O-$)
Example : Terylene :



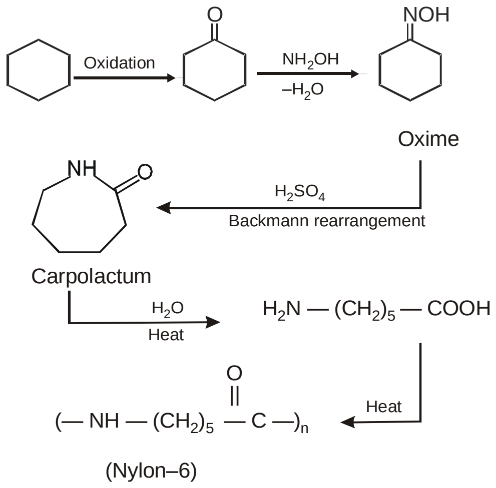
(b) Polyamides : Such polymers have amide linkage $(-\overset{O}{\overset{||}{C}}-\underset{H}{\underset{|}{N}}-)$ in the chain

(i) Nylon-66

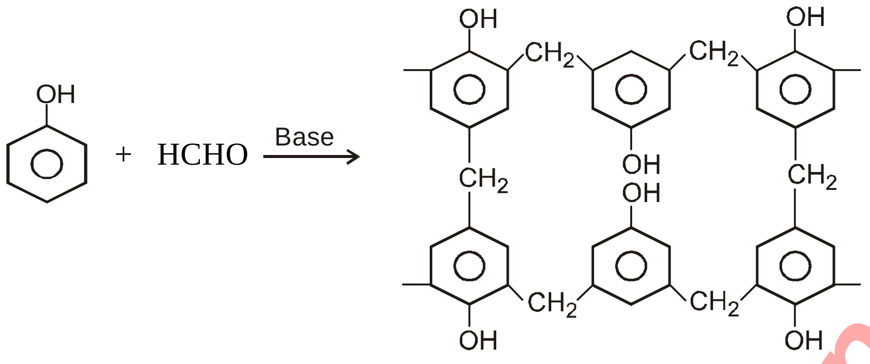


Uses : Nylon 66 have high tensile strength so it is used in the manufacture of carpets, textile fibres and bristles for brushes. It is used in making elastic hoisery.

(ii) Nylon-6



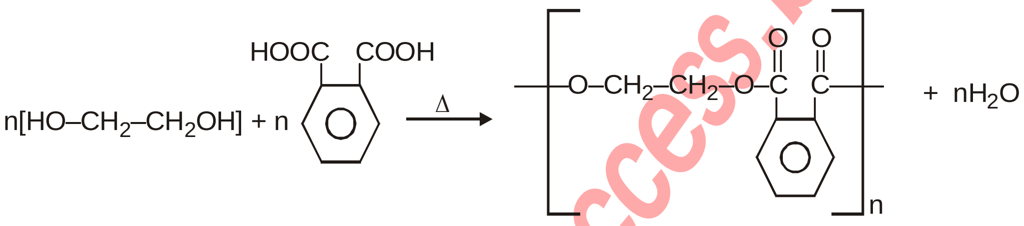
(c) Phenol-formaldehyde resins(Bakelite)



Bakelite

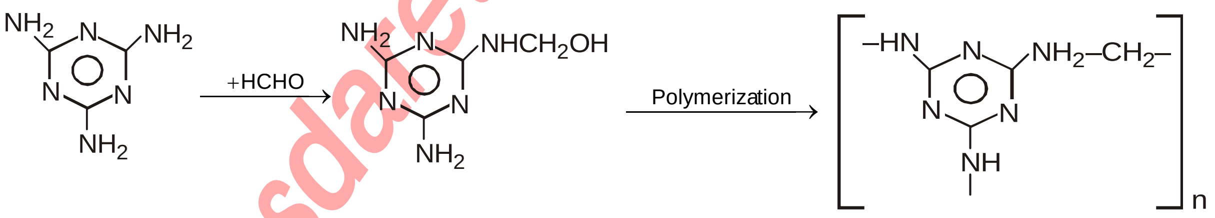
Because bakelite is hard and is a good electrical insulator, it is extensively used on making electrical switches, fuse holders, etc.

