### CARBONYL COMPOUNDS

A divalent group in which a double bond is present between carbon and oxygen atoms, is called a carbonyl group. The compounds in which two valencies of the carbon atom of the carbonyl group are saturated by hydrogen and/or hydrocarbon radical/s (or substituted hydrocarbon radical/s), are called carbonyl compounds.

Carbonyl group



### ALDEHYDE

In aldehydes, at least one hydrogen atom is attached to the carbonyl group, i.e., aldehydes can be represented by the following general

Where Z = H or hydrocarbon radical (or substituted hydrocarbon radical)

After removing Z from the above formula of aldehydes, the remaining group is called an aldehydic group or formyl group, and it is represented by the condensed fromula –CHO for convenience.

### KETONES

The carbonyl group present in ketones is called ketonic group. In ketonic group, both the valencies of carbon atom are satisfied by carbon. Therefore, ketones can be represented by the

following general formula.

Where Z = Hydrocarbon radical (or substitued hydrocarbon radical)

Ketonic group is represented by the condensed formula –CO– for convenience.

If the radicals Z attached to the ketonic group are identical, then ketones are called simple or sym or symmetrical ketones, and if they are nonidentical then they are called mixed or unsym or unsymmetrical ketones. For example :

### Simple or symmetrical ketones :

$$CH_3$$
-C-CH<sub>3</sub>  $C_2H_5$ -C-C<sub>2</sub>H<sub>5</sub>

### Mixed or unsymmetrical ketones :

$$CH_3$$
- $C-C_2H_5$   $CH_3$ - $C-C_3H_7$   $C_2H_5$ - $C-C_3H_7$ 

### PREPARATION OF CARBONYL COMPOUNDS

Methods of Preparation of Both Alkanals and Alkanones

### [a] By Oxidation of Alkanols :

Alkanals are prepared by oxidation of primary alcohols, while ketones are prepared by oxidation of secondary alcohols. Acidified dichromate is normally used as an oxidant.

$$RCH_{2}OH + [O] \xrightarrow{\text{Dil. } H_{2}SO_{4}}{K_{2}Cr_{2}O_{7}} RCHO + H_{2}O$$

$$R-CHOH + [O] \xrightarrow{\text{Dil. } H_{2}SO_{4}}{K_{2}Cr_{2}O_{7}} R-C=O + H_{2}O$$

$$R = CHOH + [O] \xrightarrow{\text{Dil. } H_{2}SO_{4}}{K_{2}Cr_{2}O_{7}} R = C = O + H_{2}O$$

On using N–bromosuccinimide (NSB) as an oxidant, the reaction takes place as follows :



$$RCHO + \begin{array}{c} CH_2 - CO \\ CH_2 - CO \\ Succinimide \end{array} NH-HBr$$

### [b] By Dehydrogenation of Alkanols :

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

$$RCH_{2}OH \xrightarrow{Cu \text{ or } ZnO} RCHO$$

$$R-CHOH \xrightarrow{Cu \text{ or } ZnO} -2H \xrightarrow{R-C=O} R$$

### [c] By Dry Distillation of Calcium Alkanoates :

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.





### [d] By Action of MnO on Alkanoic Acids :

Alkanals and alkanones can be obtained by passing vapours of alkanoic acids over heated manganous oxide at 300°.

$$\begin{array}{ccc} R_{1}^{+}CO-O-H & MnO \\ + & 300^{\circ} \end{array} \xrightarrow{R} CO + CO_{2} + H_{2}O \\ R'-CO_{1}^{+}OH & 300^{\circ} \end{array}$$

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).

[e] **By Alkaline Hydrolysis of gem–Dihalides :** Carbonyl compounds are formed on heating alkylidene dihalides with aqueous caustic alkali solution.

$$\begin{array}{c} R \\ I \\ R-C-CI \\ I \\ CI \\ \end{array} \xrightarrow{KOH} \left( \begin{array}{c} R \\ I \\ R-C-OH \\ I \\ OH \end{array} \right) \xrightarrow{\Delta} \begin{array}{c} R \\ I \\ R-C=O \\ -H_2O \end{array} \xrightarrow{R} O = O \\ Unstable \end{array}$$

Methanal is formed (in very low yield) from methylene dichloride  $(CH_2Cl_2)$ , ethanal from ethylidene dichloride  $(CH_3CHCl_2)$  and propanone from isopropylidene dichloride  $(CH_3CCl_2CH_3)$ .

Above method is appropriate for preparation of ketones because ketones are more stable towards caustic alkali whereas aldehydes are very reactive in alkaline medium and form serveral by–products.

### [f] By Oxidation of Alkyl Halide :

Alkanals are fromed on oxidation of 1° alkyl halides by dimethylsulphoxide ( $Me_2SO$ ) in the presence of a base, like triethylamine ( $Et_3N$ ). Alkanones are formed on oxidation of 2° alkyl halides.

RCH<sub>2</sub>–X + CH<sub>3</sub>–SO–CH<sub>3</sub> Primary Dimethyl alkyl halide sulphoxide

 $\xrightarrow{(C_2H_5)_3N} RCHO + CH_3 - S - CH_3 + HX$ Alkanal Dimethyl
sulphide

 $R_2CH-X + CH_3-SO-CH_3$ Secondary alkyl halide

$$\xrightarrow{(C_2H_5)_3N} R_2CO + CH_3 - S - CH_3 + HX$$
  
Alkanone

### [g] By Oxidation of Nitroalkanes :

$$\begin{array}{ccc} \text{RCH}_2\text{NO}_2 & \xrightarrow{\text{OH}^-} & \text{RCH}=\text{NO}-\text{OH} \\ & & \xrightarrow{\text{H}_3\text{O}^+} & \text{RCH}=\text{O} \\ \\ \text{R}_2\text{CHNO}_2 & \xrightarrow{\text{OH}^-} & \text{R}_2\text{C}=\text{NO}-\text{OH} & \xrightarrow{\text{H}_3\text{O}^+} \\ & & \text{R}_2\text{C}=\text{O} \end{array}$$

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

### [h] By Grignard's Reagents :

**[i] With ethyl formate :** Alkanal is formed by reaction of formic ester and an alkylmagnesium halide.

 $\begin{array}{ccc} H & H \\ I & I \\ R + C = O & \longrightarrow & R - C = O + C_2 H_5 O - Mg X \\ I & I \\ Mg X & O C_2 H_5 \end{array}$ 

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.

$$R-MgX + C_2H_5O-CO-R'$$
  

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

 $R-MgX + H_2N-CO-R'$ 

 $\rightarrow$  R–CO–R' + Mg(NH<sub>2</sub>)X

**[ii] With higher alkyl cyanides :** Alkanones are formed on hydrolysis after reaction of an alkylmagnesium halide with ethyl cyanide or its higher homologue.

Reactivity of  $\alpha$  hydrogen atom decreases due to +I effect of methyl group in ethyl cyanide. Therefore, better yield of the ketone is obtained by its reaction with an alkylmagnesium halide.

**By Ozonolysis of Alkenes :** Desired alkanals and alkanones can be obtained by ozonolysis of appropriate alkenes.

$$\underset{R}{\overset{R}{\longrightarrow}} c = c \underset{R}{\overset{R}{\longrightarrow}} \underset{R}{\overset{Ozonolysis}{\longrightarrow}} \underset{R}{\overset{R}{\longrightarrow}} c = o + o = c \underset{R}{\overset{R}{\longrightarrow}}$$

### By Hydration of Alkynes :

[i]

[i]

[i] Catalytic Acidic Hydration : Acetaldehyde is formed on passing acetylene in 40% aqueous solution of  $H_2SO_4$  at 60° in the presence of 1% HgSO<sub>4</sub>. It is called Kucherov reaction.

$$CH \equiv CH + H_2O \xrightarrow{\text{Dil } H_2SO_4} CH_3 - CHO$$

Alkanones are formed on using higher alkynes.

$$R-C \equiv CH + H_2O \longrightarrow R-CO-CH_3$$
$$R-C \equiv C-R + H_2O \longrightarrow R-CO-CH_2-R$$

### [ii] Hydration Through Hydroboronation :

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.



In the above reaction the ethanal is formed from acetylene propanal from propyne butanal from 1–butyne and butanone from 2–butyne.

[k] **By Oxidation of Glycols :** Carbonyl compounds are obtained on oxidation of vicinal alkanediols by periodic acid or lead tetraacetate

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} \text{R-CH-OH} \\ \text{R-CH-OH} \end{array} + [O] & \xrightarrow{\text{HIO}_4 \text{ or}} \\ \hline (\text{CH}_3\text{COO})_4 \text{ Pb} \end{array} \rightarrow 2\text{R-CHO} + \text{H}_2\text{O} \end{array}$$

$$\begin{array}{c} \text{R-C-OH} \\ \text{R-C-OH} \end{array} \\ \begin{array}{c} \text{R-C-OH} \\ \text{R-C-OH} \end{array} + [O] & \xrightarrow{\text{HIO}_4 \text{ or}} \\ \hline (\text{CH}_3\text{COO})_4 \text{ Pb} \end{array} \rightarrow 2\text{R-C=O} + \text{H}_2\text{O} \end{array}$$

### METHODS OF PERPARATION OF ONLY ALKANALS

[a] By 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}\\ \text{temperature}\\ \text{and pressure} \xrightarrow[\text{High}\\ \text{High}\\ \text{High}\\ \text{High}\\ \text{CHO}\\ \text{Propanal} \xrightarrow[\text{HO}\\ \text{Propanal} \xrightarrow[\text{CHO}\\ \text{Propanal} \xrightarrow[\text{CHO}\\ \text{Propanal} \xrightarrow[\text{CHO}\\ \text{CH}_{3}-CH=CH_{2}+CO+H_{2} \xrightarrow[\text{CHO}\\ \text{CHO}\\ \text{CH}_{3}-CH_{2}-CH_{2}-CHO+CH_{3}-CH-CH_{3} \xrightarrow[\text{CHO}\\ \text{CHO}\\ \xrightarrow[\text{CHO}\\ \text{CHO}\\ \text{CHO}\\ \xrightarrow[\text{CHO}\\ \text{CHO}\\ \xrightarrow[\text{CHO}\\ \text{CHO}\\ \xrightarrow[\text{CHO}\\ \text{CHO}\\ \xrightarrow[\text{CHO}\\ \text{CHO}\\ \xrightarrow[\text{CHO}\\ \text{CHO}\\ \xrightarrow[\text{CHO}\\ \xrightarrow[\xrightarrow[\text{CHO}\\ \xrightarrow[\xrightarrow[\text{CHO}\\ \xrightarrow[\xrightarrow[\text{CHO}\\ \xrightarrow[\xrightarrow[\text{CHO}\\ \xrightarrow[\xrightarrow[\text{CHO}\\ \xrightarrow[\xrightarrow[\text{CHO}\\ \xrightarrow[\xrightarrow[\xrightarrow[\text{CHO}\\ \xrightarrow[\xrightarrow[\xrightarrow[\[x]\\ \xrightarrow[\xrightarrow[x]\\ \xrightarrow[\xrightarrow[x]\\ \xrightarrow[\xrightarrow[x]\\ \xrightarrow[\xrightarrow[x]\\ \xrightarrow[x]\\ \xrightarrow[\xrightarrow[x]\\ \xrightarrow[x]\\ \xrightarrow[x]\\$$

Isobutyraldehyde

n-Butyraldehyde

Aldehydes are formed on reduction of a carboxylic acid chloride in boiling xylene medium

by hydrogen and palladised barium sulphate.

$$R-C-CI + H_2 \xrightarrow{Pd} R-C-H + HCI$$

**By Rosenmund Reaction :** 

[b]

[**c**]

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<sub>4</sub> 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.

### By Reduction of Acid Nitriles :

[i] By Stephen Reaction : 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.

$$\begin{array}{c} R-C \equiv N \xrightarrow{HCI} R-C \equiv N^{+}HCI^{-} \xrightarrow{SnCl_{2}} \\ Acid nitrile \\ \hline \\ R-CH \equiv NH_{2}I_{2}SnCI_{6}^{2-} \\ Aldimine chloros tannate \end{array}$$

$$[R-CH=NH_2]_2SnCl_6 + 2H_2O$$

$$\rightarrow$$
 2R – CH = O + (NH<sub>4</sub>)<sub>2</sub>SnCl<sub>6</sub>

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

$$\begin{array}{c} CH_{3}-C\equiv N+2H \xrightarrow{SnCl_{2}} CH_{3}-CH=NH\\ Acetal dimine \\ \hline HOH \\ Octal debude \end{array}$$

## [ii] By Reduction with Lithium Aluminium Hydride :

When calculated amount of  $\text{LiAlH}_4$  is dissolved in ethereal solution of an alkyl cyanide, followed by hydrolysis of the product then an alkanal is formed at low temperature.

$$4R-C \equiv N + LiAlH_4 \rightarrow (R-CH=N)_4LiAl$$

$$\xrightarrow{HOH} 4R-CH=O$$

[d] By Sommelet Reaction : In 1953, Angyal first obtained hexanal in 50% yield on passing steam through the aqueous solution of n-hexylamine hydrochloride in the presence of urotropine and acetic acid.

