# ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

## Ethers (R-O-R)

### Nomenclature

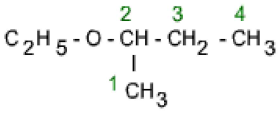
They are named by putting the names of two-alkyl groups before the word ether $CH_3$-O-$CH_3$ is named as dimethyl ether $C_2H_5$-O-$C_2H_5$ is named as diethyl ether $C_2H_5$-O-$CH_3$ is named as ethyl methyl ether $C_6H_5$-O-$CH_3$ is named as methyl phenyl ether. If same alkyl groups are there, they are called simple ether or symmetrical ether otherwise they are called mixed ether or unsymmetrical ethers

$C_2H_5$-O-$C_2H_5$ simple ether

$C_2H_5$-O-$CH_3$ mixed ether

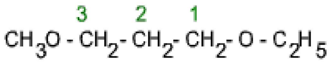
Above ethers are **aliphatic ethers** but $C_6H_5$-O-$CH_3$ is called **aromatic ether.**

| **Structure** | **Common name** | **IUPAC name** |
|---|---|---|
| $CH_3$-O-$CH_3$ | Dimethyl ether | Methoxy methane |
| $CH_3$-O-$C_2H_5$ | Ethyl methyl ether | Methoxy ethane |
| $C_6H_5$-O-$CH_3$ | Methyl phenyl ether (anisole) | Methoxy benzene |
| $C_6H_5$-O-$C_2H_5$ | Ethyl phenyl ether (phenetole) | Ethoxy benzene |



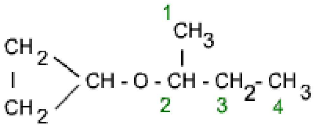
$$C_2H_5-O-\underset{\overset{|}{^1CH_3}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

— 2 ethoxy butane.

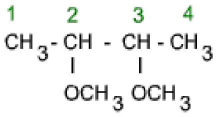


$$CH_3O-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2}-O-C_2H_5$$

— 1 - ethoxy - 3 - methoxy propane.



— 2 cyclopropoxy butane.



$$\overset{1}{CH_3}-\underset{\overset{|}{OCH_3}}{\overset{2}{CH}}-\underset{\overset{|}{OCH_3}}{\overset{3}{CH}}-\overset{4}{CH_3}$$

— 2,3 dimethoxy butane.

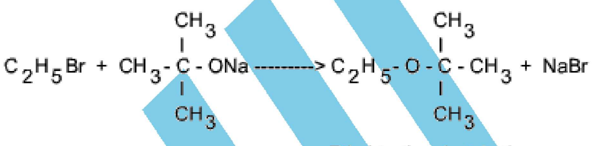
## Methods of preparation

### Willamson' synthesis

when alkyl halide is treated with sodium alkoxide, we get ether

RX + R'-O-Na ————> R-O-R' + NaX

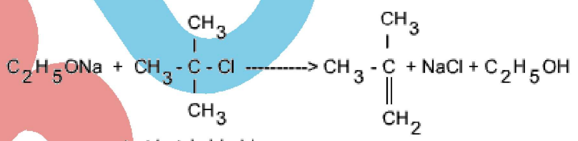
$CH_3$Br + Na$OC_2H_5$ ——————————> $CH_3$-O-$C_2H_5$ + NaBr sodium ethoxide methoxy ethan



$$C_2H_5Br + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-ONa \longrightarrow C_2H_5-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + NaBr$$

Ethyl tertiary butyl ether

Secondary or tertiary halides readily undergo elimination reaction in the presence of strong base to form alkenes.



$$C_2H_5ONa + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl \longrightarrow CH_3-\underset{\overset{\|}{CH_2}}{\overset{CH_3}{C}} + NaCl + C_2H_5OH$$

tert butyl chloride

Phenolic ethers can be prepared by the following reactions

$C_2H_5$Br + Na$OC_6H_5$ ——————> $C_2H_5$-O-$C_6H_5$ + NaBr phenetole

$CH_3$Br+Na$OC_6H_5$ ——————> $CH_3$-O-$C_6H_5$ + NaBr anisole

### Dehydration of alcohols

Alcohols are dehydrated to ethers in presence of concentrated $H_2SO_4$ at 413 K.

$$C_2H_5O\boxed{H + HO}-C_2H_5 \xrightarrow[413\ K]{H_2SO_4} C_2H_5-O-C_2H_5 + H_2O$$

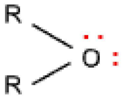
If ethyl alcohol is passed over heated catalyst like $Al_2O_3$ at 520K we get ether

$$2\,C_2H_5OH \xrightarrow[520\ K]{Al_2O_3} C_2H_5-O-C_2H_5 + H_2O$$

Ethoxy ethane

### Physical properties

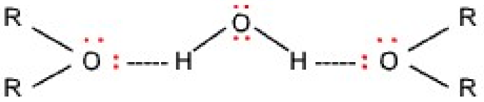
In ether central oxygen atom is $sp^3$ hybrid state.



The bond angle in C-O-C is not exactly 109°28'. The deviation in angle is caused by the repulsive force between alkyl group. C-O-C angle in dimethyl ether is 110°.

Thus ethers have bent structure and have dipole moment greater than zero. There is no H-bonding in ether.

Ethers are soluble in water, solubility of ethers is due to the capability of their molecules to form H-bond with water molecules.



## Chemical properties

### Cleavage by acids

Ether can be cleaved by the use of halogen acid, $H_2SO_4$

$$C_2H_5\text{-O-}C_2H_5 + HI \xrightarrow{373\ K} C_2H_5OH + C_2H_5I$$

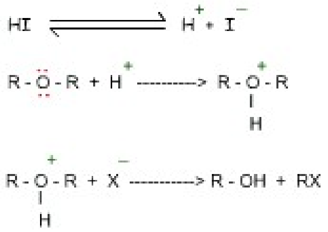
again $C_2H_5OH$ will react with HI and gives $C_2H_5I$

$$C_2H_5OH + HI \longrightarrow C_2H_5I + H_2O$$

Overall reaction is as under

$$C_2H_5\text{-O-}C_2H_5 + 2HI \xrightarrow{373\ K} 2C_2H_5I + H_2O$$

### Mechanism is as under



$$HI \rightleftharpoons \overset{+}{H} + \overset{-}{I}$$

$$R\text{-}\ddot{O}\text{-}R + \overset{+}{H} \dashrightarrow R\text{-}\underset{H}{\overset{+}{O}}\text{-}R$$

$$R\text{-}\underset{H}{\overset{+}{O}}\text{-}R + \overset{-}{X} \dashrightarrow R\text{-}OH + RX$$

another reaction is

$$C_6H_5\text{-}O\text{-}CH_3 + HI \xrightarrow{373\ K} \underset{\text{Phenol}}{C_6H_5OH} + CH_3I$$

In the above reaction, we will always get phenol and methyl iodide. It is due to fact that phenyl oxygen bond has partial double bond character due to resonance and thus its cleavage is difficult as compared to alkyl oxygen bond. Order of reactivity of halogen acids is