(d) Glyptal or (alkyd resin) : The most simple glyptal (polyethylene phthalate) formed from the polycondensation of glycol and phthalic acid.



Uses : It is used in the manufacture of paints

(e) Melamine formaldehyde resin : Melamine formaldehyde resin is formed by the co-polymerisation of melamine and formaldehyde.



Melamine intermediate

Uses : It is used for making non breakable plastic crockery i.e cup plates etc.

7. MOLECULAR WEIGHT OF POLYMERS

There are two types of average molecular weight in case of polymers.

(a) $\overline{M}_n$ = Number average molecular weight.

(b) $\overline{M}_w$ = Weight average molecular weight.

(a) **Number average molecular weight ($\overline{M_n}$)**

$$(\overline{M_n}) = \frac{\text{Total weight of the molecules}}{\text{Total number of molecules}}$$

If: n_1 molecules of mol. wt. M_1.
n_2 molecules of mol. wt. M_2.
n_3 molecules of mol. wt. M_3. Then

$$\overline{M_n} = \frac{n_1M_1 + n_2M_2 + n_3M_3 + ---}{n_1 + n_2 + n_3 + ---}$$

$$\overline{M_n} = \frac{\sum n_i M_i}{\sum n_i}$$

(b) **Weight average molecular weight $\overline{M_w}$**

$$\overline{M_w} = \frac{w_1M_1 + w_2M_2 + w_3M_3 + ---}{w_1 + w_2 + w_3 + ---}$$

[Weight = no. of molecules × molecular weight]

Where : w_1 = weight of the molecules of mol. wt. M_1
w_2 = weight of the molecules of mol. wt. M_2
w_3 = weight of the molecules of mol. wt. M_3

NOTE :– Polydispersity index (PDI) is the ratio of weight average mol mass to no. average mol mass PDI = $\overline{M}_w / \overline{M}_n$

For natural polymers PDI = 1 i.e. $\overline{M}_w = \overline{M}_n$

For Synthetic polymers PDI > 1 i.e. $\overline{M}_w > \overline{M}_n$

POLYMER THEORY

Ex.1 The product of addition polymerization reaction is -
(A) PVC (B) Nylon (C) Terylene (D) Polyamide **(Ans. A)**

Sol. PVC (polyvinyl chloride) is an addition polymer while nylon, terylene and polyamides are condensation polymers.

Ex.2 A raw material used in making nylon-6,6 is -
(A) Adipic acid (B) Butadiene
(C) Ethylene (D) Methyl methacrylate **(Ans.A)**

Sol. Nylon-6,6 is a copolymer of adipic acid [$COOH(CH_2)_4COOH$] and hexamethylene diamine.

Ex.3 Polymerisation of chloroethylene gives rise to the polymer -
(A) Polyethene (B) PVC (C) Teflon (D) Nylon **(Ans.B)**

Sol. Chloroethylene is $CH_2 = CHCl$ (vinyl chloride) whose polymer will be PVC (polyvinyl chloride).

Ex.4 Rubber is heated with sulphur and the process is known -
(A) Galvanization (B) Vulcanization (C) Bessmerization (D) Sulphonation **(Ans.B)**

Sol. It is used for making tyres.

Ex.5 Monomer of orlon is:
(A) vinyl chloride (B) styrene (C) propylene (D) acrylonitrile **(Ans.D)**

Sol. Acrylonitrile is $CH_2 = CHCN$

SOLVED EXAMPLES

BIOMOLECULES

Ex.1 Which of the following is not a reducing sugar-

(A) Glucose (B) Sucrose (C) Mannose (D) Fructose **Ans. (B)**

Sol. Sucrose is not a reducing sugar because it does not reduce fehling's solution.

Ex.2 Which one of the following is the reagent used to identify glucose-

(A) Neutral ferric chloride (B) Chloroform and alcoholic KOH

(C) Ammonical silver nitrate (D) Sodium ethoxide **Ans. (C)**

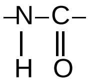
Sol. Ammonical silver nitrate (Tollen's reagent) oxidises glucose to gluconic acid and itself reduced to metallic silver.