 $\begin{array}{c} \mathsf{CH}_3(\mathsf{CH}_2)_4 \mathsf{CH}_2\mathsf{NH}_2\mathsf{.HCI} & \underbrace{(\mathsf{CH}_2)_6\mathsf{N}_4, \,\mathsf{CH}_3\mathsf{COOH})}_{\mathsf{N}-\mathsf{Hexyla min e hydrochloride}} \\ \end{array}$ 

CH<sub>3</sub> (CH<sub>2</sub>)<sub>4</sub> CHO Hexanal

### METHODS OF PREPARATION OF ONLY ALKANONES

[a] By Alkaline Hydrolysis of Acetoacetic Ester of Its Alkyl Derivatives : Acetone is formed on hydrolysis of acetoacetic ester by dilute acid or alkali.

$$\begin{array}{c} \mathsf{CH}_3\mathsf{COCH}_2 + \mathsf{CO} + \mathsf{OEt} & \underline{\mathsf{Dil. acid}} \\ \mathsf{H} + \mathsf{O} + \mathsf{H} & \underline{\mathsf{or alkali}} \end{array} \rightarrow$$

 $CH_3COCH_3 + CO_2 + EtOH$ 

Higher alkanones are formed on taking alkyl derivatives of acetoacetic ester.

 $\begin{array}{c} CH_{3} & CH_{3} \\ CH_{3}COCH-CO-OEt & \longrightarrow CH_{3}COCH_{2}-CO_{2}+EtOH \\ Methylacetoacetic ester & Butanone \end{array}$ 

[b] By 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.

$$\begin{array}{c} R-CHOH + CH_{3}-CO \xrightarrow{[(CH_{3})_{3}C-O]_{3}AI} \\ R & CH_{3} \\ R & CH_{3} \\ R-CO + CH_{3}-CHOH \\ R & CH_{3} \end{array}$$

[3] **From Dialkylcadmium :** 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-CdCl

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

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

### PHYSICAL PROPERTIES

- Formaldehyde is a colourless gas at room temperature. Members having two to eleven carbon atoms are colourless liquids, while higher members are colourless solids.
- [ii] Lower alkanals have unpleasant pungent odour, but higher alkanals have pleasnt fruity odour. Ketones have pleasant odour.
- Lower members are soluble in water, but solubility decreases with increase in molecular weight. They are completely soluble in organic solvent.
- [iv] Their boiling points increase with increase in molecular weight.
- [v] Their boiling points are lower than those of the alkanols having approximately same molecular weight; intermolecular hydrogen bonding is stronger in alkanols but higher than those of the alkanes, because alkanes are non-polar.

### REACTIONS

It would be appropriate to learn the reactions of carbonyl compounds under the following points.

- [A] Reactions of both alkanals and alkanones
- [B] Reactions of alkanals only
- [C] Reaction of alkanone only

**Reaction Similar in Aldehydes and Ketones:** 

[a] Nucleophilic additon	[b] Halogenation
[c] Oxidation	[d] Reduction
[e] Pyrolysis	[f] Polymerisation

[a] Nucleophilic Addition : Representative mechanism of carbonyl compounds is nucleophilic addition. Addition of a reagent E– Nu on carbonyl group of carbonyl compound can be exhibited as follows :



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

 $HCHO > CH_3CHO > CH_3COCH_3 > C_6H_5-CHO$ 



Acetone cyanohydrin is formed on reacting acetone with HCN.



[2] With Sodium bisulphite :



Bisulphite adducts of carbonyl compounds are white crystalline solids. Whose melting points are high. Pure parent carbonyl compounds can again be obtained on their hydrolysis.

### [3] With Grignard's Reagents :



In the above reaction, HCHO forms primary alcohols, other aldehydes form secondary alcohols and ketones form tertiary alcohols.

### [4] With Alcohols :

Acetals are obtained by the reaction of alkanals with alkanols in the presence of dry HCl gas. Hemiacetals are formed as intermediates, which are hydroxy ethers. Acetals are dialkoxyalkanes. Anhydrous  $ZnCl_2$  can also be taken in place of dry HCl gas.

$$C=O + H \xrightarrow{\text{In}} OR \xrightarrow{\text{Dry}} C \xrightarrow{\text{OH}} OH \xrightarrow{\text{ROH}} C \xrightarrow{\text{OR}} OR \xrightarrow{\text{OR}}$$

Methylal is the common name of the acetal formed by the reaction of acetaldehyde and methanol.

CH<sub>3</sub>CHO+ 2HOCH<sub>3</sub> 
$$\xrightarrow{\text{Dry}}$$
 CH<sub>3</sub>CH $\stackrel{\text{OCH}_3}{\longleftarrow}$  H<sub>2</sub>O  
Methylal

An acetal obtained by the reaction of acetaldehyde and ethanol is simply known as acetal, whose systematic IUPAC name is 1,1–diethoxyethane.

CH<sub>3</sub>-CH=O + 2HOC<sub>2</sub>H<sub>5</sub> 
$$\xrightarrow{\text{Dry}}$$
 CH<sub>3</sub>-CH $\stackrel{OC_2H_5}{\swarrow}$  + H<sub>2</sub>O  
Acetal

### [5] With Mercaptans :

Thiols (Mercaptans) are stronger nucleophiles than alcohols. Therefore, they react with aldehydes as well as ketones to form thioacetals (or mercaptals) and thioketals (or mercaptols).



Sulphonals are formed on the oxidation of thioacetal and thioketal by acidified permanganate. Sulphonals are used as hypnotics.



### [6] With Ammonia :

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



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



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.

$$-C=0 + H_2N-Z$$
  $\xrightarrow{\Delta}$   $-C=N-Z$ 

[i]

[ii]

With Formaldehyde: When ammonia is added to formalin (40% aqueous solution of formaldehyde), then beautiful shining white crystals of urotopine are obtained at low temperature.

$$6\mathrm{CH}_{2}\mathrm{O} + 4\mathrm{NH}_{3} \rightarrow (\mathrm{CH}_{2})_{6}\mathrm{N}_{4} + 6\mathrm{H}_{2}\mathrm{O}$$

Urotropine is known by other trivial names also. i.e aminoform, hexamethylene tetramine and hexamine. Its structural formula is perfectly symmertrical, and is placed in the class of nonaromatic polyheterocyclic compounds.



With Acetaldehyde : The reaction between acetaldehyde and ammonia takes place at room temperature and an adduct acetaldehyde– ammonia is obtained.

$$CH_3$$
  
H  
C=O + NH<sub>3</sub>  $\longrightarrow$   $CH_3$   
H  
C  
NH<sub>2</sub>  
Acetaldehyde-ammonia

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.

[iii] With Acetone : Diacetoneamine is formed on heating acetone with ammonia carefully and slowly.



#### [8] With Ammonia Derivatives

#### [i] With Hydroxylamine :

$$C=O + H_2NOH \longrightarrow C=NOH$$

[ii] With Hydrzaine :

$$C=O + H_2NNH_2 \xrightarrow{-H_2O} C=NNH_2$$
  
Hydrazone

With Phenylhydrazine : [iii]



#### With 2,4–Dinitrophenylhydrazine : [iv]



#### [**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 with reaction hydroxylamine, hydrazine phenylhdrazine and semicarbazide. The pure parent carbonyl compound can be obtained by hydrolysis of the above five derivatives.

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

#### [9] With Dilute Alkali:

In the presence of small amounts of hydroxide ions two molecules of the carbonyl compound containing  $\alpha$ -hydrogen atims, give a  $\beta$ -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<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, KOH, Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub> etc. are added.

$$\begin{array}{cccc} H & H & \\ I & |\alpha \\ CH_3 - C & + CH - CH = O & \xrightarrow{low [OH]} & CH_3 - C - CH - CH = O \\ II & I & \\ O & H & OH \\ Acetaldehyde & Acetaldol \\ (two moles) & & \end{array}$$

A  $\alpha$ ,  $\beta$ -unsaturated aldehyde crotonaldehyde is formed by the elimination of a water molecule on heating acetaldol (3-hydroxybutanal)



Aldol condensation of two nonidentical 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.

F

$$CH_{3} - CHO + CH_{3} - CH_{2} - CHO \longrightarrow$$
Actaldehyde
$$CH_{3}-CH-CH-CHO \longrightarrow$$

$$OH CH_{3}$$

$$3-Hydroxy-2-methylbutanal$$

$$CH_{3}CH_{2} - CHO + CH_{3}CHO \longrightarrow$$

$$Pr opionaldehyde$$

$$CH_{3}CH_{2}-CH-CH_{2}CHO$$

ĊН 3-Hydoxypentanal

### [b] Halogenation

### [1] With Halogen :

The carbonyl compounds have reactive  $\alpha$  hydrgoen atoms, which are readily substituted on reacting with halogens. Halogenation of ketones takes place more satisfacorily as compared to aldehydes, because aldehydes readily undergo oxidation as well as polymerisation.

$$CH_{3}COCH_{3} + 6Cl_{2} \xrightarrow{hv} CCl_{3}COCCl_{3} + 6HCl \\ \xrightarrow{Hexachloroacetone}$$

Monobromoactone is formed by bromination of acetone in the presence of  $CaCO_3$ .

$$CH_{3}COCH_{3} + Br_{2} \xrightarrow{\text{CaCO}_{3}} CH_{3}COCH_{2}Br + HBr$$

On trichlorination of acetaldehyde in the presence of antimony trichloride, chloral is formed, which is an important intermediate in the manufacture of D.D.T. and chloroform.

$$CH_{3}CHO + 3Cl_{2} \xrightarrow{SbCl_{3}} CCl_{3}CHO (Chloral) + 3HCl$$

### [2] With Phosphorus Pentachloride :

Geminal dichlorides are formed by the reaction of  $PCl_5$  with carbonyl compounds.

$$C=O + PCl_5 \longrightarrow C Cl_{Cl} + POCl_3$$
  
gem Dichloride

$$\begin{array}{l} \mathrm{CH}_{3}-\mathrm{CH}=\mathrm{O} \xrightarrow{\mathrm{PCl}_{5}} \mathrm{CH}_{3}-\mathrm{CHCl}_{2}+\mathrm{POCl}_{3}\\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}=\mathrm{O} \xrightarrow{\mathrm{PCl}_{5}} \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CHCl}_{2}\\ +\mathrm{POCl}_{3} \end{array}$$

$$CH_{3} - COCH_{3} \xrightarrow{PCI_{5}} CH_{3} CCI_{2} + POCI_{3}$$

### [3] Haloform Reaction :

Acetaldehyde and all methyl ketones (acetone, butanone, 2–pentanone, 3–methylbutanone, etc.) give haloform on heating with halogen in alkaline medium.

$$CH_{3}-CH=O \xrightarrow{l_{2}+Na_{2}CO_{3}} CHI_{3}$$
$$CH_{3}-CO-CH_{3} \xrightarrow{Cl_{2}+OH^{-}} CHCl_{3}$$

Oxidation :

[c]

Oxidation of aldehydes takes place readily, whereas ketones resist oxidation and are oxidised under high energy conditions.

### [1] With Inorganic Oxidants :

Alkanal gives alkanoic acid of same number of carbon atoms at room temperature on oxidation with even very weak oxidising agents, like Tollen's reagent, Fehling's solution. Benedict's solution, mercuric chloride, etc., as also with strong oxidants, like acidified permanganate, acidified dichromate, chromic acid, conc. HNO<sub>3</sub>, etc., Oxidation of alkanones takes place only on heating with strong oxidants, and alkanoic acids having less number of carbon atoms are formed.

$$R-C-H+[O] \longrightarrow R-C-OH$$

$$CH_{3}CHO \xrightarrow{\Lambda} CH_{3}COOH$$

$$CH_{3}-CO-CH_{3}+3[O] \xrightarrow{\Lambda} CH_{3}-COOH +$$

$$HCOOH$$

$$R-CO \stackrel{!!}{=} CH_{2}-R'+3[O] \xrightarrow{\Lambda} R-COOH +$$

HOOC - R'

When two nonidentical alkanoic acids are formed on oxidation of alkanone then CO group of alkanone remains attached to the smaller alkyl group. This is called Popoff's rule.

 $\begin{array}{c} CH_{3}COCH_{2}C_{2}H_{5} \xrightarrow{3[O]} CH_{3}COOH + \\ HOOC-C_{2}H_{5} \end{array}$ 

The  $\alpha$  CH<sub>2</sub> group gets converted to CO group at room temparature by selenium dioxide.

$$CH_3CHO + SeO_2 \longrightarrow |_{CHO}^{CHO}$$

### **Baeyer–Villiger Reaction :**

[2]

Oxidation of aldehyde and ketones by a peracid is called Baeyer–villiger reaction.