HI > HBr > HCl

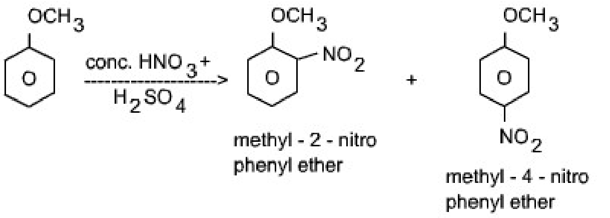
### Reaction with $PCl_5$

$$C_2H_5\text{-O-}C_2H_5 + PCl_5 \xrightarrow{\text{heat}} 2C_2H_5Cl + POCl_3$$

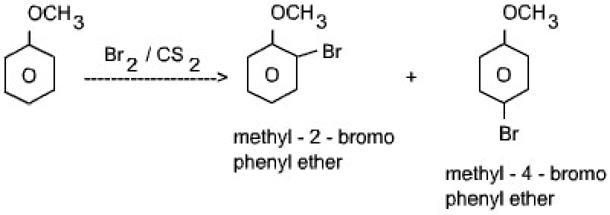
phosphoryl chloride

### Ring substitution in aromatic ethers

Aromatic ether undergo electrophilic substitution in the benzene ring at the ortho and para positions.



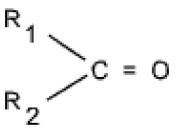
Simillar reaction will take place with $Br_2$ dissolved in $CS_2$



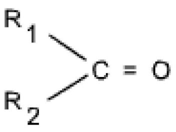
### User of ethers

1. Diethyl ether is used as an industrial solvent for oils, gums, resins etc..
2. An anaesthetic in surgery.

## Aldehydes and ketones



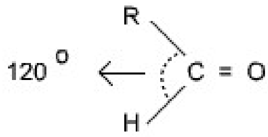
Ketone

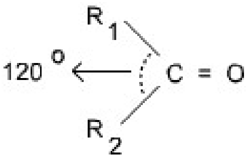


Aldehyde

Aldehydes and ketones are the compounds which contain a carbonyl group $>C=O$.

The group $R_1$, $R_2$, R may be aliphatic or aromatic. The general formula of aldehyde and ketones are RCHO and $R_1R_2CO$ respectively. Here carbon is $sp^2$ hybridized and bond angle is 120°.



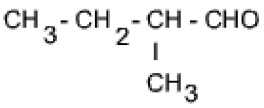


### Nomenclature of aldehyde and ketone

IUPAC name of aldehydes are alkenals and for ketones it is alkanones.

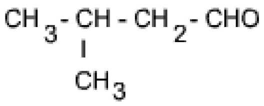
### NAMING OF ALDEHYDE

| Formula | Common name | IUPAC name |
|---|---|---|
| HCHO | formaldehyde | methanal |
| $CH_3CHO$ | acetaldehyde | ethanal |



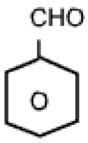
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CHO$

α methy butyraldehyple 2 methyl butanal

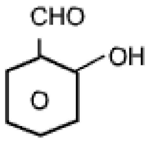


$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CHO$

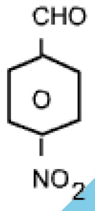
β Methyl Butyraldehyde 3 methylbutanal



benzaldehyde benzaldehyde



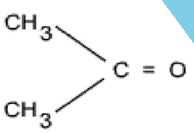
o-hydroxy benzaldehyde 2-hydroxy benzaldehyde



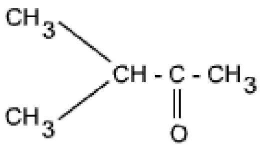
P-nitrobenzaldehyde 4 - nitro benzaldehyde

**Naming of Ketones**

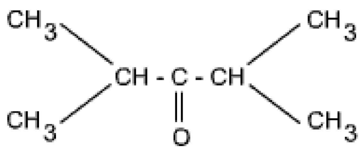
**Formulae Common name IUPAC name**



Dimethyl keton Propanone

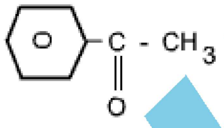


Methyl isopropyl ketone 3-methyl 2-butanone

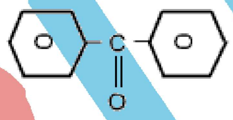


Di-isopropyl-ketone 2,4-dimethyl 3pentanone

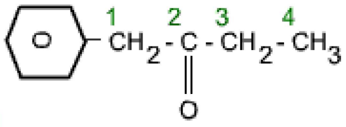
**Example of some aromatic ketones**



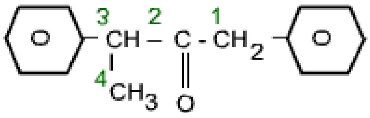
Methyl phenyl ketone or acetophenone



Diphenyl ketone or benzophenone



Ethyl benzyl ketone or 1 phenyl 2 butanone



1,3 diphenyl 2 butanone

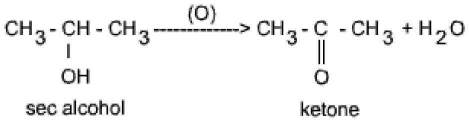
**General methods of preparation of aldehydes and ketones From alcohols**

Aldehyde and ketones are prepared by direct oxidation of alcohols. Acidic $KMnO_4$ or $K_2Cr_2O_7$ are used as oxidising agents. **Primary alcohols give aldehydes**.

$$\underset{\text{primary alcohol}}{CH_3-CH_2-OH} \xrightarrow{(O)} \underset{\text{ethanol}}{CH_3CHO} + H_2O$$

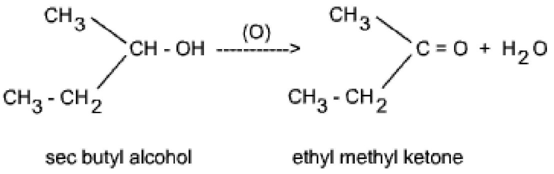
$$\underset{\text{n butyl alcohol}}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow{(O)} \underset{\text{butanal}}{CH_3CH_2CH_2CHO} + H_2O$$

**Ketones can be prepared by using similar oxidising agents from secondary alcohols**.

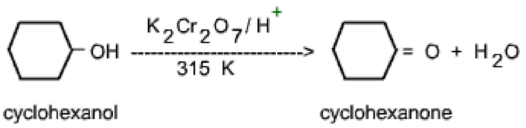


$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{(O)} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + H_2O$$

sec alcohol ketone



sec butyl alcohol ethyl methyl ketone



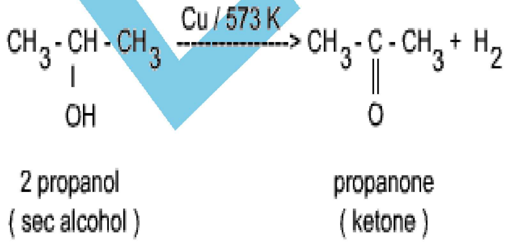
cyclohexanol cyclohexanone

Aldehydes undergo further oxidation to carboxylic acids very easily. So oxidaiton of alcohols to aldehyde is carried out under controlled reactron conditions. When alcohol vapours are passed over heated metallic catalyst such as Cu, Ag, we get aldehydes, ketones. **Primary alcohols give aldehyde and secondary alcohols give ketone**.