Ex.3 Following is/are the oligosaccharides-

(A) Glucose (B) Sucrose (C) Lactose (D) Cellulose **Ans. (B,C)**

Sol. Oligosaccharides are the compounds which give 2 to 10 monosaccharides on hydrolysis. For example - sucrose, lactose, maltose etc

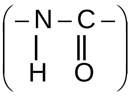
Ex.4



$\underset{H}{\underset{|}{-N}}-\underset{O}{\underset{\|}{C}}-$ group is characteristic of -

(A) Cellulose (B) Nucleic acid (C) Proteins (D) Phospholipids **Ans. (C)**

Sol. Peptide bond



$\left(\underset{H}{\underset{|}{-N}}-\underset{O}{\underset{\|}{C}}-\right)$ is characteristic of proteins.

Ex.5 The pH value of a solution in which a polar amino acid does not migrate under the influence of electric field is called -

(A) Isoelectronic point (B) Isoelectric point

(C) Neutralisation point (D) None **Ans. (B)**

Sol. Isoelectric point is the pH at which structure of amino acid has no charge.

Ex.6 The simplest amino acid is -

(A) Glycine (B) Alanine (C) Guanine (D) All the above **Ans. (A)**

Sol. Simplest amino acid is glycine (α– amino acetic acid H_2N-CH_2-COOH).

Ex.7 The main structural feature of protein is–

(A) Ester linkage (B) Ether linkage (C) Peptide linkage (D) All of these **Ans. (C)**

Sol. The main structural feature of proteins is the presence of peptide linkage.

Ex.8 The primary structure of a polypeptide is determined by-

(A) The numer of disulphite bonds in the polypeptide

(B) The number of amino acids in the polypeptide

(C) The order of amino acids in the polypeptide

(D) The length of the polypeptide **Ans. (C)**

Sol. The primary structure of a polypeptide is the information of order of different amino acids in that polypeptide.

Ex.9 DNA molecule consists of units of-

(A) Base–sugar (B) Base – sugar– phosphate

(C) Base – phosphate (D) None of these **Ans. (B)**

Sol. DNA has nucleotide unit, i.e., Sugar + base + H_3PO_4.

Ex.10 The process of formation of RNA from DNA is known as-

(A) Translation (B) Transcription (C) Replication (D) Mutation **Ans. (B)**

Sol. The process of formation of RNA from DNA is called transcription.

Ex.11 The organic compound which will answer Fehling's solution test is-

(A) Ethanol (B) Acetone (C) Maltose (D) Benzaldehyde **Ans. (C)**

Sol. Maltose, being reducing sugar, reduces Fehling solution.

Q.12 The main point of difference between DNA and RNA is-

(A) Presence of thymine in DNA and RNA

(B) Presence of deoxyribose and thymine in DNA, ribose and uracil in RNA

(C) Presence of ribose and thymine in DNA, deoxybribose and uracil in RNA

(D) Presence of deoxyribose in DNA and ribose in RNA **Ans. (B)**

Sol. DNA has deoxyribose sugar, RNA has ribose sugar with three bases common as adenine, guanine and cytosine. DNA has fourth base thymine ; RNA has uracil.

POLYMER

Ex.13 Which one is used as a heterogeneous catalyst in the polymerization of ethylene into polyethene-

(A) Walker catalyst (B) Ziegler-Natta catalyst

(C) Wilkinson's catalyst (D) Ruthenium catalyst **(Ans.B)**

Sol. In the polymerisation of ethylene into polyethylene Zeigler–Natta catalyst (Triethyl aliminium + Titanium tetrachloride) is used as heterogeneous catalyst.

Ex.14 Natural polymer is-

(A) Polyester (B) Glyptal (C) Starch (D) Nylon-6 **(Ans.C)**

Sol. Starch is natural polymer of D glucose.