 $CH_3CHO + RCOCOOH$ 

$$\longrightarrow$$
 CH<sub>3</sub>COOH + RCOOH

### [d] Reduction :

### [1] Hydrogenation :

The carbonyl group (–CO–) gets converted to alcoholic group (–CHOH–) on hydrogenation. Thus, aldehydes form primary alcohols, while ketones form secondary alcohols on hydrogenation.

 $RCHO + 2H \longrightarrow RCH_2OH$ 

The following reagents can be used for hydrogenation of aldehydes and ketones.

### [2] With Red Phsophrous and HI :

Alkanals and alkanones are converted to alkanes having same number of carbon atoms on reducing them with red phosphrous and HI.

 $RCHO + 4H \xrightarrow{\text{RedP/HI}} RCH_3 + H_2O$ 

### [3] Clemmensen's Reaction :

The CO group of alkanones is converted to  $CH_2$  group on reduction of alkanones by zinc amalgam and concentrated hydrochloric acid.

$$CH_{3}COCH_{3} + 4H \xrightarrow[Conc. HCl]{Zn-Hg} CH_{3}CH_{2}CH_{3} + H_{2}O$$

Alkanals do not undergo Clemmensen's reduction because they readily polymerise in the presence of conc, acid. However, benzaldehyde undergoes Clemmensen reduction because it is inert towards concentrated hydrochloric acid.

### [4] Wolff–Kishner Reaction :

In this reaction, an alkanal or an alkanone is reacted with hydrazine (or hydrazine hydrate) to first obtain their crystalline hydrazone derivative. Alkane having same number of carbon atoms is obtained on heating the hydrazone with sodium ethoxide at 100°.

$$>C = O \xrightarrow{\text{NH}_2\text{NH}_2} >C = N-NH_2$$
$$\xrightarrow{C_2H_5ONa} >CH_2 + N_2$$

### Pyrloysis :

[e]

On heating carbonyl compounds at 600° or above, they undergo decomposition as follows :

HCHO 
$$\xrightarrow{\Lambda}$$
 H<sub>2</sub> + CO  
CH<sub>3</sub>CHO  $\xrightarrow{\Lambda}$  CH<sub>4</sub> + CO

 $CH_3COCH_3 \xrightarrow{\Delta} CH_4 + CH_2 = C = O$  (Ketene)

### [f] Polymerisation :

Carbonyl compounds form several polymerisation products. Alkanals generally undergo addition polymerisation reactions, whereas alkanones undergo condensation polymerisation reactions.

### Addition polymerisation :

### Formaldehyde :

### [1] In Neutral Medium

[i] White crystalline soild, paraformaldehyde is obtained on evaporation (not boiling) of formalin (40% aqueous solution of formaldehyde) carefully. It is a linear additon polymer, which is also called polyoxymethylene, because there is a repetition of oxymethylene ( $-CH_2-O-$ ) units in its structure.

$$n CH_2 = O \xrightarrow{Evaporation}$$

$$-[CH_2 - O -]_n$$
 (n = 6 to about 100)  
Paraformaldehyde

Paraformaldehyde undergoes depolymerisation on heating with dilute alkali or alone, and its monomer formaldehyde gas is liberated out.

$$-[CH_2 - O - ]_n \xrightarrow{\Delta} n CH_2 = O$$

[ii] Metaformaldehyde is formed by trimerisation on leaving formaline at room temperature.

 $3CH_2O=O \longrightarrow (CH_2-O)_3$ 

Metaformaldehyde is also called trioxymethylene, because it contains three  $CH_2O$  units bonded together. It has a nonaromatic six-membered heterocyclic structure, in which it may be regarded as a trioxa analogue of cyclohexane. Therefore, it is also called 1,3,5-trioxan or sym-trioxan.



### [2] In Weak Alkaline Medium :

Leaving formalin in a weak alkali (lime water or baryta water) for a few days, a mixture of mainly hexoses (sugars containing six carbon atoms) is forms by repeated aldol condenstion. This mixture is called formose or  $\alpha$ acrose Pentoses (five carbon sugars) are also present in small amount in 'formose'.

$$6CH_2O \xrightarrow[Ormotion]{Ormotion} C_6H_{12}O_6$$

$$Ba(OH)_2$$

Formation of hexose sugars from formaldehyde is an example of hexamerisation.

### Acetaldehyde :

[1] On adding a few drops of concentrated sulphuric acid to acetaldehyde and leaving it at room temperature for some time, paraldehyde is formed by addition trimerisation.

$$3CH_{3}CHO \xrightarrow[Conc. H_{2}SO_{4}]{} (CH_{3}CHO)_{3}$$
(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.

Addition tetramerisation of acetaldehyde takes place at 0° in the presence of dry hydrogen chloride gas and metaldehyde is formed.

$$4CH_{3}CHO \xrightarrow{\text{Dry HCl gas}} (CH_{3}CHO)_{4}$$

Metaldehyde has the following nonaromatic eight–memebred heterocyclic structure.



Metaldehyde is used as smokeless powder.

### **Condensation Polymerisation**

### Acetone

[2]

[1] On heating with conc.  $H_2SO_4$  mesitylene is formed by liberation of three water molecules from three molecules of acetone.



[2] A mixture of mesityl oxide and phorone is obtained from acetone in the presence of dry HCl gas.



Reactions Different in Aldehydes and Ketones

[A] Reactions of only Aldehydes :

### [1] **Reducing Properties :**

Aldehyde readily undergo oxidation. Therefore, they behaves as strong reducing agents.

With Schiffs Reagent : Colourless solution obtained on passing SO<sub>2</sub> gas in deepred-coloured aqueous solution of magenta dye (also called fuchsine and rosaniline hydrochloride) is known as Schiff's reagent. All aldehydes restore the pink colour of dilute Schiff's reagent *in cold*. Therefore, it is a specific test of aldehydes, which is called *Schiffs test*.

Cold dilute Schiff's reagent (Colourless oxidised form)

Aldehyde

Pink Colour (Coloured reduced form)

[ii] With Tollen Reagent : Ammoniacal silver nitrate ( $AgNO_3 + NH_4OH$ ) is called *Tollen's reagent*. Silver mirror is formed on carefully heating an aldehyde with Tollen's reagent in a test tube on a water-bath. Greyish-black precipitate of silver is formed on heating directly and rapidly.

 $Ag^{+1} + 2NH_4OH \longrightarrow Ag^{+1} (NH_3)_2 + 2H_2O$   $2Ag^{+1} (NH_3)_2 + H_2O \longrightarrow Ag_2O + 2NH_4^{+1} + 2NH_3$   $RCHO + Ag_2O \longrightarrow RCOOH + 2Ag$ 

 $\begin{array}{c} \text{RCHO} + 2\text{Ag}^{+1} (\text{NH}_3)_2 + 3\text{OH}^{-1} \longrightarrow \\ \text{RCOOH} + 4\text{NH}_3 + 2\text{H}_2\text{O} + \text{Ag} \end{array}$ 

For convenience silver mirror test can be written as follows.

 $\begin{array}{c} AgNO_3 + NH_4OH \longrightarrow AgOH + NH_4NO_3 \\ 2AgOH \longrightarrow Ag_2O + H_2O \\ RCHO + Ag_2O \longrightarrow RCOOH + 2Ag \end{array}$ 

[iii] With Fehling's Reagent : In laboratory. Fehling's solution is kept in two bottles, labeled as Fehling's Solution' A' and Fehling's solution 'B'.

Fehling solution'A' - Aqueous solution of CuSO<sub>4</sub> (Blue)

Fehling solution 'B' - Alkaline solution (NaOH or  $Na_2CO_3$ ) of sodium potassium tartarate (Rochelle's salt) (Colourless)

On mixing Fehling's solutions'A' and 'B' in equal amounts, the colour of solution becomes deep blue.

 $CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$ 



On heating the dark blue solution after adding aldehyde to it, cupric ions get separated from the complex, and oxidise the aldehyde to the corresponding carboxylic acid in the presence of hydroxide ions. The cupric ions get reduced to cuprous ions which get precipitated as insoluble cuprous oxide (red precipitate).

RCHO + 4OH<sup>-</sup> + 2Cu<sup>2+</sup>  $\longrightarrow$  RCOOH + 2H<sub>2</sub>O + Cu<sub>2</sub>O (Red precipitate)

### [iv] With Benedict's Solution :

Benedict's solution (like Fehling's solution) also gives a red precipitate of  $Cu_2O$  on heating with aldehydes. The only difference between these two reagents is that in Fehling's solution there is tartrate ion, whereas in Benedict's solution there is citrate ion.

For Convenience, Benedict's test and Fehling's test can be expressed as follows :

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$
$$Cu(OH)_2 \longrightarrow CuO + H_2O$$
$$R-CHO + 2CuO \longrightarrow R-COOH + Cu_2O$$

### [v] With Mercuric Chloride Solution :

On adding aldehydes to mercuric chloride solution, a white precipitate first appears, which turns dark grey due to mixing up of a black precipitate of mercury formed.

$$\begin{array}{c} \text{RCHO} + 2\text{HgCl}_2 + \text{H}_2\text{O} \\ & \longrightarrow \text{RCOOH} + \text{Hg}_2\text{Cl}_2 + 2\text{HC} \\ & \text{White precipitate} \end{array}$$

$$\frac{\text{RCHO} + \text{Hg}_2\text{Cl}_2 + \text{H}_2\text{O}}{\longrightarrow} \text{RCOOH} + 2\text{Hg} + 2\text{HCI}$$

Black precipitate

### [2] Resinification :

On adding a strong alkali to the aldehydes having at least one  $\alpha$  hydrogen atom, a viscous sticky product called resin is formed by polymerisation due to repeated aldol condensation.

$$nCH_3COH \xrightarrow{\text{NaOH}} CH_3[CH(OH)CH_2]_nCHO$$
  
Resin

### [3] Cannizzaro's Reaction :

On adding sufficient amounts of concentrated solution of a caustic alkali to an aldehyde having no  $\alpha$  hydrogen atom, a mixture of corresponding primary alcohol and corresponding carboxylate ion is obtained at room temperature.

 $2HCHO + OH^{-}$ 

$$\xrightarrow[Conc. caustic alkali]{Room temperature} CH_3OH + HCOO^-$$

In Cannizzaro's reaction, two molecules of aldehyde reacts in such a way that one molecules gets oxidised and the other gets reduced. This process is called *disproportionation*. The following aldehydes, besides methanal, also give Cannizzaro's reaction.

Chloral, Benzaldehyde, Trimethylacetaldehyde.

### [4] 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.



### [5] With Primary Amines :

On heating an aldehyde with a primary amine, a Schiff's base is formed by liberation of a water molecule.

$$R-CH=O + H_2 N-R \xrightarrow{\Delta} R - CH = N - R + H_2 O$$

Secondary amines are formed on reduction of Schiff's bases.

$$R-CH=N-R+2H \longrightarrow R-CH_2-NH-R$$
(Secondary amine)

### [B] Reactions of Ketones Only :

### [1] With Nitrous Acid :

[2]

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

 $CH_3COCHH_2 + O=NOH$ 

$$\longrightarrow CH_3COCH = NOH + H_2O$$
Oximinoacetone

### **Bimolecular Reductive Condenstion :**

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

$$\begin{array}{c} CH_{3} & CH_{3} \\ CH_{3}-C=O \\ CH_{3}-C=O \\ I \\ CH_{3}-C=O \\ I \\ CH_{3} \end{array} + \begin{array}{c} H \\ H \\ C_{6}H_{6} \end{array} + \begin{array}{c} CH_{3} \\ CH_{3}-C-OH \\ I \\ CH_{3}-C-OH \\ I \\ CH_{3} \end{array}$$

The derivative name of pinacol is tetramethylethylene glycol, and its IUPAC name is 2,3–dimethyl–2,3–butanediol.

### [3] With Chloroform :

Chloretone is formed by nucleophilic addition of chloroform on acetone.

$$\begin{array}{ccc} CCI_{3} & CCI_{3} \\ CH_{3}-C=O & + \begin{array}{c} I \\ H \\ CH_{3} \end{array} & CH_{3}-C-OH \\ CH_{3} \\ CH_{3} \end{array}$$

### Formaldehyde, Methanal, CH<sub>2</sub>O, HCHO:

Formaldehyde can be prepared by the general methods of preparation of alkanals. In order to obtain it in laboratory, catalytic dehydrogenation of methyl alcohol is carried out by platinised asbestos at 250°-300° or by copper at 300°.

 $\mathrm{CH_{3}OH} \xrightarrow{\mathrm{Pt \ or \ Cu}} \mathrm{HCHO} + \mathrm{H_{2}}$ 

For the manufacture of formaldehyde on industrial scale. dehydrogenation of methanol is carried out by Cu at 300° or by controlled, air oxidation of methane in the presence of molybdenum oxide.

 $CH_4 + O_2 \xrightarrow{MoO_2} HCHO + H_2O$ 

Formaldehyde is a colourless gas having a characteristic pungent odour. It is highly soluble in water, alcohol and ether. Its 40% aqueous solution (in which 5-12% is methanol) is called *formalin*.