$$CH_3-CH_2-OH \xrightarrow{Cu\,/\,573\,K} CH_3-CHO + H_2$$

$$CH_3-CH_2-CH_2-OH \xrightarrow{Cu\,/\,573\,K} CH_3-CH_2-CHO + H_2$$

1 - propanol propanal



$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{Cu\,/\,573\,K} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + H_2$$

2 propanol
( sec alcohol )

propanone
( ketone )

**From carboxylic acid chlorides** Acid chlorides (RCOCl) are converted to aldehyde by catalytic hydrogenation

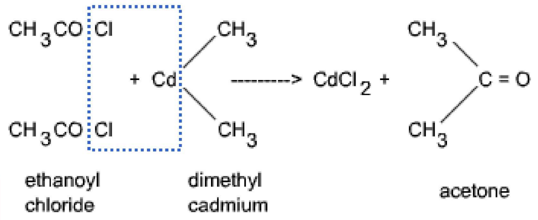
$$CH_3COCl + H_2 \xrightarrow{Pd\,/\,BaSO_4} CH_3CHO + HCl$$

acetyl chloride acetaldehyde

$$C_6H_5COCl + H_2 \xrightarrow{Pd\,/\,BaSO_4} C_6H_5CHO + HCl$$

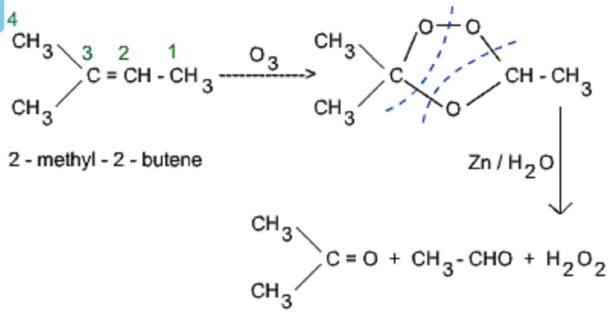
benzaldehyde

The above reaction is called Rosenmund's reduction. Ketones are obtained by treating acid chlorides with dialkyl cadmium.

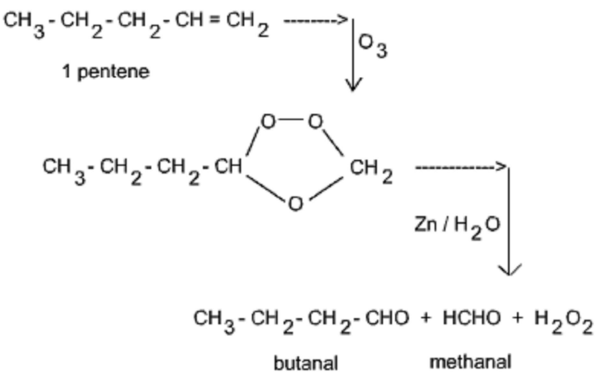


ethanoyl chloride dimethyl cadmium acetone

**By the ozonolysis of alkenes** Alkene react with ozone to form ozonides which on subsequent reductive cleavage with Zn/$H_2O$. It gives carbonyl compounds. Reaction will proceed as under



2 - methyl - 2 - butene

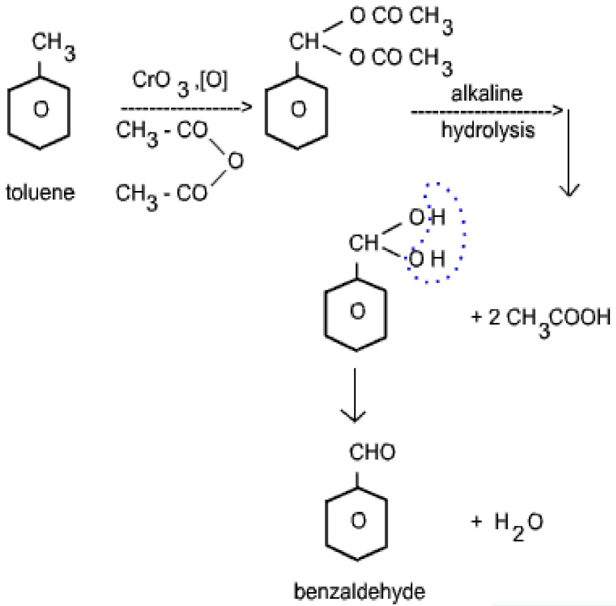


1 pentene

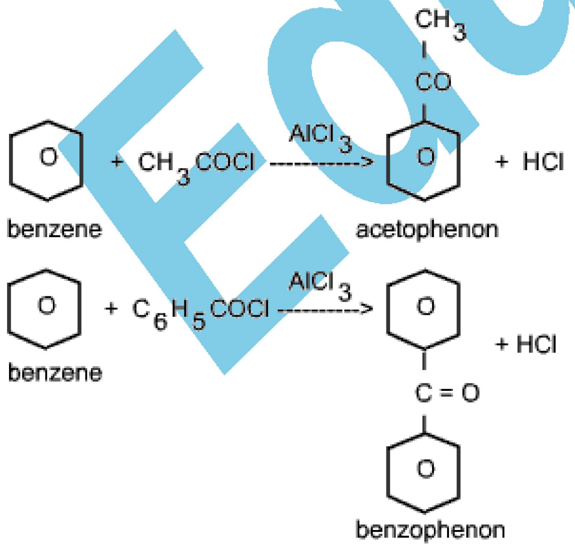
butanal methanal

### Preparation of aromaic carbonyl compounds

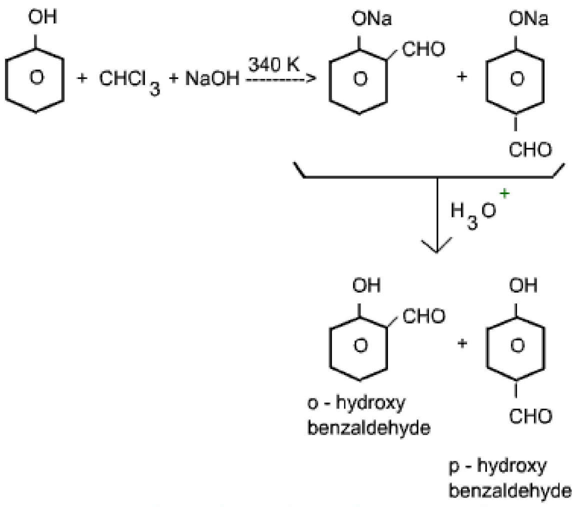
**Oxidation of toluene** always yields benzaldehyde. Further oxidation of benzaldehyde is avoided by trapping the aldehyde with acetic anhydride which form benzal diacetate. **$CrO_3$ is used as a oxidising reagent.**



**By Friedal crafts reaction** aromatic ketone can be obtained by this method as follows :

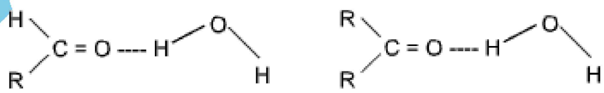


Aromatic aldehyde contaning hydroxy groups is prepared by **Reimer Tiemann reaction**



**Physical properties of aldehydes and ketones**

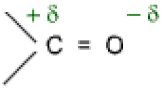
Formaldehyde is a gas and other aldehydes are liquids. The lower ketone are colourless liquids and have pleasant smell. The higher members are colourless solids, Aromatic ketones are generally solid with a pleasant smell. Aldehyde and ketones are polar in nature so they have intermolecular dipole dipole interaction. Hence they have higher boiling points than non-polar compounds of comparable molecular masses. Lower members of aldehydes and ketone [methanal, ethanal, propanone] are soluble in water because they form H bond with water.