Ex.15 Which is a synthetic rubber-

(A) Buna-S (B) Neoprene (C) Both the above (D) None **(Ans.C)**

Sol. Buna – S and neoprene are synthetic rubber.

Ex.16 Thermosetts are-

(A) Cross-linked polymers

(B) Do not melt (or soften) on heating

(C) Cross-linking is usually developed at the time of moulding where they harden irreversibly

(D) All **(Ans.D)**

Sol. Ex of thermosetts is bakelite

Ex.17 Di–n–butyl phthalate is -

(A) Plastisizer (B) Thermoplastic

(C) Polymer (D) Thermosetting plastic **(Ans.A)**

Sol. Di–n–butylphthalate is plastisizer added to PVC to make it soft.

Ex.18 Natural rubber is-

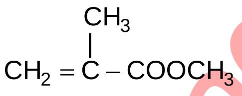
(A) Trans polyisoprene (B) Cis polyisoprene

(C) Cis and trans isoprene (D) None of these **(Ans.B)**

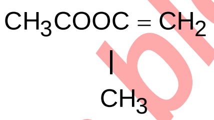
Sol. Natural rubber is a homopolymer of cis-isoprene.

Ex.19 The structual formula of monomer of poly methymethacrylate (PMMA) is -

(A) $CH_2=CHCOOCH_3$

(B) 
$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-COOCH_3$

(C) $CH_3COOCH=CH_2$

(D) 
$\underset{\underset{\displaystyle CH_3}{|}}{CH_3COOC}=CH_2$ **(Ans.B)**

Sol. Formula 2nd is of methyl methacrylate, the monomer of PMMA. or Plexiglass.

Ex.20 Which one of the following compounds is polyester-

(A) Bakelite (B) Nylon 6,6 (C) Terylene (D) Rubber **(Ans.C)**

Sol. Terylene is a polyester fibre made up of by the polymerisation of ethylene glycol and pterephthalic acid.

Ex.21 Nylon is classified as a condensation polymer because-

(A) In its preparation a solid is formed from liquid monomers

(B) Its structure contains the peptide linkage, –CONH–

(C) It can be prepared from aqueous solutions of its monomers

(D) A small molecule is eliminated in its formation from its monomers **(Ans. D)**

Sol. Nylon is a condensation polymer because in the reaction of adipic acid with hexamethylene diamine, small molecule H_2O is eliminated in its formation.

Ex.22 The primary structure of a polypeptide is determined by-

(A) The number of disulphide bonds in the polypeptide

(B) The number of amino acids in the polypeptide

(C) The order of amino acids in the polypeptide

(D) The length of the polypeptide **(Ans. C)**

Sol. The primary structure of a polypeptide is the information of order of different amino acids in that polypeptide.

EXERCISE – I

BIOMOLECULES

Q.1 Which of the following bonds determines the secondary structure of proteins ?
(A) Electrovalent bond (B) Covalent bond (C) Hydrogen bond (D) Coordinate bond

Q.2 Which of the following is called the power house of the living cell ?
(A) Golgi bodies (B) Nucleus (C) Mitochondria (D) Lysosome

Q.3 Which of the following part of the cell is the centre of protein synthesis?
(A) Plasma membrane (B) Golgi bodies (C) Ribosome (D) Lysosome

Q.4 Which of the following bonds is responsible for the coiled structure of proteins ?
(A) Dipeptide bond (B) Peptide bond (C) Hydrogen bond (D) Ionic bond

Q.5 Which of the following diseases is due to the deficiency of vitamin A ?
(A) Scurvy (B) Nightblindness (C) Beri-beri (D) Anemia

Q.6 Which of the following compounds is not the component of a balanced diet ?
(A) Vitamin (B) Hormone (C) Carbohydrate (D) Fat

Q.7 Insulin belongs to which of the following families ?
(A) Antiseptic (B) Vitamin (C) Hormone (D) Enzyme

Q.8 Which of the following acts as a biocatalyst ?
(A) Enzyme (B) Amino acid (C) Nitrogen molecule (D) Carbohydrate

Q.9 Which of the following enzymes convert starch to maltose ?
(A) Invertase (B) Zymase (C) Maltase (D) Diastase