1. With Phenol :

A mixture of p-hydroxybenzyl alcohol (80%) and o-hydroxybenzyl alcohol (20%) is foemed by the reaction of

formaldehyde and phenol. This reaction is called *LedererManasse Reaction*. Synthetic resin or plastic called *phenol formaldehyde resin* or *bakelite* is formed by condensation polymerisation when a small amount of ammonia is added to the above mixture.

$$C_6H_5OH + CH_2O \longrightarrow$$

HOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH o- + p-Hydroxylbenzyl alcohol  $NH_3 \downarrow \Delta$ Bakelite (phenol-formaldehyde resin)

### With urea :

2.

3.

4.

5.

6.

Reaction of formaldehyde and urea takes place very fast and methylolurea and after that dimethylolurea are formed.

 $CH_2O + HNHCONH_2 \longrightarrow$ 

$$\label{eq:HOCH2NHCONH2} \begin{split} & \text{HOCH}_2\text{NHCONH}_2\,(\text{Methylolurea}) \\ & \text{HOCH}_2\text{NHCONH}_2 + \text{CH}_2\text{O} & \longrightarrow \end{split}$$

HOCH<sub>2</sub>NHCONHCH<sub>2</sub>OH (Dimethylolurea) A product, urea formaldehyde resin is obtained on the condensation polymerisation of dimethylolurea.

n HOCH<sub>2</sub>NHCONHCH<sub>2</sub>OH  $\xrightarrow{-nH_2O}$ 

Urea-formaldehyde resin

### With Fehling Solution :

Being the most reactive member of the alkanal family, formaldehyde gives red-brown precipitate of copper on further reduction of cuprous oxide formed by reduction of Fehling's' solution and Benedict's solution.

 $HCHO + 2CuO \longrightarrow$ 

 $HCOOH + Cu_2O$  (Red ppt)

HCHO +  $Cu_2O \longrightarrow$ 

HCOOH + 2Cu (Red-brown ppt)

### Halogenation :

Due to the absence of alkyl group, halogenation of formaldehyde does not take place.

### With PCl<sub>5</sub>:

Dichloromethane is not obtained by the reaction of  $PCl_5$  on formal dehyde.

### With Proteins :

When protein chains comes in contact with formaldehyde, many methylene bridges are established between them. Due to this, the proteins get hardened and precipitated. This process is called denaturation of proteins.

A plastic galolith or milksone is prepared from milk protein, casein by the above process.

### Uses:

- [1] As an antiseptic and a disinfectent.
- [2] In preservation of zoological specimens.
- [3] In the manufacture of urinary antiseptic. urotropine.
- [4] In the manufacture of bakelite, ureaformaldehyde-resin. galolith, *etc*.
- [5] In the manufacture of chewable tablet, formamint, which is a mixture of lactose and formalin.
- [6] In hardening of proteins.

### Acetaldehyde, Ethanal, CH<sub>3</sub>CHO

### Uses :

- [1] As an antiseptic.
- [2] In the preparation of silver mirrors.
- [3] In the manufacture of mild hypnotic drug, paraldehdye.
- [4] In the manufacture of smokeless solid fuel, named metaldehyde.
- [5] In the manufacutre of important industrial products, like chloral, iodal, chloroform, iodoform, ethyl alcohol, acetic acid, ethyl acetate. etc,.

### Acetone, Propanone, CH<sub>3</sub>COCH<sub>3</sub>:

[1] Meerwein–Pondorff Oppenauer–Verley Reaction :

> When acetone is heated with a primary or secondary alcohol in benzene or toluene solution in the presnce of a weak base (aluminium alkoxide), then the ketone is reduced to secondary alcohol, Primary alcohols are oxidised to aldehydes and secondary alcohols are oxidised to ketones.

 $\begin{array}{c} \text{CH}_{3}\text{COCH}_{3} + \text{RCH}_{2}\text{OH} \rightleftharpoons \begin{array}{c} (\text{RO})_{3}\text{Al} \\ \longleftarrow \end{array} \begin{array}{c} \text{CH}_{3}\text{CH}_{3}\text{CHOHCH}_{3} + \text{RCHO} \\ \text{Acetone} & 1^{\circ} \text{Alkanol} & \text{Isopropyl alcohol} \end{array}$ 

 $\begin{array}{c} CH_{3}COCH_{3}+R_{2}CHOH \xrightarrow{(RO)_{3}Al} CH_{3}CHOHCH_{3}+R_{2}CO\\ 2^{o} Alcohol & Alkanone \end{array}$ 

The above reaction is reversible. Reduction of ketone by this reaction is called Meerwein–Pondorff–Verley reaction whereas oxidation of alcohol is called Oppenauer reaction.

### [2] Condensation With Phenol :

Bisphenol–A is formed by liberation of water molecule when phenol is heated with acetone in the presence of conc. HCl.



Bisphenol–A is useful in the manufacutre of dyes in the dye industry.

Uses :

- [1] As an industrial solvent for silk varnishes, paints, lacquers, cellulose acetate, nail pollishes, etc.
- [2] For cleaning dry parts of instruments in electronic industry.
- [3] In the manufacture of industrial produts like chloroform, iodoform, chloretone, bisphenol–A, sulphonal, perspex, etc.
- [4] In storage of acetylene.
- [5] As a medium while preparing smokeless powder, cordite.

### Tests for Acetone :

- 1. No reaction takes place with Schiff's reagent. Tollen's reagent, Fehling's solution. Bendict solution and mercuric chloride solution (distinction form aldehydes), but reacts with HCN, NaHSO<sub>3</sub>, NH<sub>2</sub>OH, NH<sub>2</sub>NH<sub>2</sub>, NH<sub>2</sub>NHC<sub>6</sub>H<sub>5</sub> and NH<sub>2</sub>NHCONH<sub>2</sub> (Similarity with aldehydes and ketones)
- 2. **Iodoform test :** Gives a yellow precipitate of iodoform on heating with iodine and alkali (Similarity with acetaldehyde and all methyl ketones, but distinction from other carbonyl compounds)

### Aldehydes, Ketones and Carboxylic Acids By Alkaline Hydrolysis of Benzal Chloride :

### **3.** Legal's Test :

When sodium nitroprusside is added to acetone and basified with dilute NaOH, a red violet colour is obtained. This test is also given by other methyl ketones.

Distinction of formaldehyde and Acetaldehyde :

- 1. Odour : Formaldehyde has a characteristic pungent odour, but the pungent odouor of acetaldehyde is not characteristic.
- 2. **Iodoform Test :** Acetaldehyde gives iodoform test, but formaldehyde does not.
- 3. Fehling's Solution : Acetaldhyde gives red precipitate of  $Cu_2O$ , whereas formaldehyde gives red-brown precipitate of Cu.
- 4. Benedict's Solution : Acetaldehyde gives red precipitate of  $Cu_2O$ , whereas formaldehyde gives red-brown precipitate of Cu.

### BENZALDEHYDE, C<sub>6</sub>H<sub>5</sub>CHO, 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°.

$$C_6H_5CH_2OH \xrightarrow{Cu \text{ or } ZnO} C_6H_5CHO + H_2$$

Benzaldehyde is obtained by hydrolysis of benzal chloride, i.e., benzylidine chloride using dilute alkali.

 $C_6H_5CHCl_2 + 2KOH$  —

$$[ \text{C}_6\text{H}_5\text{CH(OH)}_2 ] \ + \ 2KCl \\ \underset{\text{Unstable}}{\text{Unstable}}$$

$$[C_6H_5CH(OH)_2] \longrightarrow C_6H_5CHO + H_2O$$

[4] **By Ozonolysis of Styrene :** A mixture of benzaldehyde and formaldehyde is obtained on ozonolysis of styrene.

$$C_6H_5CH=CH_2 + O_3 \longrightarrow C_6H_5-CH \longrightarrow C_6H_2$$
  
Styrene ozonide

$$\xrightarrow{H_2O} C_6H_5CH=O+CH_2=O$$

[7]

[3]

### 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 :

$$C_6H_5-MgBr + EtO-C-H \longrightarrow O$$
  
 $C_6H_5-C-H + EtO-MgBr$ 

### By Rosenmund's Reaction :

Benzaldehyde is formed by the reduction of benzoyl chloride in the presence of palladised barium sulphate.

$$C_6H_5-C_6H_2 \xrightarrow{Pd} BaSO_4 \rightarrow C_6H_5-C_6H + HCl$$

### [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.

$$C_6H_5-C\equiv N+2H \longrightarrow C_6H_5-CH=NH$$
  
Benzaldimine  
 $\longrightarrow C_6H_5-CH=O$ 

[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.

$$C_{6}H_{5}CH_{2}Cl \xrightarrow{H_{2}O} C_{6}H_{5}CH_{2}OH$$
$$\xrightarrow{Cu(NO_{3})_{2}} C_{6}H_{5}CHO$$

### [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.

$$\begin{split} \mathrm{C_6H_5CH_2Cl} + \mathrm{(CH_2)_6N_4} & \xrightarrow{\mathrm{H_2O}} \\ & \{\mathrm{C_6H_5CH_2(CH_2)_6N_4}\}^+ \\ \mathrm{Cl^-} & \xrightarrow{\mathrm{H^+}} \mathrm{[C_6H_5CH_2-N=CH_2]} & \longrightarrow \end{split}$$

C<sub>6</sub>H<sub>5</sub>CH=N–CH<sub>3</sub>(N–Methylbenzaldimine)

$$\xrightarrow{H_3O^+} C_6H_5CH=O$$

[11] By Gattermann–Koch Aldehyde Synthesis: Benzaldehyde is formed on heating a mixture of benzene, carbon monoxide and HCl in nitrobenzene medium in the presence of anhydrous AlCl<sub>3</sub>. It is assumed that an unstable formyl chloride is formed as intermediate, which forms formyl cation (an electrophile).

$$CO + HCl \longrightarrow [H-CO-Cl]$$

$$H-C-Cl + AlCl_{3} \longrightarrow$$

$$H-C^{+}(Formyl carbocation) + AlCl_{4}^{-}$$

$$C_6H_5H + CH^+ = O \longrightarrow C_6H_5 - CH = O + H^+$$

### [12] By Gattermann Aldehyde Synthesis :

Benzaldehyde can also be obtained by heating benzene, HCN and HCl in the presence of anhydrous  $AlCl_3$ .

$$C_{6}H_{5}H + [HCN + HC1] \longrightarrow$$

$$C_{6}H_{5}CH = NH + HC1$$

$$C_{6}H_{5}CH = NH \longrightarrow C_{6}H_{5}CH = O$$

[13] By Etard's Reaction :

An addition complex is formed on reacting toluene with chromyl chloride solution in carbon tetrachloride. The complex compound gives bezaldehyde on decompsotion by water.

$$C_{6}H_{5}CH_{3} + 2CrO_{2}Cl_{2} \longrightarrow C_{6}H_{5}CH_{3}.2CrO_{2}Cl_{2}$$
$$C_{6}H_{5}CH_{3}.2CrO_{2}Cl_{2} \longrightarrow C_{6}H_{5}CHO$$

### 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.

$$C_{6}H_{5}-CH=O + \overset{\delta_{+}}{\mathsf{E}} - \overset{\delta_{-}}{\mathsf{Nu}} \longrightarrow$$

$$C_{6}H_{5} - \overset{\mathsf{Nu}}{\mathsf{CH}} - O^{-} + \mathsf{E}^{+} \longrightarrow C_{6}H_{5} - \overset{\mathsf{Nu}}{\mathsf{CH}} - \mathsf{OE}$$

$$\overset{\mathsf{Nu}}{\overset{\mathsf{Oxide ion}}{\overset{\mathsf{Oxide ion}}}{\overset{\mathsf{Oxide ion}}{\overset{\mathsf{Oxide ion}}}{\overset{\mathsf{Oxide ion}}}{\overset{\mathsf{$$

### [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 Hydrogen Cyanide :

Mandelic acid is obtained on hydrolysis of mandelonitrile i.e., benzaldehyde cyanohydrin, formed by addition of hydrogen cyanide on benzaldehyde.



### With Sodium Bisulphite :

[4]

[5]

The reaction of sodium bisulphite with benzaldehyde gives benzaldehyde-sodium bisulphite adduct, which is a white crystalline solid.