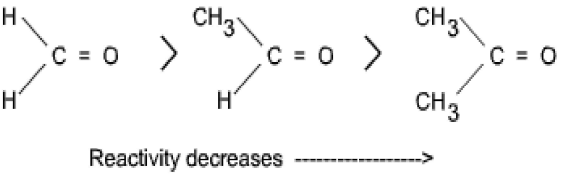
Aldehydes and ketones are fairly soluble in organic solvents.

**Chemical properties of aldehydes and ketones**

Both are having $>C=O$ group. Carbonyl group is polar because oxygen is more electronegative than carbon.



Nucleophiles can attack at carbon of carbonyl group.

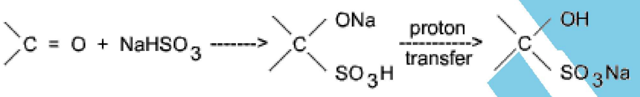


Acetone is less reactive towards nucleophiles because in acetone, the carbonyl carbon is attached to two methyl group which are electron releasing nature, These methyl groups push electrons towards carbonyl carbon and thus, decrease the magnitude of positive charge on carbon and make it less susceptile to nucleophilic. Both aldehydes and ketones react with hydrogen cyanide (HCN) to form cyanohydrins as addition products

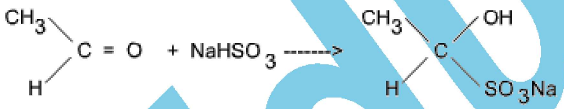
Ethanal ethanal cyanohydrin

Acetone acetone cyanohydrin

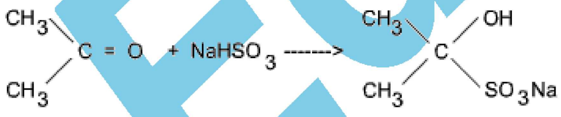
**Reaction with NaHSO** Both aldehyde and ketons form addition product.



Some examples are:

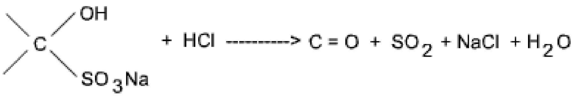


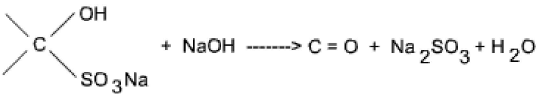
acetaldehyde acetaldehyde sodium bisulphite



acetone acetone sodium bisulphite

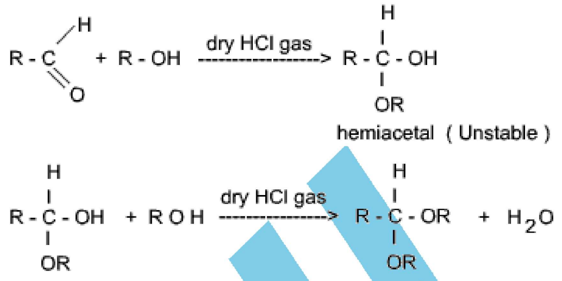
The hydrogen bisulphite addition compound can be converted back in to the original aldehyde or ketone by treating it with dilute acid or alkali.





Addition with grignard reagent, we get alcohols

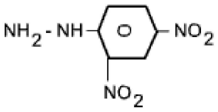
**Addition of alcohols** Aldehydes react with alcohols in the presence of dry HCl and give acetals. Reaction proceeds as follows



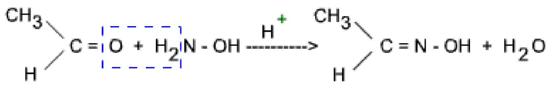
hemiacetal ( Unstable )

hemiacetal acetal

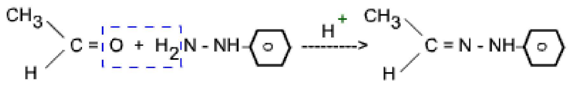
**Addition of ammonia derivatives** Aldehydes and ketones react with ammonia derivatives. The addition compounds and water molecule give a compound containing $>C = N$ -group. Some of the ammonia derivaties are as under

| | |
|---|---|
| $NH_2 - OH$ | Hydroxylamine |
| $\begin{array}{c}NH_2\\ \mid\\ NH_2\end{array}$ | Hydrazine |
| $NH_2 - NH - C_6H_5$ | Phenyl hydrazine |
| $NH_2 - NH - \underset{\underset{O}{\|}}{C} - NH_2$ | Semi carbazide |
|  | 2,4 dinitro phenyl hydrazine |

Some of the reaction are written as under.



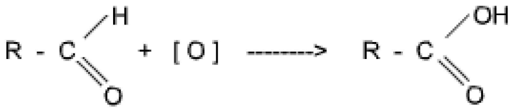
Ethanal oxime



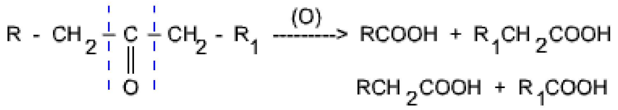
Ethanal phenyl hydrazone

+ $H_2O$

**Oxidation** Aldehydes are easily oxidised to carboxylic acid.



Ketones are not easily oxidised. They can be oxidised under vigorous condition using powerful oxidising agents such as HNO$_3$ KMnO$_4$/H$^+$, K$_2$Cr$_2$O$_7$/H$^+$ etc. On oxidation of ketones, cleavage of carbon-carbon bond takes place and a number of carboxylic acids having less number of carbon atoms than the parent ketone are formed.



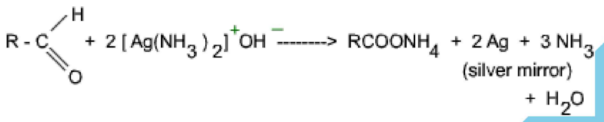
$$R-CH_2-\underset{\overset{\|}{O}}{C}-CH_2-R_1 \xrightarrow{(O)} RCOOH + R_1CH_2COOH$$
$$RCH_2COOH + R_1COOH$$

**Oxidation reaction can be used to distinguish between aldehyde and ketones by using the reagent like Tollen's reagent, Fehling's soluiton. Tollen's reagent.** It is a ammoniacal solution of AgNO$_3$

AgNO$_3$ + NH$_4$OH $\longrightarrow$ AgOH + NH$_4$NO$_3$

AgOH + 2NH$_4$OH $\longrightarrow$ [Ag(NH$_3$)$_2$]$^+$OH$^-$ + 2H$_2$O

On treating the Tollen's reagent with aldehyde we get silver mirror.



$$R-C\overset{H}{\underset{O}{\lessgtr}} + 2[Ag(NH_3)_2]^+OH^- \longrightarrow RCOONH_4 + 2Ag + 3NH_3 + H_2O$$

**Fehling solution**

Alkaline soluiton of CuSO$_4$ containing sodium potassium tartrate (Rochelle salt) as the complexing agent. Aldehyde on warming with this solution give a red precipitate of Cu$_2$O.