Q.10 Which of the following is an example of an aldohexose ?
(A) Fructose (B) Glucose (C) Sucrose (D) Ribose

Q.11 Glucose and fructose are .... of each other
(A) homologues (B) functional group isomers
(C) mirror image isomers (D) nonisomers

Q.12 Which of the following disaccharides is found in the milk?
(A) Sucrose (B) Galactose (C) Lactose (D) Maltose

Q.13 Which of the following is invert sugar ?
(A) Mixture of glucose and galactose (B) Mixture of glucose and fructose in equimolar ratio
(C) A type of cane sugar (D) Optically inactive form of sugar

Q.14 Which of the following factors is not a denaturant of enzymes ?
(A) Heat (B) Mechanical energy
(C) High salt concentration (D) pH 7

Q.15 Which of the following is an example of a pentose sugar?
(A) Fructose (B) Arabinose (C) Glucose (D) Galactose

POLYMER

Q.16 Which of the following is not a copolymer-

(A) Plexiglass (B) Buna-S (C) Nylon-66 (D) Dacron

Q.17 Polymerisation in which two or more chemically different monomers take part is called-

(A) Addition polymerisation (B) Copolymerisation

(C) Chain polymerisation (D) Homopolymerisation

Q.18 Chemical name of melamine is-

(A) 2,4-Diamino-1,3,5-triazine (B) 2-Amino-1,3,5-triazine

(C) 2,4,6 -Triamino-1,3,5-triazine (D) 1,3,5-Triamino-2,4,6-triazine

Q.19 Carprolactum is used to prepare which of the polymer-

(A) Nylon – 66 (B) Melamine (C) Nylon–6 (D) PMMA

Q.20 The fibre obtained by the condensation of hexamethylene diamine and adipic acid is-

(A) Dacron (B) Nylon 66 (C) Rayon (D) Teflon

Q.21 Of the following which is a step growth polymer-

(A) Bakelite (B) Polyethylene (C) Teflon (D) PVC

Q.22 Bekelite is:

(A) Addition polymer (B) Elastomer (C) Thermoplastic (D) Thermosett

Q.23 Perlon is:

(A) Rubber (B) Nylon (C) Terylene (D) Orlon

Q.24 Nylon-6, 6 is made by the polycondensation of:

(A) Adipic acid + Hexamethylene diamine (B) Phthalic acid + Glycerol

(C) Phenol + Formaldehyde (D) Urea + Formaldehyde

Q.25 An example of a natural biopolymer is-

(A) Teflon (B) Neoprene (C) Nylon-66 (D) DNA

Q.26 Natural silk is a-

(A) Polypeptide (B) Polyacrylate (C) Polyester (D) Polysaccharide

Q.27 Peptide bond is a key feature in-

(A) Polysaccharide (B) Proteins (C) Nucleotide (D) Vitamins

Q.28 Neoprene rubber is obtained by the polymerization of :

(A) 1, 3-Butadiene (B) 2- Methyl -1, 3-butadiene

(C) 2- Chloro -1, 3 butadiene (D) Styrene and butadiene

Q.29 Which of the following is not a natural polymer

(A) Starch (B) Cellulose (C) Glyptal (D) Glycogen

Q.30 Which of the following is natural polymer:

(A) Polyisoprene (B) Polybutadiene

(C) Polyethylene terephthalate (D) Polyethylene

EXERCISE–II

BIOMOLECULES

Q.1 RNA contains - **[AIEEE-2002]**
(A) Urasil, Ribose (B) Thiamine, Ribose
(C) Cytocine, Deoxyribose (D) Adenine, Deoxyribose

Q.2 Complete hydrolysis of cellulose gives – **[AIEEE-2003]**
(A) D-glucose (B) L-glucose (C) D-fructose (D) D-ribose

Q.3 The reason for double helical structure of DNA is operation of – **[AIEEE-2003]**
(A) Hydrogen bonding (B) Electrostatic attractions
(C) vander Waal's forces (D) Dipole-dipole interaction