 $C_6H_5CHO + NaHSO_3 \xrightarrow{} C_6H_5CH(OH)SO_3Na$ 

### With Alcohols :

An aromatic acetal is obtained on heating a mixture of benzaldehyde and alcohol in the presence of dry HCl gas.

$$C_{6}H_{5}CHO + 2HOC_{2}H_{5} \xrightarrow{\text{Dry HCl gas}} C_{6}H_{5}CH(OC_{2}H_{5})_{2} + H_{2}O$$

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.

$$C_{6}H_{5}CHO + 2HSC_{2}H_{5} \xrightarrow{\text{Dry HCl gas}} C_{6}H_{5}CH(SC_{2}H_{5})_{2} + H_{2}O$$

### [7] With Ammonia :

On heating benzaldehyde with ammonia a complex compound called hydrobenzamide is formed.

$$C_{6}H_{5}CH \neq O + H_{2} | N + H$$

$$O = CH - C_{6}H_{5} \xrightarrow{\Delta} C_{6}H_{5}CH = N$$

$$C_{6}H_{5}CH \neq O + H_{2} | N + H$$

$$C_{6}H_{5}CH = N$$

$$Hydrobenzamide$$

### [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.

$$\begin{array}{c} C_{6}H_{5}\text{--}CH=O+H_{2}N-C_{6}H_{5}\\ & \xrightarrow{\Delta} C_{6}H_{5}-CH=N-C_{6}H_{5} + H_{2}O\\ & \xrightarrow{benzylideneaniline}\end{array}$$

### [9] With Hydroxylamine :

Benzaldoxime is formed by the reaction of benzaldehyde and NH<sub>2</sub>OH.

$$C_{6}H_{5}-CH=O + H_{2}N-OH$$
$$\longrightarrow C_{6}H_{5} - CH = N - OH + H_{2}O$$

### [10] With Hydrazine :

Benzladehydehydrazone is formed by the reaction of benaldehyde and  $NH_2NH_2$ .

Benzaldoxime

$$C_{6}H_{5}-CH=O + H_{2}N-NH_{2}$$

$$\longrightarrow C_{6}H_{5} - CH = N - NH_{2} + H_{2}O$$
Benzaldehydehydrazone

### [11] With Phenylhydrazine :

The reaction of benzladehyde and  $C_6H_5NHNH_2$  gives benzaldehydephenylhydrazone.

$$C_6H_5CH=O + H_2N-NHC_6H_5 \longrightarrow$$
  
 $C_6H_5CH=N-NHC_6H_5 + H_2O_{benzaldehydephenylhydrazone}$ 

### [12] With Semicarbazide :

The reaction of benzaldehyde and semicarbazide gives benzaldehyde semicarbazone.

$$C_6H_5$$
-CH=O +  $H_2N$ -NH-CO-N $H_2$ 

 $\longrightarrow C_6H_5 - CH = N - NH - CO - NH_2 + H_2O$ Benaldehyde semicarbzaone

### [13] With Phosphorus Pentachloride :

Benzaldehyde reacts with  $PCl_5$  to form benzal chloride, which is also called benzylidene dichloride.

[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  $\alpha$  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

 $2C_6H_5CHO + OH^-$ 

$$\rightarrow C_6H_5COO^- + C_6H_5CH_2OH$$

### [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.



### [18] Benzoin Condensation :

(

When benzaldehyde is heated with aqueous alcoholic KCN solution, a ketonic secondary alcohol, benzoin is formed by bimolecular condensation.

$$C_6H_5CHO + C_6H_5CHO$$
  
 $\xrightarrow{KCN}$   $C_6H_5COCH(OH)C_6H_5$ 

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.

$$C_6H_5COCHOHC_6H_5 + [O] \xrightarrow{Conc.HNO_3} C_6H_5COCOC_6H_5 (Benzil) + H_2O$$

### [19] Claisen Reaction :

An  $\alpha$ , $\beta$ -unsaturated aldehyde (or ketone) is formed on the condensation of benzaldehyde with an aldehyde (or a ketone) having at least two  $\alpha$ hydrogen atoms, in the presence of dilute alkali cinnamaldehyde is obtained on the condensation of benzaldehyde with acetaldehyde.

$$C_6H_5CH=O + H_2CH-CHO \longrightarrow$$
  
 $C_6H_5CH = CH - CHO + H_2O$   
Cinnamaldehyde

Benzalacetone, i.e. benzlideneacetone is obtained on condensation of benzaldehyde with acetone.

$$\begin{array}{c} C_{6}H_{5}CH{=}O+H_{2}CHCOCH_{3}\\\\ \xrightarrow{\text{Dil. alkali}} C_{6}H_{5}CH=CHCOCH_{3}+H_{2}O\\\\ \xrightarrow{\text{Benzalacetone}}\end{array}$$

### [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.

$$\begin{array}{c} C_{6}H_{5}CH=O+H_{2}CH-CO \\ CH_{3}-CO' \\ Acetic anhydride \end{array} \xrightarrow{O} \begin{array}{c} CH_{3}COO \\ -H_{2}O \\ Benzalacetic anhydride \end{array} \xrightarrow{O} \begin{array}{c} C_{6}H_{5}CH=CH-CO \\ CH_{3}-CO' \\ Benzalacetic anhydride \end{array}$$

$$\xrightarrow{\text{HOH}} C_6\text{H}_5\text{CH}=\text{CH}-\text{COOH} + \text{CH}_3-\text{COOH}$$
  
Cinnamuc acid

### [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.

$$\begin{array}{ccc} C_{6}H_{5}-CH & CH_{2}-COOEt \xrightarrow{\text{Ether}} C_{6}H_{5}-CH-CH_{2}-COOEt \\ I & I \\ O+Zn+Br & OZnBr \end{array}$$

 $C_6H_5-CH-CH_2-COOH \xrightarrow{\Delta} C_6H_5-CH=CH-COOH$ Ч Cinnamic acid

#### **[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<sub>3</sub>.



### 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 :

Nitration :

m-Nitrobenzaldehyde is formed on nitration of benzaldehyde by fuming nitric acid.



#### [25] **Sulphonation :**

[24]

Benzaldehyde undergoes sulphonation on heating with conc. sulphuric acid to form mformylbenzensulphonic 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.

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

Aldehyde Ketone Test Schiff's reagent Pink colour Х Х Silver mirror Tollen's reagent Fehling Solution Red ppt. Х Х NaOH solution Brown resin Mercuric chloride Х Black ppt.

Distinction between Aldehydes and Ketones :

2.

### Carboxylic Acid:

The organic compounds containing carboxyl

(-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

[c]

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

### 1. Classification :

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

[a] Aliphatic carboxylic acid = 
$$R - C - OH$$

$$(R = H atom or alkyl group).$$

 $\cap$ 

[b] Aromatic carboxylic acid = 
$$Ar-C-OH$$
  
( $Ar = Aryl group$ )

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

	No. of -COOH	I group
[a] Mono carboxylic ac	cids	1
[b] Dicarboxylic acids		2
[c] Tricarboxylic acids		3

General formula is  $C_n H_{2n} O_2$  or  $C_n H_{2n+1}$  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  $\mathrm{sp}^2$ 

### METHOD OF PREPARATION

- 1. By the oxidation of alcohols, aldehydes and ketones :
- [a]  $1^{\circ}$  Alcohol  $\xrightarrow{[0]}$  corresponding carboxylic acids.

$$R-CH_2-OH+[O]$$

$$\xrightarrow{\text{KMnO4 or}} R-CHO \xrightarrow{[O]} R-C-OH$$

 $\sim$ 

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

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

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

$$R-C-CH_{2}-R' + [O] \xrightarrow{Acidic K_{2}Cr_{2}O_{7}}{\Delta} \rightarrow R-C-OH + R'-COOH$$

### 2. By the hydrolysis of cyanides (nitriles) :

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

5.

$$R - C \equiv N + HOH \longrightarrow \begin{pmatrix} OH \\ I \\ R - C = NH \end{pmatrix} \longrightarrow Unstable$$

 $\begin{array}{c} O \\ II \\ R - C - NH_2 \end{array} \xrightarrow{HOH} R - C \\ \hline -NH_3 \end{array} \xrightarrow{O} R - C \\ -OH + NH_3 \end{array}$ 

3. From hydrolysis of acid derivatives :

$$\begin{array}{c} O \\ R-C-Z + H-OH \longrightarrow R-C-OH + HZ \end{array}$$

[a] **From acyl halides :** 

$$\begin{array}{c} O \\ R-C-Cl + HOH \longrightarrow R-C-OH + HCl \end{array}$$

[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 :**

$$\begin{array}{c} O \\ R-C-OR' + HOH \longrightarrow R-C-OH + R' - OH \end{array}$$

[d] **From acid amides :** 

$$\begin{array}{c} & & O \\ R-C-NH_2 + HOH \xrightarrow{\quad \text{dil. HCl}} & R-C-OH + NH_4Cl \end{array}$$

4. By alkaline hydrolysis of alkylidyne trihalides :



By passing CO<sub>2</sub> in ether Solution of Grignard's reagent

$$\begin{array}{ccc} & \delta \Theta \\ R & \longleftarrow & MgX \\ & H \\ & 0 \\ & & H \\ & O \end{array} \xrightarrow{HOH} & R - C - OMgX \\ & & H \\ & &$$

- Note : Formic acid can not be prepared by this method.
- 6. Partial decarboxylation of gem dicarboxylic acids :

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

$$\begin{array}{c} \mathsf{COOH} \\ \mathsf{COOH} \end{array} \xrightarrow{ \mathsf{Glycerol} } \mathsf{HCOOH} + \mathsf{CO}_2 \end{array}$$

In absence of glycerol

$$\begin{array}{c} \mathsf{COOH} \\ \mathsf{COOH} \end{array} \xrightarrow{\Delta} \mathsf{CO}_2 + \mathsf{CO} + \mathsf{H}_2\mathsf{O} \end{array}$$

### Carbonylation of :

7.

[b]

[a] Sodium alkoxides or sodium hydroxide :

H–O Na + CO 
$$\xrightarrow{\text{High temp.}}$$
 H–COONa

$$\xrightarrow{\text{dil. HCl}} \text{HOH} H - C - OH$$

$$R-ONa + CO \xrightarrow{\text{High temp.}} R-COONa$$
$$\xrightarrow{\text{dil. HCl}} R-C-OH$$

$$R-OH + CO \xrightarrow{BF_3/HOH} R-C-OH$$

$$H-OH + CO \xrightarrow{BF_3/HOH}_{High temp. \& press} H-C-OH$$

### [c] Alkenes [Koch Reaction] :

$$CH_2 = CH_2 + CO + H_2O \xrightarrow{H_3PO_4} 300-400^{\circ}C, \text{ high press} \rightarrow O$$

$$CH_3-CH_2-C-OH$$
 (Propanoic acid)

$$CH_{3}-CH=CH_{2}+CO+H_{2}O \xrightarrow{H_{3}PO_{4}} \xrightarrow{H_{3}PO_{4}}$$

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

### 8. Oxidation of alkenes and alkynes :

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

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

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

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

### 9. Arndt–Eistert reaction :

$$R - C - CI + H - CH - N_2 \rightarrow \underbrace{R - C - CH}_{(Acyl diazomethane)} \stackrel{\text{O}}{\stackrel{\text{II}}}{\stackrel{\text{II}}{\stackrel{\text{II}}{\stackrel{\text{II}}{\stackrel{\text{II}}{\stackrel{\text{II}}}\stackrel{\text{II}}{\stackrel{\text{II}}{\stackrel{\text{II}}{\stackrel{\text{II}}{\stackrel{\text{II}}{\stackrel{\text{II}}}\stackrel{\text{II}}{\stackrel{\text{II}}\stackrel{\text{II}}{\stackrel{\text{II}}}\stackrel{\text{II}}{\stackrel{\text{II}}\stackrel{\text{II}}{\stackrel{\text{II}}}\stackrel{\text{II}}\stackrel{\text{II}}{\stackrel{\text{II}}\stackrel{\text{II}}{\stackrel{\text{II}}\stackrel{\text{II}}{\stackrel{\text{II}}}\stackrel{\text{II}}{\stackrel{\text{II}}}\stackrel{\text{II}}\stackrel{\text{II}}{\stackrel{\text{II}}}\stackrel{\text{II}}\stackrel{\text{II}}{\stackrel{\text{II}}}\stackrel{\text{II}}{\stackrel{\text{II}}}\stackrel{\text{II}}\stackrel{\text{II}}{\stackrel{\text{II}}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}}\stackrel{\text{II}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}\stackrel{\text{II}}\stackrel{\text{II}\stackrel{\text{II}}\stackrel{\text{II}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{II}}\stackrel{\text{I$$

$$\begin{array}{c} 0 \\ \parallel \\ R - CH = C \\ - HOH \\ H \\ - CH_2 - C \\ - OH \\ \end{array}$$

(A,Ketene)

**Note :** [i] The method can be used in ascending up a homolgous series.

[ii] The method can be used only for the synthesis of carboxylic acids having three or more carbon atoms and HCOOH or  $CH_3COOH$  are not prepared by this reaction.

**10.** From acetoacetic ester :

$$CH_{3} - \overset{O}{C} - CH_{2} - \overset{O}{C} - OC_{2}H_{5} \xrightarrow{Conc.}{2KOH} 2 CH_{3} - \overset{O}{C} - OK + C_{2}H_{5}OH$$

$$CH_{3} - \overset{O}{C} - OK + HCI \longrightarrow CH_{3} - \overset{O}{C} - OH + KCI$$

### PHYSICAL POPERTIES

1.

3.

4.

 $C_1$  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.

### 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.

$$\overset{\delta_{\Phi}}{H} - \overset{\check{\mathfrak{S}}}{\overset{I}{O}} = - - - - \overset{\delta_{\Phi}}{H} - O - C = \overset{\check{\mathfrak{S}}}{O} - - - - \overset{\delta_{\Phi}}{H} - \overset{\check{\mathfrak{S}}}{\overset{I}{O}} :$$

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.