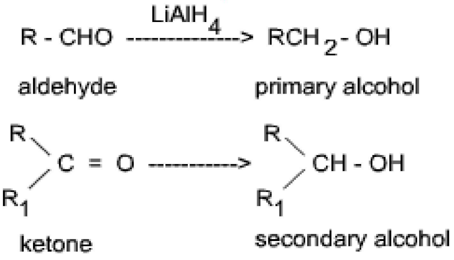
R-CHO + 2Cu(OH)$_2$ + NaOH $\longrightarrow$ RCOONa + Cu$_2$O + 3H$_2$O red ppt

It may be noted that Tollen's reagent and Fehling solution are very weak oxidising agent. They can oxidise aliphatic aldehyde. Tollen's reagent will oxidise aromatic aldehyde also but fehling solution is not capable to oxidise aromatic aldehyde.

Both reagents will not oxidise ketones. Both reagents may be used to distinguish between aldehyde and ketone.

**Reduction**

Aldehydes and ketones are reduced to primary and secondary alcohol respectively by mild reduction.

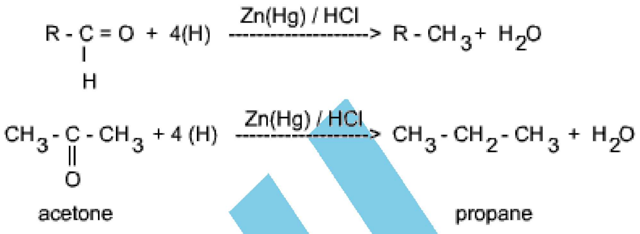


$$R-CHO \xrightarrow{LiAlH_4} RCH_2-OH$$

$$\begin{matrix}R\\R_1\end{matrix}\rangle C=O \longrightarrow \begin{matrix}R\\R_1\end{matrix}\rangle CH-OH$$

Aldehyde and ketones are converted to their corresponding hydrocarbon by the following methods :

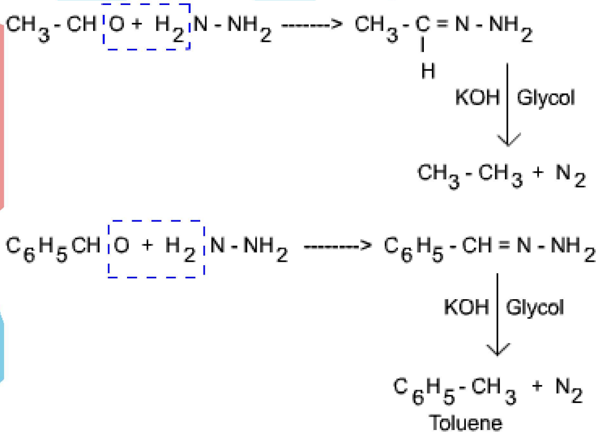
**Clemmensen reduction** Aldehyde and ketone are reduced to the corresponding hydrocarbon by treatment with amalgamated zinc and concentrated HCl.



$$R-\underset{\underset{H}{|}}{C}=O + 4(H) \xrightarrow{Zn(Hg)/HCl} R-CH_3 + H_2O$$

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 4(H) \xrightarrow{Zn(Hg)/HCl} CH_3-CH_2-CH_3 + H_2O$$

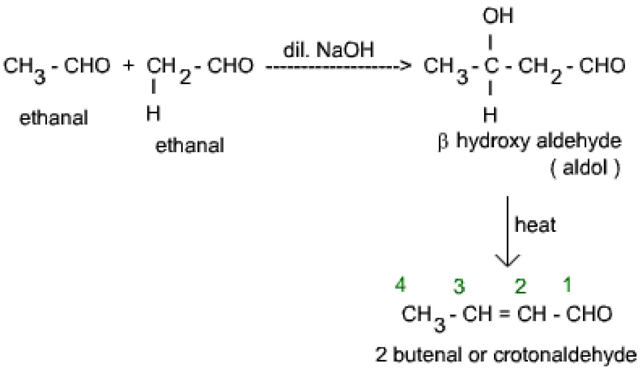
**Wolff-Kishmer reduction** Aldehyde and ketones are reduced to the corresponding hydrocarbon by the reaction with hydrazine followed by reaction with glycol and KOH



$$CH_3-CH\boxed{O + H_2}N-NH_2 \longrightarrow CH_3-\underset{\underset{H}{|}}{C}=N-NH_2 \xrightarrow{KOH\ |\ Glycol} CH_3-CH_3 + N_2$$

$$C_6H_5CH\boxed{O + H_2}N-NH_2 \longrightarrow C_6H_5-CH=N-NH_2 \xrightarrow{KOH\ |\ Glycol} C_6H_5-CH_3 + N_2$$

**Aldol condensation** Aldehydes and ketones which have at least one α hydrogen atom when treated with dilute NaOH, they undergo condensation to form β hydroxy aldehydes or ketones. This is known as aldol condensation.



$$CH_3-CHO + \underset{\underset{H}{|}}{CH_2}-CHO \xrightarrow{dil.\ NaOH} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-CHO \xrightarrow{heat} \overset{4}{CH_3}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CHO}$$

Aldol formed above when heated undergo dehydration to form α - β unsaturated aldehyde.

**Cannizygaro reaction** Aldehydes which do not have α hydrogen atom, such as formaldehyde and benzaldehyde, when heated with concentrated NaOH (50%) solution, gives a mixture of alcohol and the salt of a carboxylic acid.

$$2HCHO \xrightarrow{\text{conc.NaOH}} CH_3OH + HCOO^-Na$$

sodium acetate

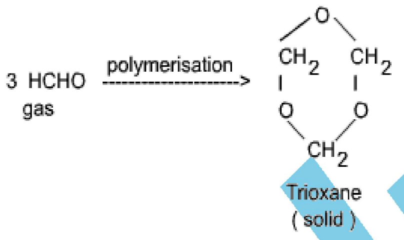
$$2C_6H_5CHO \xrightarrow{\text{conc. NaOH}} C_6H_5CH_2OH + C_6H_5COONa^+$$

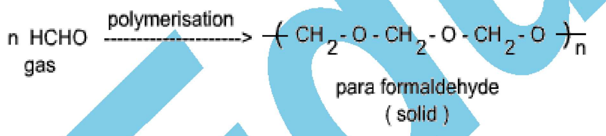
Formaldehyde reacts with ammonia to form hexamethylene tetramine.