Q.4 Coordination compounds have great importance in biological systems, In this context which of the following statements is incorrect ? **[AIEEE-2004]**
(A) Chlorophylls are green pigments in plants and contain calcium
(B) haemoglobin is the red pigment of blood and contains iron
(C) Cyanocobalamin is B_{12} and contains cobalt
(D) Carboxypeptidase–A is an enzyme and contains zinc

Q.5 Which base is present in RNA but not in DNA ? **[AIEEE-2004]**
(A) Uracil (B) Cytosine (C) Guanine (D) Thymine

Q.6 Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which of the following categories ? **[AIEEE-2004]**
(A) A co-enzyme (B) A hormone (C) An enzyme (D) An antibiotic

Q.7 Identify the correct statement regarding enzymes : **[AIEEE-2004]**
(A) Enzymes are specific biological catalysts that can normally function at very high temperatures (T~ 1000 K)
(B) Enzymes are normally heterogeneous catalysts that are very specific in their action
(C) Enzymes are specific biological catalysts that cannot be poisoned
(D) Enzymes are specific biological catalysts that possess well-defined active sites

Q.8 In both DNA and RNA, heterocylic base and phosphate ester linkages are at – **[AIEEE-2005]**
(A) C_2' and C_5' respectively of the sugar molecule
(B) C_5' and C_2' respectively of the sugar molecule
(C) C_5' and C_1' respectively of the sugar molecule
(D) C_1' and C_5' respectively of the sugar molecule

Q.9 The pyrimidine bases present in DNA are – **[AIEEE 2006]**
(A) cytosine and guanine (B) cytosine and thymine
(C) cytosine and uracil (D) cytosine and adenine

Q.10 The term anomers of glucose refers to – **[AIEEE 2006]**
(A) a mixture of (D)-glucose and (L)-glucose
(B) enantiomers of glucose
(C) isomers of glucose that differ in configuration at carbon one (C-1)
(D) isomers of glucose that differ in configurations at carbons one and four (C-1 and C-4)

Q.11 The secondary structure of a protein refers to – **[AIEEE 2007]**

(A) α-helical backbone

(B) hydrophobic interactions

(C) sequence of α-amino acids

(D) fixed configuration of the polypeptide backbone

Q.12 α-D-(+)-glucose and β-D-(+)-glucose are **[AIEEE 2008]**

(A) epimers (B) anomers (C) enantiomers (D) conformers

Q.13 The two functional groups present in a typical carbohydrate are : **[AIEEE 2009]**

(A) – OH and –COOH (B) – CHO and –COOH

(C) > C = O and –OH (D) – OH and –CHO

POLYMER

Q.14 Monomers are converted to polymer by – **[AIEEE-2003]**

(A) Hydrolysis of monomers

(B) Condensation reaction between monomers

(C) Protonation of monomers

(D) None is correct

Q.15 Nylon threads are made of – **[AIEEE-2003]**

(A) Polyamide polymer (B) Polyethylene polymer

(C) Polyvinyl polymer (D) Polyster polymer

Q.16 Which of the following is a polyamide ? **[AIEEE-2005]**

(A) Nylon-66 (B) Teflon (C) Bakelite (D) Terylene

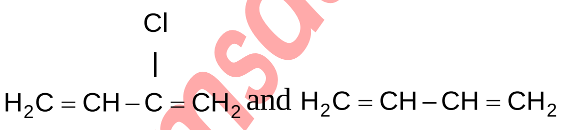
Q.17 Which of the following is fully fluorinated polymer- **[AIEEE-2005]**

(A) Teflon (B) Neoprene (C) PVC (D) Thiokol

Q.18 Bakelite is obtained from phenol by reacting with **[AIEEE 2008]**

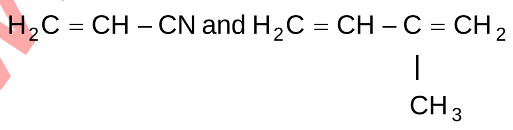
(A) CH_3CHO (B) CH_3COCH_3 (C) HCHO (D) $(CH_2OH)_2$