### 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.



### 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 <sub>2n</sub>	>	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.

 $CH_2$   $CH_2$  COOH Provide more effective

packing of the molecule in the lattice.

While in acids of odd no. of carbon atoms

$$CH_3$$
  $CH_2$   $CH_2$   $COOH$  Less effective packing

### CHEMICAL PROPERTIES

Carboxylic acids give following reactions :

- (1) Due to alkyl group
- (2) Due to acidic hydrogen
- (3) Due to >C = O group
- (4) Due to OH group
- (5) Due to COOH group
- (6) Special reaction of alkanoic acid

### 1. Reactions due to alkyl group :

[a] **Halogenation :** Acids having  $\alpha$  –H atom give this reaction. The  $\alpha$  –H atoms are easily replaced by chlorine or bromine atoms, forming halogen derivatives of acids.

$$\begin{array}{c} H \\ R - C - COOH \xrightarrow{Cl_2} R - CH - COOH \xrightarrow{Cl_2} R - CH - COOH \xrightarrow{Cl_2} R - C - COOH \\ H \end{array}$$

**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  $\alpha - H$  atom.

### 2. Due to acidic hydrogen :

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



**Note :** Acids liberate  $CO_2$  with NaHCO<sub>3</sub>. This reaction is used to distinguish carboxylic acid from phenol which does not react with NaHCO<sub>3</sub>.

### [b] **Reaction with Ketene :**

$$\begin{array}{cccc} R-C-OH + C &= CH_2 \longrightarrow R-C-O &- C &- CH_3 \\ \parallel & 0 & 0 & 0 \\ & 0 & 0 & 0 \end{array}$$
(Anhydride)

[c] **Reaction with diazomethane :** 

$$\begin{array}{c} O \\ \parallel \\ R - C - OH + CH_2 - N = N \longrightarrow R - C - OCH_3 + N_2 \\ 0 \\ \end{array}$$
Methyl ester

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

[d] **Reaction with alkene and alkyne :** 

$$R - C - OH + CH_{2} = CH_{2} \xrightarrow{BF_{3}} R - C - OCH_{2} - CH_{3}$$

$$R - C - OH + R - CH = CH_{2} \xrightarrow{BF_{3}} R - CH - CH_{3}$$

$$R - C - OH + CH = CH \xrightarrow{Hg^{+2}} CH_{2} O$$

$$R - C - OH + CH = CH \xrightarrow{Hg^{+2}} CH_{2} O$$

$$R - C - OH + CH = CH \xrightarrow{Hg^{+2}} CH_{2} O$$

3. Reaction due to 
$$(>C = O)$$
 group :

$$[a] \qquad \begin{array}{c} O \\ R - C - OH + 4 H \xrightarrow{\text{LIAIH}_4 \text{ or}} R - CH_2 - OH + H_2O \end{array}$$

$$[b] \qquad R - C - OH + 6HI \xrightarrow{\text{RedP}} A - CH_3 + 2H_2O + 3I_2$$

- 4. Reactions due to (–OH) group :
- [a] With  $P_2O_5$  (Dehydrations)

$$\begin{array}{c} 0 \\ R - C - OH_{1} \\ r - 1 \\ R - C + OH_{1} \\ H \end{array} \xrightarrow{P_{2}O_{5}} R - C \\ R - C \\ H \end{array} \xrightarrow{R - C} O + H_{2}O$$

[b] **Esterification**:

$$R - C_{+} \xrightarrow{f - OH + H_{+}} OR' \xrightarrow{Conc.H_2SO_4} R - C_{-} OR' + H_2O$$

- **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 :**

$$\begin{array}{ccc} & & & & & \\ & & & \\ 3R-C-OH+PCI_3 & \longrightarrow & & \\ & & & \\ & & & \\ & & & \\ R-C-OH+PCI_5 & \longrightarrow & & \\ &$$

[d] With Thionyl Chloride :

$$\begin{array}{ccc} O & & O \\ \parallel & & \parallel \\ R-C-OH+SOCI_2 & \underline{Pyridine} & R-C-CI+HCI+SO_2 \uparrow \end{array}$$

- **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 :

$$\begin{array}{c} O & O \\ \parallel \\ R - C - OH + NH_3 & \stackrel{\Delta}{\longrightarrow} & R - C - ONH_4 & \stackrel{\Delta}{\longrightarrow} \\ O \\ \parallel \\ R - C - NH_2 & \stackrel{\Delta}{\longrightarrow} & R - C \equiv N + H_2O \end{array}$$

With Hydrazoic acid (Schmidt reaction) :  

$$N_3H = Hydrazoic acid$$
  
 $0 \qquad 0 \qquad \parallel$   
 $R-C-OH+HN_3 \xrightarrow{H_2SO_4} R-C-N_3+H_2O$   
 $\longrightarrow R - NH_2 + CO_2 + N_2$ 

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 :

[f]

$$\begin{array}{c} \underset{CH_{3} - C - OH + N_{3}H}{\overset{\Delta}{\xrightarrow{}}} & \underset{(-H_{2}O)}{\overset{}{\xrightarrow{}}} & CH_{3} - \overset{O}{C} - N_{3} \xrightarrow{-N_{2}} \end{array}$$
Ethanoic acid
$$\begin{array}{c} \underset{CH_{3} - C - N:}{\overset{}{\xrightarrow{}}} \\ & \underset{Reamangement}{\overset{}{\xrightarrow{}}} \\ CH_{3} - N = C = O \\ (Methyliso cyanate) \end{array}$$

 $CH_3 - NH_2 \leftarrow CO_2^{\uparrow} CH_3 - NH - COOH \leftarrow H_2O$ Methanamine

### 5. Reaction due to (-COOH) group :

[a] **Decarboxylation :** 

[b] Kolbe's electrolytic synthesis :

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

**Note :** Kolbe synthesis undergoes free radical mechanism.

### [c] Hundsdiecker reaction :

$$\begin{array}{c} O \\ \parallel \\ R - C - OAg + X_2 \end{array} \xrightarrow{CCl_4} \\ R - X + CO_2 \uparrow + Agx \downarrow \\ (X = Cl_2 \text{ or } Br_2) \end{array}$$

- **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 :

$$R > C = O + H_2O + CO_2$$

(Carbonyl compounds)

### 6. Special reaction of alkanoic acid :

### [a] **Oxidation**:

 $\rightarrow$  By SeO<sub>2</sub>  $\alpha$  keto acid is formed

 $\rightarrow$  By  $H_2O_2$  –OH group comes at  $\beta$  –C atom.

 $\begin{array}{c} CH_3 - CH_2 - CH_2 - COOH & \xrightarrow{H_2O_2} \\ (Butanoic acid) & & (O) \end{array}$ 

 $CH_3 - CH - CH_2 - COOH$ OH (3 - Hydroxy Bu tan oic acid)

[b] **Pyrolysis**:



### 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.



- [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<sub>4</sub>
- [f] It converts the orange colour of acidic  $K_2Cr_2O_7$ into green colour.
- [g] It reduces Fehling solution.
- [h] Dehydration HCOOH

$$\xrightarrow{\Delta} H_2O + CO_2$$

[i] Effect of heat :

$$[a] \text{HCOOH} \xrightarrow{160^{\circ}\text{C}} \text{CO}_2 + \text{H}_2$$

$$[b] 2HCOONa \xrightarrow{380^{\circ}C} 2 | COONa \\ \xrightarrow{\Delta} 2 | COONa \\ \xrightarrow{COONa} \\ \xrightarrow{Sodium oxalate} + H_2$$

### DISTINCTION BETWEEN FORMIC ACID AND ACETIC ACID

S. NO.	НСООН		CH₃COOH
1.	Decomposed on heating to give carbon		Stable
	dioxide and hydrogen.		
2.	With concentrated sulphuric acid gives		Stable
	carbon monoxide and water.		
3.	With halogens, there is not action.		Substituted acids are formed.
4.	Reduces ammonical silver nitrate and		No action.
	Fehling's solution.		
5.	Calcium salt on heating gives formaldehyde.	$z_{r}$	Calcium salt on heating gives acetone.
6.	Sodium salt on heating gives sodium oxalate		No action.
	hydrogen.	-	
7.	Sodium salt + soda lime gives hydrogen on		Methane is produced.
	heating.		5. 1
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		No action.
	solution.		

### FORMIC ACID (HCOOH)

### 1. Lab Reaction :

### ACETIC ACID CH<sub>3</sub>COOH

Industrial methods :

$$\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} \xrightarrow{\text{Glycerol}} \text{HCOOH} + \text{CO}_2 \end{array}$$

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 +  $PbCO_3 \longrightarrow$ 

$$(\text{HCOO})_2\text{Pb} + \text{CO}_2 + \text{H}_2\text{O}$$

$$(\text{HCOO})_2\text{Pb} + \text{H}_2\text{S} \xrightarrow{100^{\circ}\text{C}} 3$$
  
 $2\text{HCOOH} + \text{PbS} (\text{PPT})$ 

### 2. Industrial method :

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

 $CO + NaOH \xrightarrow{473K} HCOONa$  $\xrightarrow{H_2O} HCOOH + NaOH$ 

[a] From ethyne :  

$$HC = CH + H_2O \xrightarrow{40\% H_2SO_4}{1\% HqSO_4} CH_3CHO$$
  
(Acetaldehyde)  
Magnous acetate [O] air oxid<sup>n</sup>  
CH\_3COOH

### ] From ethyl alcohol

[i] By dehydrogenation :  $CH_3CH_2OH \xrightarrow[(-H_2)]{300^{\circ}C}$ 

$$CH_{3}CHO \xrightarrow{[O]} CH_{3}COOH$$

[ii] By fermentation (Quick vinegar process)

$$CH_{3}CH_{2}OH + O_{2} \xrightarrow{\text{Acetobector bacteria}} (Mycoderma acetail) \rightarrow$$

 $CH_3COOH + H_2O$ 

[dilute form 8 – 10% Called **VINEGAR**] [iii] From CH<sub>3</sub>OH

 $CH_{3}OH + CO \xrightarrow{\text{BF}_{3}} CH_{3}COOH$ 

[b]

### ACID DERIVATIVES

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.

$$R - C - OH \xrightarrow{+X (X = CI, Br, I)}{-OH} \xrightarrow{R - C - X} (Acyl halide)$$

$$R - C - OH \xrightarrow{-OH} \xrightarrow{R - C - O - C - R} (Acid Anhydride)$$

$$\xrightarrow{+NH_2} \xrightarrow{-OH} \xrightarrow{R - C - NH_2} (Acid Amide)$$

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.

$$R-C-Z$$
 [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

$$R-C-X > R-C-O-C-R > R-C-OR > R-C-NH_{2}$$
  
\* Order of stability

$$\mathbf{R} - \mathbf{C} - \mathbf{NH}_2 > \mathbf{R}\mathbf{COOR} > \mathbf{R} - \mathbf{C} - \mathbf{O} - \mathbf{C} - \mathbf{R} > \mathbf{R} - \mathbf{C} - \mathbf{X}$$

Derivatives regenerate the parent acid on hydrolysis.

### ACETYL CHLORIDE

1. Method of preparation : Laboratory method :

$$3CH_3 - C - OH + PCl_3 \rightarrow 3CH_3 - C - Cl + H_3PO_3$$

$$CH_{3}-COH + PCl_{5} \rightarrow CH_{3}-CO+POCl_{3} + HCl^{1}$$
$$CH_{3}COOH + SOCl_{2} \rightarrow CH_{3}-CO-Cl + SO_{2} + HCl^{1}$$

### From Sodiumacetate :

$$\begin{array}{c} \mathrm{CH}_{3}\mathrm{-}\mathrm{COONa} + \mathrm{PCl}_{5} \rightarrow \\ \mathrm{CH}_{3}\mathrm{-}\mathrm{CO}\mathrm{-}\mathrm{Cl} + \mathrm{POCl}_{3} + \mathrm{NaCl} \\ \mathrm{3CH}_{3}\mathrm{-}\mathrm{COONa} + \mathrm{PCl}_{3} \rightarrow \mathrm{3CH}_{3}\mathrm{-}\mathrm{CO}\mathrm{-}\mathrm{Cl} + \mathrm{Na}_{3}\mathrm{PO}_{3} \\ \mathrm{2CH}_{3}\mathrm{-}\mathrm{COONa} + \mathrm{POCl}_{3} \rightarrow \\ \mathrm{2CH}_{3}\mathrm{-}\mathrm{CO}\mathrm{-}\mathrm{Cl} + \mathrm{NaPO}_{3} + \mathrm{NaCl} \\ \mathrm{CH}_{3}\mathrm{-}\mathrm{COONa} + \mathrm{SOCl}_{2} \rightarrow \mathrm{CH}_{3}\mathrm{-}\mathrm{CO}\mathrm{-}\mathrm{Cl} + \mathrm{SO}_{2} + \mathrm{NaCl} \end{array}$$

## By the reaction of sulpuryl chloride on calcium ethanoate :

$$\begin{array}{c} CH_{3} - C \\ CH_{3} - C \\ CH_{3} - C \\ O \\ CH_{3} - C \\ O \\ O \end{array} \rightarrow Ca + SO_{2}CI_{2} \rightarrow 2CH_{3} - C - CI + CaSO_{4} \end{array}$$

### 2. Physical Properties :

[i] Colourless liquid, having pungent odour.