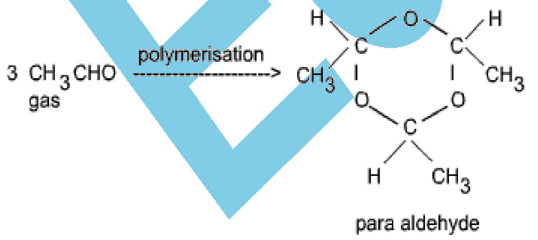
$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$

Hexamethylene tetramine

Hexamethylene tetramine is known as urotropine is used as medicine to treat urimary inflection. By the polymerisaiton of formaldehyde and acetaldehyde we get polymers in solid forms

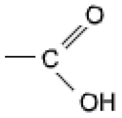






**Carboxylic acid**

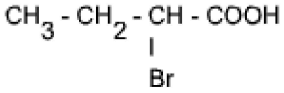
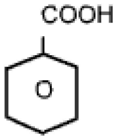
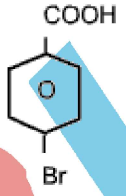
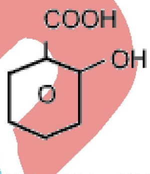
Organic compounds containing carboxyl groups



are termed as carboxylic acid.

Acid may be aliphatic or aromatic depending upon the group alkyl or aryl attached to carboxylic group.

**Nomenclature**

| **Formula** | **Common name** | **IUPAC name** |
|---|---|---|
| HCOOH | Formaic acid | Methanoic acid |
| $CH_3CH_2\text{-}COOH$ | Propionic acid | Propanoic acid |
|  $CH_3\text{-}CH_2\text{-}\underset{\underset{Br}{\mid}}{CH}\text{-}COOH$ | α bromobutyric acid | 2-bromobutanoic acid |
|  | ______ | benzoic acid |
|  | P bromo benzoic acid | 4-bromo benzoic acid |
|  | salicylic acid | 2-hydroxybenzoic acid |
| $CH_3\text{-}CH{=}CH\text{-}COOH$ | ____ | 2-buteneoic acid |

**Methods of preparation By the oxidation of primary alcohols** By the oxidation of primary alcohols with $KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$ we can get the acids

$$R\text{-}CH_2\text{-}OH + 2(O) \xrightarrow{KMnO_4/H^+} RCOOH + H_2O$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH + 2(O) \xrightarrow{KMnO_4/H^+} CH_3CH_2\text{-}CH_2\text{-}COOH + H_2O$$

**By the oxidation of aldehyde**

By the usual oxidizing agent we get acids.

$$R\text{-}CHO + (O) \xrightarrow{KMnO_4/H^+} RCOOH$$

$$CH_3CHO + (O) \xrightarrow{KMnO_4/H^+} CH_3COOH$$

**From alkyl cyanides**

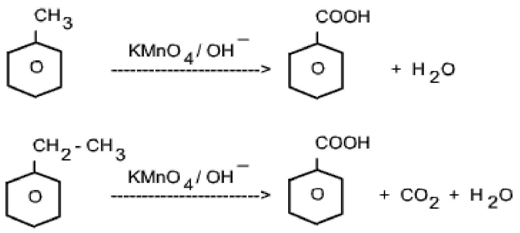
Alkyl cyanides on hydrolysis with dilute acid or alkalies give carboxylic acids

$$R\text{-}CN + 2H_2O \xrightarrow{H^+} RCOOH + NH_4^+$$

$$CH_3\text{-}CN + 2H_2O \xrightarrow{\text{dilute HCl}} CH_3COOH + NH_4Cl$$

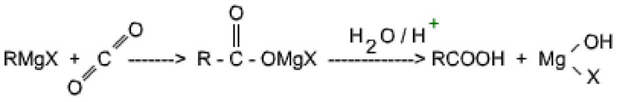
### From alkyl benzenes

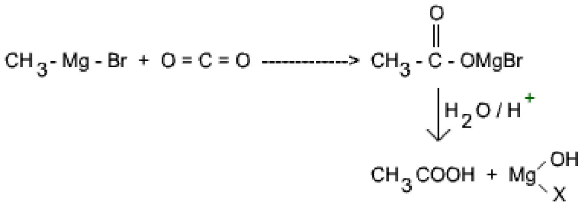
Benzoic acid can be prepared by oxidaiton of alkyl benzene with alkaline $KMnO_4$, Chromic anhydride or concentrated $HNO_3$.

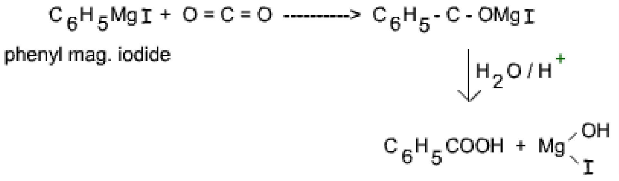


### From Grignard reagent

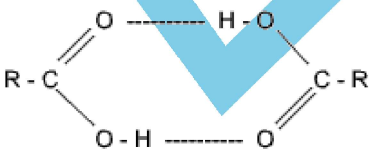
Grignard reagents when treated with $CO_2$ give carboxylic acid.



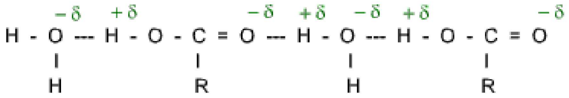




**Physical properties** The first three aliphatic acids are colourless liquids with pungent smell. The next six are oily liquids while higher members are colourless, odourless waxy solids. Benzoic acid is a crystalline solid. Carboxylic acids form dimer in which two acid molecules are held by two H bonds.



Due to H bonding they have higher boiling points. Lower members are soluble in water due to formation of H bonding.



### Chemical properties

Carboxylic acids are acidic in nature. **They ionise in water**

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

Hydronium ion

Acidic strength of carboxylic acid is much less than mineral acid. The carboxylate ion is stablised by resonance.

Chloroacate acid is stronger than acetic acid because chlorine is electron withdrawing atom, it will decrease the electron density over carbonyl carbon. It favours delocalisation of negative charge. Thus chloroacetic ion is stablised relative to the acetate ion. Hence chloroacetic acid in stronger than acetic acid.

**All carboxylic acids turn blue litmus red.**

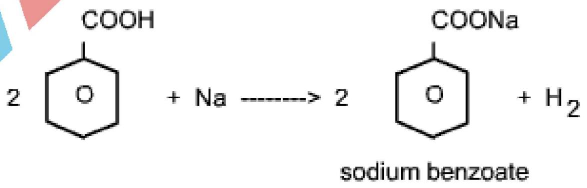
**Reactions with metals**

Like Na, K, Ca, Mg, Zn etc. is as follows :

$2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2$

$2CH_3COOH + Zn \longrightarrow (CH_3COO)_2Zn + H_2$

zinc acetate



**Reaction with alkalies**

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

**Reduction**

Carboxylic acid are reduced to primary alcohols on treatment with $LiAlH_4$

$$RCOOH \xrightarrow{LiAlH_4} RCH_2\text{-}OH$$

**Reaction with $PCl_5$, $PCl_3$ and $SOCl_2$**

$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

acetylchloride

$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$

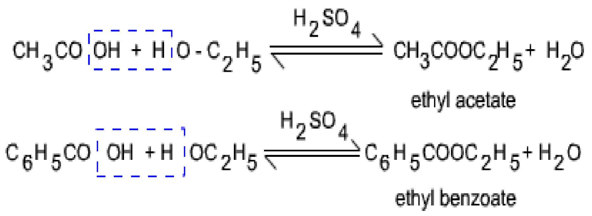
acetyl chloride

$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2\uparrow + HCl\uparrow$

$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2\uparrow + HCl\uparrow$

**Formation of esters and reaction with alcohols**

When carboxylic acids are heated with alcohols in presence of concentrated $H_2SO_4$, esters are formed. The reaction is called esterificaion.