Q.19 Buna-N synthetic rubber is a copolymer of - **[AIEEE 2009]**

(A) 
$H_2C=CH-\underset{}{\overset{\displaystyle Cl \atop |}{C}}=CH_2$ and $H_2C=CH-CH=CH_2$

(B) $H_2C=CH-CH=CH_2$ and $H_5C_6-CH=CH_2$

(C) $H_2C=CH-CN$ and $H_2C=CH-CH=CH_2$

(D) 
$H_2C=CH-CN$ and $H_2C=CH-\underset{\displaystyle | \atop CH_3}{C}=CH_2$

Q.20 The disaccharide present in milk is :
(A) Maltose (B) Lactose (C) Sucrose (D) Cellobiose

Q.21 Insulin is :
(A) An amino acid (B) Protein (C) A carbohydrate (D) A lipid

Q.22 Glucose when heated with CH_3OH in presence of dry HCl gas gives α and β–methyl glucosides because it contains :
(A) An aldehyde group (B) A–CH_2OH group (C) A ring structure (D) Five hydroxyl groups

Q.23 The commonest disaccharide has the molecular formula :
(A) $C_{10}H_{18}O_9$ (B) $C_{10}H_{20}O_{10}$ (C) $C_{18}H_{22}O_{11}$ (D) $C_{22}H_{22}O_{11}$

Q.24 It is best to carry out reactions with sugars in neutral or acid medium and not in alkaline medium. This is because in alkaline medium sugars undergo one of the following changes :
(A) Racemisation (B) Decomposition (C) Inversion (D) None of these

Q.25 The fibre obtained by the condensation of hexamethylene diamine and adipic acid is :
(A) Dacron (B) Nylon '66' (C) Rayon (D) Teflon

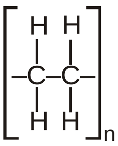
Q.26 Natural rubber is basically a polymer of or the monomer of natural polymer rubber is :
(A) Neoprene (B) Isoprene (C) Chloroprene (D) Butadiene

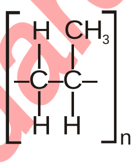
Q.27 Rayon yarns are obtained from :
(A) Polymethylene (B) Polyesters (C) Cellulose (D) Styrene

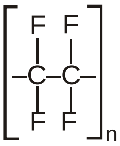
Q.28 Polymerisation in which two or more chemically different monomers take part is called :
(A) Addition polymerisation (B) Copolymerisation
(C) Chain polymerisation (D) Homopolymerisation

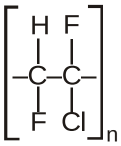
Q.29 Which of the following polymers contains nitrogen :
(A) Nylon (B) Polythene (C) PVC (D) Terylene

Q.30 Which of the following is teflon :

(A) 
$\left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\right]_n$

(B) 
$\left[-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\right]_n$

(C) 
$\left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\right]_n$

(D) 
$\left[-\overset{H}{\underset{F}{C}}-\overset{F}{\underset{Cl}{C}}-\right]_n$

ANSWER KEY

EXERCISE – I

Q.1	C	Q.2	C	Q.3	C	Q.4	C	Q.5	B	Q.6	B	Q.7	C
Q.8	A	Q.9	D	Q.10	B	Q.11	B	Q.12	C	Q.13	B	Q.14	D
Q.15	B	Q.16	A	Q.17	B	Q.18	C	Q.19	C	Q.20	B	Q.21	A
Q.22	D	Q.23	B	Q.24	A	Q.25	D	Q.26	A	Q.27	B	Q.28	C
Q.29	C	Q.30	A										

EXERCISE – II

Q.1	A	Q.2	A	Q.3	A	Q.4	A	Q.5	A	Q.6	B	Q.7	D
Q.8	D	Q.9	B	Q.10	C	Q.11	A	Q.12	B	Q.13	C	Q.14	B
Q.15	A	Q.16	A	Q.17	A	Q.18	C	Q.19	B	Q.20	B	Q.21	B
Q.22	C	Q.23	D	Q.24	C	Q.25	B	Q.26	B	Q.27	C	Q.28	B
Q.29	A	Q.30	C										