Slowly soluble in water, soluble in organic solvents like CHCl<sub>3</sub>, CCl<sub>4</sub>, CH<sub>3</sub>-CO-CH<sub>3</sub>, etc.

[iii] Produces bilster on skin and its vapour causes irritation in eyes.

[iv] Boiling point is 51°C.

[V]

Fumes strongly in moist air.

**3.** Chemical properties :

$$\begin{array}{c} O \\ CH_3 - C - CI + HOH \rightarrow CH_3 - C - OH + HCI \\ \text{on alkaline hydrolysis} \end{array}$$

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - CI + 2NaOH \rightarrow CH_3 - C - ONa + NaCI + H_2O \end{array}$$

- [2] Reduction :
  - $\begin{bmatrix} i \end{bmatrix} CH_3 C CI + H_2 \xrightarrow{Pd}_{BaSo_4} CH_3 C = O + HCI$

(Rosenmund's reduction, partial reduction)

$$\begin{bmatrix} ii \end{bmatrix} CH_3 - C - CI + 4H \xrightarrow[]{\text{LiAlH}_4} or NaBH_4 CH_3 - CH_2 - OH + HCI (Complete reduction)$$

[3] Curtius Reaction :

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - CI + NaN_3 \longrightarrow CH_3 - C - N_3 \xrightarrow{\Delta/HOH} \\ Acetazide \end{array}$$

$$CH_3 - NH_2 + N_2 + CO_2$$

[4] Friedel Craft's reaction :

 $\begin{array}{c} O \\ \parallel \\ CH_3 - C - C\ell + H - C_6H_5 \xrightarrow{\text{Anhyd.}} CH_3 - C - C_6H_5 + HC\ell \\ (Acetophenone) \end{array}$ 

$$\begin{array}{c} 0 \\ CH_3 - C - CI + R - Mgx \longrightarrow CH_3 - C - R + Mg < X \\ CH_3 - C - CI + R - Mgx \longrightarrow CH_3 - C - R + Mg < X \\ CI \end{array}$$

[6] Halogenation :

[5]

$$CH_3 - C - CI + CI_2 \xrightarrow{\text{reor}} CI - CH_2 - C - CI + HCI_2$$
  
Chloroacetylchloride

[7] With Ether :

$$CH_{3} - C - CI + C_{2}H_{5} - O - C_{2}H_{5} \xrightarrow{Anhyd.}{ZnCl_{2}}$$

[8] With Sodium Ethoxide :

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - CI + NaOC_2H_5 \end{array} \longrightarrow \begin{array}{c} O \\ \parallel \\ CH_3 - C - OC_2H_5 + NaCI \end{array}$$

[9] With Sodium Acetate :

$$\begin{array}{c} O & O & O \\ \parallel & \parallel \\ CH_3 - C - CI + NaO - C - CH_3 \rightarrow CH_3 - C - O - C - CH_3 + NaCI \end{array}$$

Aceticanhydride

[10] Acetylation of Compounds having reactive hydrogen atom :

$$\begin{array}{c} 0 \\ \parallel \\ R - C - CI + H - Z \end{array} \xrightarrow{} \begin{array}{c} 0 \\ \parallel \\ R - C - Z + HCI \end{array}$$

$$\mathbf{Ex.}$$

# $\begin{array}{c} O \\ || \\ CH_3 - C - CI + CH_2 = CH_2 \xrightarrow{Anhyd.} \\ \hline AlCI_3 \end{array}$



### **ACETIC ANHYDRIDE**

$$\begin{bmatrix} CH_3 - C - O - C - CH_3 \end{bmatrix}$$

$$CH_3 - C - OH \xrightarrow{O}_{-OH} CH_3 - C - O - C - CH_3$$

1. Method of prepatation : From Acetyl chloride :

$$CH_{3} - C - CI + H - O - C - CH_{3} \rightarrow CH_{3} - C - O - C - CH_{3} + HCI$$

$$CH_{3} - C - CI + Na - O - C - CH_{3} \rightarrow CH_{3} - C - O - C - CH_{3} + NaCI$$

$$(Laboratory Method)$$

From Acetic acid :

 $\begin{array}{cccccccc} O & O & O & O \\ \parallel & \parallel & \parallel & \parallel \\ CH_3 - C - OH + & H - O - C - CH_3 & \xrightarrow{P_2O_5} & CH_3 - C - O - C - CH_3 + & H_2O \end{array}$ 

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

$$8CH_{3}COONa + SCI_{2} + 2CI_{2} \longrightarrow COONa$$

$$4CH_3 - \ddot{C} - O - \ddot{C} - CH_3 + 6NaCl + Na_2SO_4$$

### From Ketene :

$$\begin{array}{ccc} H & OH \\ | & | \\ CH_2 - C = O \xrightarrow{AIPO_4} CH_2 = C = O + H_2O \\ \hline & & (ketene) \end{array}$$

$$CH_2 = C = O + H - O - C - CH_3 \longrightarrow CH_3 - C - O - C - CH_3$$
  
$$\| \qquad \qquad \| \qquad \qquad \\ O \qquad O \qquad \qquad O$$

### Aldehydes, Ketones and Carboxylic Acids



### With $N_2O_5$ :



### With Benzene [Friedel-Craft's Reaction]:

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ C_6H_5H + CH_3 - C - O - C - CH_3 & \xrightarrow{\text{Anhyd.}} \\ \hline \text{AlCl}_3 \end{array}$$

$$\begin{array}{c} O\\ \parallel\\ C_6H_5-C-CH_3 + CH_3 - COOH\end{array}$$

Acetophenone

### With Acetaldehyde :

$$\begin{array}{ccc} O & O \\ \parallel & \parallel \\ CH_3 - C - O - C - CH_3 + CH_3 - CHO \longrightarrow CH_3CH(OCOCH_3)_2 \end{array}$$

Ethylidene diacetate

### With Dry HCl gas :

$$\begin{array}{ccc} & O & O \\ \parallel & \parallel \\ CH_3 - C - O - C - CH_3 + HCI \longrightarrow & CH_3 - C - CI + CH_3COOH \end{array}$$

### **Perkin's Reaction :**

$$\begin{array}{ccc} O & O & O \\ \parallel & \parallel & \parallel \\ CH_3 - C - O - C - CH_3 + C_6H_5 - CH & \longrightarrow \end{array}$$

$$\begin{array}{ccc} O & O & O \\ \parallel & \parallel & \parallel \\ CH_3 - C - O - C - CH_3 + C_6H_5 - CH & \longrightarrow \end{array}$$

(Benzaldehyde)

(

$$\rightarrow C_6H_5 - CH = CH-COOH + CH_3COOH$$
  
(Cinnamic acid)

### **Reduction :**

 $CH_3 - CH_2 - OH_2 + 8H \xrightarrow{\text{LIAIH}_4} 2CH_3 - CH_2 - OH + H_2O$ With Compounds having reactive H-atom :

 $\begin{array}{c} O & O \\ \parallel \\ CH_3 - C - O - C - CH_3 + H - Z \longrightarrow CH_3 - C - Z + CH_3COOH \end{array}$ 

Acetylderivative

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

### ACETAMIDE

 $\begin{bmatrix} CH_{3}-C-NH_{2} \end{bmatrix}$   $CH_{3}-C-OH \xrightarrow{+NH_{2}} CH_{3}-C-NH_{2}$ 

1. Method of Preparation : From Acetychloride :

 $\begin{array}{c} \mathsf{O} & \mathsf{O} \\ \mathbb{I} \\ \mathsf{CH}_3 \mathsf{-} \mathsf{C} \mathsf{-} \mathsf{CI} \mathsf{+} \mathsf{2NH}_3 \longrightarrow \mathsf{CH}_3 \mathsf{-} \mathsf{C} \mathsf{-} \mathsf{NH}_2 \mathsf{+} \mathsf{NH}_4 \mathsf{CI} \end{array}$ 

### From Acetic Acid :

 $\begin{array}{c} O \\ \parallel \\ CH_3 - C - OH + NH_3 \end{array} \xrightarrow{\Delta} CH_3 - C - NH_2 + H_2O \end{array}$ 

From acetic Anhydride :

$$\begin{array}{ccc} O & O \\ \parallel & \parallel \\ CH_3 - C - O - C - CH_3 + 2H - NH_2 \longrightarrow & 2CH_3 - C - NH_2 + H_2O \end{array}$$

### From Ethyl Acetate :

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - OC_2H_5 + NH_3 \end{array} \longrightarrow \begin{array}{c} O \\ \parallel \\ CH_3 - C - NH_2 + C_2H_5OH \end{array}$$

Partial hydrolysis of Acetonitrile :

$$\xrightarrow{\text{Dil} \text{HCl}} \text{CH}_3 - \overrightarrow{\text{C}} - \text{NH}_2 \xrightarrow{\text{Conc. HCl}} \text{CH}_3 - \overrightarrow{\text{C}} - \text{NH}_2$$

By thermal decomposition of Ammonium acetate :

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - ONH_4 \end{array} \xrightarrow{\Delta} CH_3 - C - NH_2 + H_2O \end{array}$$

### Physical properties :

2.

[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 82°C and boiling point is 222°C.

### 3. Chemical properties : Hydrolysis :

### **Dehydration :**

$$\begin{array}{c} O \\ \parallel \\ 3CH_{3} - \overset{O}{C} - NH_{2} + P_{2}O_{5} & \stackrel{\Delta}{\longrightarrow} 3CH_{3}CN + 2H_{3}PO_{4} \\ CH_{3} - \overset{O}{C} - NH_{2} + PCI_{5} & \stackrel{\Delta}{\longrightarrow} [CH_{3}CCI_{2}NH_{2}] + POCI_{3} \xrightarrow{-2HCI} CH_{3}CN + 2HCI \\ CH_{3} - \overset{O}{C} - NH_{2} + POCI_{3} \xrightarrow{\Delta} 3CH_{3}CN + H_{3}PO_{4} + 3HCI \\ CH_{3} - \overset{O}{C} - NH_{2} + SOCI_{2} & \stackrel{\Delta}{\longrightarrow} CH_{3}CN + SO_{2} + 2HCI \end{array}$$

### **Reduction :**

Reducing Agent : Metal Catalyst +  $H_2$ , Na + Ethanol, LiAl $H_4$  etc.

 $\begin{array}{c} O \\ \parallel \\ CH_3 - C - NH_2 + 4H \longrightarrow CH_3CH_2OH + NH_3 \longrightarrow P \end{array}$ 

$$CH_3 - CH_2 NH_2 + H_2O$$

With Nitrous Acid :

 $\begin{array}{c} O\\ \parallel\\ CH_3 - C - NH_2 + HONO \end{array}$ 

$$\longrightarrow$$
 CH<sub>3</sub> – COOH + N<sub>2</sub> + H<sub>2</sub>O

### 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 :

O || CH<sub>3</sub> - C - NH<sub>2</sub> + NaNH<sub>2</sub>

O || CH<sub>3</sub> - C - NH - Hg - OCOCH<sub>3</sub> + CH<sub>3</sub>COOH

Acetamidomercuriacetate

Weak basic behaviour :

[ii]

С

$$\begin{array}{ccc} & & & & & \\ & \parallel & \\ H_3 - C - NH_2 + HCI & \longrightarrow & CH_3 - C - NH_3CI \end{array}$$

Hofmann Bromamide Reaction or Hypobromite Reaction :

$$CH_3 - C - NH_2 + Br_2 + 4KOH$$
(or NaOH)

$$CH_3 - NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

**Slightly Mechanism :** 

**Bromination:** 



### **Dehydrobromination :**

$$\begin{array}{c} \mathsf{CH}_{3} - \mathsf{C} = \mathsf{O} + \mathsf{KOH} \longrightarrow \begin{bmatrix} \mathsf{CH}_{3} & \mathsf{C} = \mathsf{O} \\ & & \mathsf{I} \\ & & \mathsf{N} - \mathsf{Br} \\ & & \mathsf{H} \end{bmatrix}$$

+ KBr +  $H_2O \xrightarrow{\text{Rearrangement(step 3)}} CH_3 - \underbrace{N=C=O}_{..}$ Methylisocyanate