**Decarboxylation**

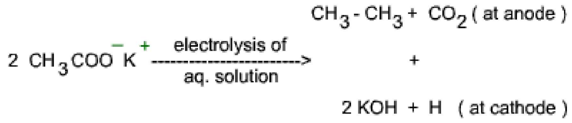
Carboxylic acid lose $CO_2$ under the following condition.

Sodium or potashium salt of carboxylic acid on heating with sodalime (CaO + NaOH) give alkanes

$$CH_3COONa + NaOH \xrightarrow{CaO,\ Heat} CH_4 + Na_2CO_3$$

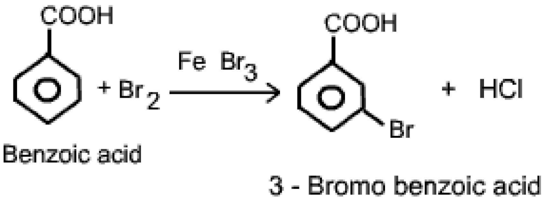
When two COOH groups are attached to same carbon atom decarboxylation takes place simply on heating

Alkali metal salts of carboxylic acid undergo decarboxylation on electrolysis (Kolbe's eletrolysis)

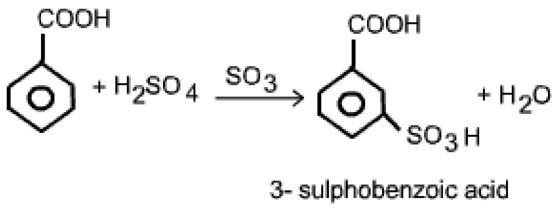


**Ring substitution in aromatic acids** Carboxylic group in benzoic acids is an electron withdrawing group and therefore it is m-directing. The electrophilic substitution takes place at meta position.i.

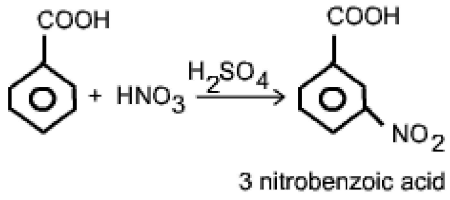
**i. Bromination**



**ii. Sulphonation**



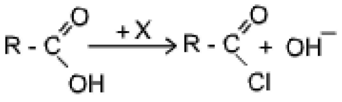
**iii. Nitration**



**Derivatives of carboxylic acids** If we replace hydroxyl group by other group, we get derivatives of carboxylic acids.

**Acyl halides**

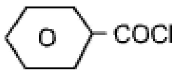
These are derivatives of carboxylic acids in which -OH group of carboxylic acid has been replaced by halogen atoms.



**Nomenclature**

This **ic** of the acids is replaced by **yl** and name of halogen is added in the nomenclature. For example $CH_3COCl$. Its name will be ethanoyl chloride.

$$\underset{\text{ethanoic acid}}{CH_3COOH} \xrightarrow{Cl^-} \underset{\text{ethanoyl chloride}}{CH_3COCl + OH^-}$$

| **Formula** | **Common name** | **IUPAC name** |
|---|---|---|
| $CH_3COCl$ | Acetyl chloride | Ethanoyl chloride |
| $CH_3CH_2CH_2COCl$ | n- butyryl chloride | Butanoyl chloride |
|  | Benzoyl chloride | Benzoyl chloride |

**Preparation**

From carboxylic acid we will get acyl chloride

$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$

$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$

## Properties

### Physical properties

The lower acyl chlorides are colourless liquids while the higher members are colourless solid with low melting point, They fume in air due to the formation of HCl by hydrolysis.

Acyl chloride have no hydrogen bond (intermolecular) so they are having low boiling points.

### Chemical properties

**They are hydrolysed by water to give carboxylic acid.**

$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$

$C_6H_5COCl + H_2O \longrightarrow C_6H_5COOH + HCl$

**With alcohols, they form esters**

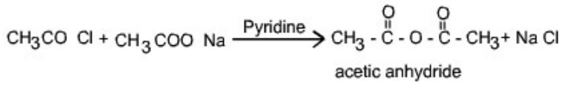
$CH_3CH_2COCl + CH_3CH_2\text{-}OH$

$\longrightarrow CH_3CH_2COOCH_2CH_3 + HCl$

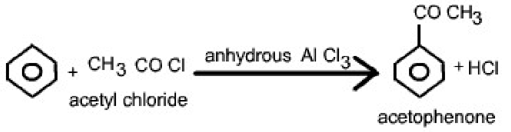
prpanoylchloride Ethyl Propionate

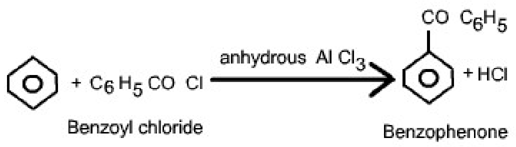
**Reaction with salts of carboxylic acid**

In presence of pyridine, they form acid anhydride



**Reaction with benzene** In presence of anhydrous $AlCl_3$, acyl halide react with benzene and form ketones, this reaction in called **Friedal Craft acylation reaction.**





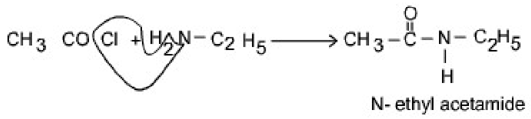
**Reaction with ammonia or amines**

The acyl chlorides react with ammonia to form acid amides

$CH_3COCl + 2NH_3$ ———> $CH_3CONH_2 + NH_4Cl$

$C_6H_5COCl + 2NH_3 - C_6H_5CONH_2 + NH_4Cl$

However acyl chloride react with amines to from substituted amides



**Reduction**

Acyl halides are reduced to aldehyde by the action of hydrogen in the presence of $Pd/BaSO_4$

$CH_3COCl + H_2 \xrightarrow{Pd/BaSO_4} CH_3CHO + HCl$

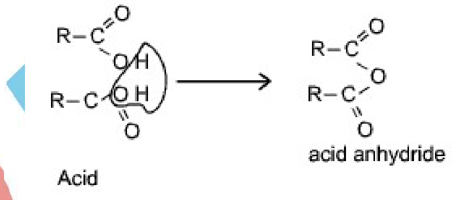
This reaction is called Rosenmund reduction.

### Uses of acyl chlorides

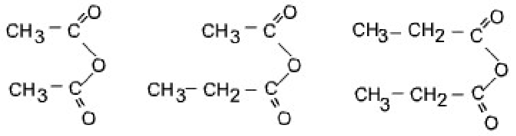
- They are used for the preparation of ketones on Friedel craft reaction.
- They are used in dyestuffs and pharmaceuticals.

### Acid anhydrides

Acid anhydrides are the acid derivatives which are derived from carboxylic acids by the removal of water from molecules of the acid.