### Hydrolysis :

$$CH_3 - N = C = O + 2KOH \longrightarrow CH_3 - NH_2 + K_2CO_3$$
  
Methylamine

**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.

### ETHYLACETATE AND ACETIC ESTER

$$[CH_{3}-C-OC_{2}H_{5}]$$

$$O$$

$$H_{3}-C-OH \xrightarrow{OC_{2}H_{5}} CH_{3}-C-OC_{2}H_{5}$$

$$O$$

$$H_{3}-C-OH \xrightarrow{OC_{2}H_{5}} CH_{3}-C-OC_{2}H_{5}$$

1. Methods of preparation : By liquid phase Esterification :

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - OH + HOC_2H_5 \end{array} \xrightarrow{Conc.H_2SO_4} \end{array}$$

$$CH_3 - C - OC_2H_5 + H_2O$$

### By vapour phase Esterification :

$$\begin{array}{c} O\\ \parallel\\ CH_3-C-OH + HOC_2H_5 & \xrightarrow{ThO_2}\\ \hline\\ (vapour) & (vapour) \end{array}$$

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - OC_2H_5 + H_2O \end{array}$$

### By Aceylation of Ethanol :

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - CI + HOC_2H_5 \xrightarrow{Pyridine} CH_3 - C - OC_2H_5 + HCI \end{array}$$

$$CH_{3} - C \rightarrow O + HOC_{2}H_{5} \xrightarrow{Anhyd} CH_{3} - C - OC_{2}H_{5} + CH_{3}COOH$$

$$CH_{3} - C = OC_{2}H_{5} + CH_{3}COOH$$

### **Tischenko Reaction :**



Ethylation of Silver halides :

$$CH_3 - C - OAg + I - C_2H_5 \longrightarrow$$

0 || CH₃ - C - OC₂H₅ +AgI↓

**Ethanolysis of Ethanenitrile :** 

$$CH_3 - C \equiv N + C_2H_2OH + H_2O \longrightarrow$$

By addition of Acetic acid on Ethylene :

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - OH + CH_2 = CH_2 \xrightarrow{BF_3} CH_3 - C - O - CH_2 - CH_3 \end{array}$$

By reaction of sodium Ethoxide on Acetyl chloride :

$$\begin{array}{cccc} O & O \\ \parallel \\ CH_3 - C - CI + NaOC_2H_5 & \longrightarrow & CH_3 - C - OC_2H_5 + NaCI \end{array}$$

### **Baeyer–Villiger Oxidation :**

Ethyl acetate is formed on reacting butanone with a peracid, Methyl propionate is also formed in small amounts.

$$CH_3 - C - C_2H_5 + CH_3 - C - OOH \longrightarrow$$
  
Peracetic acid

$$\begin{array}{c} O & O \\ \parallel \\ CH_3 - C - OC_2H_5 + CH_3 - C - OH \end{array}$$

$$CH_3 - C - CH_2 - CH_3 + [O] \longrightarrow CH_3 - CH_2 - C - OCH_3$$
  
Methyl propionate

### 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°.

### 3. Chemical Properties :

### Hydrolysis :

 $CH_{3} - C - OC_{2}H_{5} + HOH \xrightarrow{H_{2}SO_{4}} CH_{3} - COOH + C_{2}H_{5}OH$   $CH_{3} - C - OC_{2}H_{5} + NaOH \longrightarrow CH_{3} - C - ONa + C_{2}H_{5}OH$ 

**Note :** In esters caustic alkalies hydrolysis is rapid and complete. Alkaline hydrolysis of esters is called "Saponification".

### **Reduction :**

$$CH_{3} - C - OC_{2}H_{5} + 4H \xrightarrow{\text{RedP} + HI}{\text{or LiAlH}_{4}} 2 CH_{3}CH_{2}OH$$

$$O_{\parallel} \\ CH_{3} - C - OC_{2}H_{5} + 4H \xrightarrow{\text{Na}+C_{2}H_{5}OH}{2CH_{3}CH_{2}OH}$$
(Bouveault-Blanc reduction)

Ammonolysis :

$$CH_3 - C - OC_2H_5 + H - NH_2 \xrightarrow{\Delta} CH_3 - C - NH_2 + C_2H_5OH$$

With Grignard's Reagent :

$$CH_3 - C - OC_2H_5 + R - Mg X \longrightarrow CH_3 - C - R + Mg < X \xrightarrow{O_{\parallel}}{U}$$

**Note :** The product will be tertiary alcohol when 2 mole of Grignard's reagent are taken.

### With Hydazine :

$$CH_3 - C - OC_2H_5 + H - NH - NH_2 \longrightarrow O_1 \\ CH_3 - C - NH NH_2 + C_2H_5OH$$

Acetyl hydrazine

### With Hydroxyl Amine :

$$CH_3 - C - OC_2H_5 + H-NH-OH \longrightarrow$$



With PCl<sub>5</sub>:



$$CH_3 - C - CI + POCI_3 + C_2H_5CI$$

### **Claisen Ester Condensation :**

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - OC_2H_5 + H - CH_2 - C - OC_2H_5 \underline{\quad C_{2H_5ONa}} \end{array}$$

$$CH_3 - C - CH_2 - C - OC_2H_5 + C_2H_5OH$$
  
Acetoaceticester

### Pyrolysis or Thermal decomposition :

$$CH_3 - C - O H \xrightarrow{500^\circ-600^\circ} CH_3 - C - OH + CH_2 = CH_2$$

Acidolysis :

$$CH_{3} - C - OC_{2}H_{5} + C_{5}H_{10} - COOH \longrightarrow$$

$$O_{5}H_{11} - C - OC_{2}H_{5} + CH_{3} - C - OH$$

### BENZOIC ACID (C<sub>6</sub>H<sub>5</sub>COOH)

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<sub>6</sub>H<sub>5</sub>CONHCH<sub>2</sub>COOH

### PREPARATION

### [1] Oxidation of Benzyl Alcohol :

Benzoic acid is formed on permanganate [6] oxidation of benzyl alcohol.

$$\frac{C_6H_5CH_2OH}{\longrightarrow}C_6H_5CHO(Benzaldehyde)$$

 $\xrightarrow{[0]} C_6H_5COOH$  (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.

$$C_6H_5^ C \leftarrow [0] \rightarrow C_6H_5COOH$$
  
Side chain

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.) Aldehydes, Ketones and Carboxylic Acids

### 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.

$$C_6H_5MgBr \xrightarrow{CO_2} C_6H_5COOMgBr$$
  
 $\xrightarrow{HOH} C_6H_5COOH$ 

Carboxylation of Benzene :

[4]

[5]

[7]

[9]

Benzoylglycine

Benzoic acid is obtained on heating benzene and carbon dioxide in nitrobenzene medium in the presence of anhydrous aluminium chloride.

$$C_6H_5H + CO_2 \xrightarrow{AlCl_3} C_6H_5COOH$$

### Alkaline Hydrolysis of Benzotrichloride :

Benzoic acid is formed on hydrolysis of benzotrichloride by lime water in the presence of iron catalyst.

$$C_6H_5CCl_3$$
 (Benzotrichloride) 3 OH<sup>-</sup>  
 $\xrightarrow{Ca(OH)_2} C_6H_5COOH + H_2O + 3 Cl^-$ 

### 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.

$$\begin{array}{c} C_{6}H_{5}H+\text{ CI-CO-CI} \xrightarrow{\text{ AlCI}_{3}} C_{6}H_{5}COCI+HC1 \\ \text{Phosgene} \end{array}$$

[8] Hydrolysis of Cyanobenzene :

Benzoic acid is formed on hydrolysis of cyanobenzene i.e., benzonitrile by dilute hydrochloric acid.

 $C_6H_5CN + 2HOH + HCl \longrightarrow$ 

$$C_6H_5COOH + NH_4Cl$$

## 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.

 $\begin{array}{c} \text{HO-C}_{6}\text{H}_{4}\text{-COOH} + \text{Zn} \xrightarrow{} \\ \\ \text{H-C}_{6}\text{H}_{4}\text{-COOH} + \text{ZnO} \\ \\ \\ \text{Benzoic acid} \end{array}$ 

### [10] Decarboxylation of Phthalic Acid :

o–Benzendicarboxylic acid is called phthalic acid. On heating its zinc of nickel or chromium salt at 200–300° with water vapours, benzoic acid is formed by partial decarboxylation.



 $\xrightarrow{\Delta} +H_2O \rightarrow O + CO_2$ 

### [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.

$$C_{6}H_{5}COCl + H_{2}O \longrightarrow C_{6}H_{5}COOH + HCl$$
$$(C_{6}H_{5}CO)_{2}O + H_{2}O \longrightarrow 2C_{6}H_{5}COOH$$

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.

$$C_{6}H_{5}CONH_{2} + H_{2}O + HCl \longrightarrow$$

$$C_{6}H_{5}COOH + NH_{4}Cl$$

$$C_{6}H_{5}CONH_{2} + NaOH \longrightarrow$$

$$C_{6}H_{5}COONa + NH_{2}$$

Liberation of ammonia gas on heating the solution after adding sodium hydroxide solution is the test for amides.

### PHYSICAL PROPERTIES

Benzoic acid is a crystalline solid (melting point 122°) 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.

### **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

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.

$$C_6H_5COOH + NaOH \longrightarrow$$
  
 $C_6H_5COONa + H_2O$ 

$$2C_{6}H_{5}COOH + Na_{2}CO_{3} \longrightarrow$$

$$2C_{6}H_{5}COONa + H_{2}O + CO_{2}$$

$$C_{6}H_{5}COOH + NaHCO_{3} \longrightarrow$$

$$C_{6}H_{5}COONa + H_{2}O + CO_{2}$$

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<sub>3</sub>.

$$2C_{6}H_{5}COOH + Ca(OH)_{2} \xrightarrow{} (C_{6}H_{5}COO)_{2}Ca$$

$$C_{6}H_{5}COOH + NH_{3} \xrightarrow{} C_{6}H_{5}COONH_{4}$$

$$C_{6}H_{5}COOH + NH_{4}OH \xrightarrow{} C_{6}H_{5}COONH_{4} + H_{2}O$$

### 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  $H_2SO_4$ .

$$C_6H_5COOH + HOR \xrightarrow{H^+} C_6H_4COOR + H_2O$$

### 3. With Inorganic Chloride :

Benzoyl chloride is formed on the reaction of benzoic acid with phosphrous pentachloride or phsophrous trichloride or thionyl chloride.

$$C_{6}H_{5}COOH + PCl_{5} \longrightarrow$$

$$C_{6}H_{5}COCl + POCl_{3} + HCl$$

$$3C_{6}H_{5}COOH + PCl_{3} \longrightarrow$$

$$C_{6}H_{5}COCl + H_{3}PO_{4}$$

$$C_{6}H_{5}COOH + SOCl_{2} \longrightarrow$$

$$C_{6}H_{5}COCl (Benzoyl chloride) + SO_{2} + HCl$$

### 4. With $P_2O_5$ :

Benzoic anhydride is formed on heating benzoic acid with  $P_2O_5$ .

$$2C_6H_5COOH \xrightarrow{P_2O_5} (C_6H_5CO)_2O + H_2O$$

Acetic anhydride also dehydrates two molecules of benzoic acid to give benzoic anhydride.

### With Ammonia :

5.

8.

9.

[**B**]

Benzamide is formed on heating benzoic acid with ammonia.

$$C_6H_5COOH + NH_3 \longrightarrow [C_6H_5COONH_4]$$
  
 $\xrightarrow{\Delta} -H_2O \rightarrow C_6H_5CONH_2$ 

Benzonitrile or cyanobenzne can be obtained by heating benzamide with  $P_2O_5$ .

$$C_6H_5CONH_2 \xrightarrow{P_2O_5} C_6H_5CN + H_2O$$

### 6. With Soda Lime :

Benzene is obtained on dry distillation of sodium salt of benzoic acid with sodalime.

 $C_6H_5COONa + NaOH \longrightarrow C_6H_6 + Na_2CO_3$ 

### 7. Dry Distillation of Calcium Salt :

Benzophenone is obtained on dry distillation of calcium salt of benzoic acid.

$$(C_6H_5COO)_2Ca \xrightarrow{\Delta} C_6H_5COC_6H_5 + CaCO_3$$

### Hunsdiecker Reaction :

Bromobenzene is formed on heating the silver salt of benzoic acid with bromine in carbon tetrachloride solution

$$C_6H_5COOAg + Br_2 \xrightarrow{CCl_4} C_6H_5Br + CO_2 + AgBr$$

## Reduction by Lithium Aluminium Hydride :

Benzyl alcohol is formed on reduction of benzoic acid by lithium aluminium hydride (LiAlH<sub>4</sub>).

$$C_6H_5COOH + 4H \xrightarrow{\text{LiAlH}_4} C_6H_5CH_2OH + H_2O$$

### 10. Reduction by Sodium and Ethanol :

Toluene is formed on reduction of benzoic acid by sodium and ethanol.

$$C_6H_5COOH + 6H \xrightarrow[EtOH]{Na} C_6H_5CH_3 + 2H_2O$$

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-nitrobenzoic

3,5-Dinitrobenzoic acid

NO<sub>2</sub>



**Note :** Due to the presence of a deactivating m-directing COOH group in benzoic acid, the latter does not give Friedel–Crafts reaction.

### TESTS

2.

### 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.

### **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.

### 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.