Formula



**Common name** acetic anhydride acetic propanoic anhydride propionic anhydride

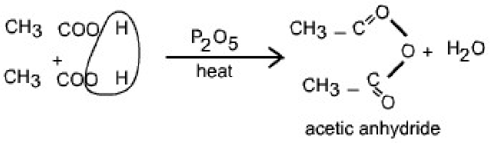
**IUPAC name** ethanoic anhydride ethanoic propanoic anhydride propanoic anhydride

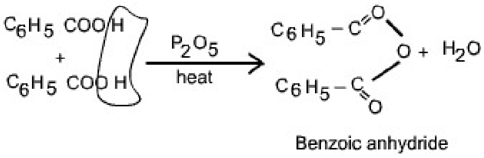
### Methods of preparation

### From carboxylic acids

Acid anhydride are obtained by heating carboxylic acid with $P_2O_5$.

**For example.**

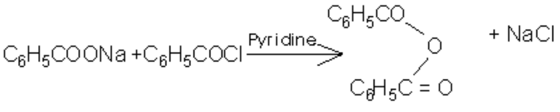




### From carboxylic acid salt and acyl chloride

Carboxylic acid are treated with acid chlorides in the presence of pyridine

$$CH_3COONa + CH_3COCl \xrightarrow{Pyridine} CH_3COOCOCH_3 + NaCl$$



Benozoic anhydride

### Properties

### Physical properties

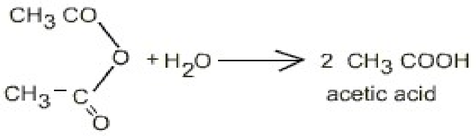
1. Lower members are colourless liquids. Higher members as well as aromatic acid anhydrides are solid.

2. They have higher boiling points than the corresponding acid. It is due to greater molecular size.

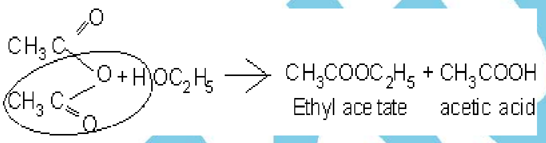
### Chemical properties

### Hydrolysis

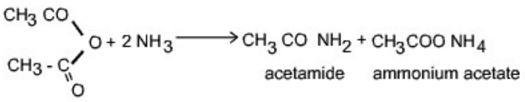
They are hydrolysed to give acids



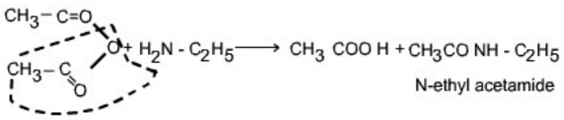
### They react with alchohols and form esters



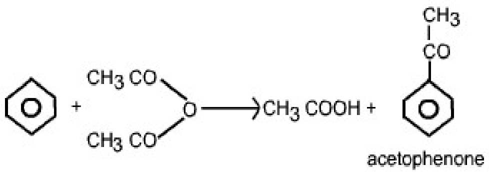
### Reaction with ammonia and amines



with amines, they form substituted amides

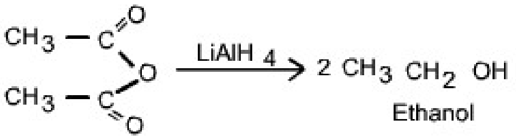


### Reaction with $C_6H_6$



### Reduction

Aanhydrides are reduced by $4AlH_4$ togive alcohols

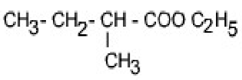
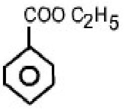
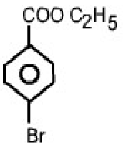


### Esters

Esters are the derivatives of carboxylic acids in which the -OH group of the carboxylic acid has been replaced by -OR group (Where R may be alkyl or aryl group)

### Nomenclature

An esters is named on the basis of the corresponding acid by changing **ic** to **ate** and preceeding this with the name of alkyl or aryl groups

| Formula | Trivial Name | IUPAC Name |
|---|---|---|
| $HCOOC_2H_5$ | Ethyl Formate | Ethyl methanoate |
| $CH_3COOC_2H_5$ | Ethyl acetate | Ethyl ethanoate |
|  $CH_3-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-COOC_2H_5$ | Ethyl α methyl buty rate | Ethl -2- methyl Butanoate. |
|  | Ethyl benzoate | Ethyl benzoate |
|  | Ethyl -4- Bromobenzoate | Ethyl -4- Bromobenzoate |

### Preparation

### From carboxylic acids

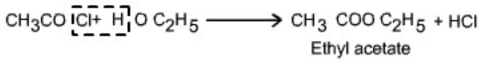
Esters are generally prepared by heating carboxylic acid with alcohols in the presence of few drops of conc. $H_2SO_4$ or dry HCl gas.

Ethyl acetate

The above reaction is called **esterifications**.

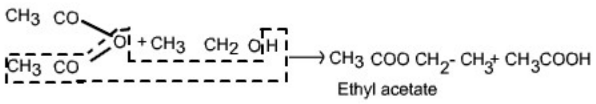
**From acid chlorides or acid anhydrides**

Esters are easily prepared by the action of alcohols on acid chlorides or acid anhydrides.



$CH_3CO\boxed{Cl + H}O\,C_2H_5 \longrightarrow CH_3\,COO\,C_2H_5 + HCl$

$C_6H_5CO\boxed{Cl + H}O\,C_2H_5 \longrightarrow C_6H_5\,COOC_2H_5 + HCl$



### Properties

### Physical properties

Esters have pleasant fruity odours. Esters do not form hydrogen bonds and hence they have lower boiling point than the corresponding acids. They are less soluble in water but readily soluble in organic solvents.

### Chemical properties

They are hydrolysed by water. The reaction is accelerated by dilute mineral acids (HCl, $H_2SO_4$) or alkalies. Hydrolysis of ester by using alkalies is known as **saponification**.

$$CH_3\,COO\,C_2H_5 + H_2O \xrightleftharpoons{\text{dil acid}} CH_3\,COOH + C_2H_5OH$$

$$CH_3\,COO\,C_2H_5 + Na\,OH \longleftrightarrow CH_3\,COO\,Na + C_2H_5OH$$

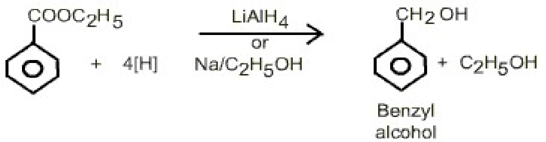
### Reaction with ammonia

$$CH_3CO\boxed{OC_2H_5 + H}NH_2 \longrightarrow \underset{\text{actamide}}{CH_3CONH_2} + C_2H_5OH$$

### Reduction

Esters are reduced to alcohols with $LiAlH_4$ or refluxing with $Na/C_2H_5OH$.

$$CH_3\,COOCH + 4[H] \xrightarrow[\text{Na/C}_2\text{H}_5\text{OH}]{\text{LiAlH}_4 \text{ or}} 2C_2H_5OH$$



### Reaction with alcohols

When ester is treated with an alcohol in the presence of an acid ($H_2SO_4$ or HCl) a new ester with the alkyl group of new alcohol part is obtained.

$$RCOOR_1 + R_2\text{-}OH \xrightarrow{H^+} RCOOR_2 + R_1\text{-}OH$$

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + CH_3OH \xrightarrow{H^+} \underset{\text{methyl acetate}}{CH_3COOCH_3} + C_2H_5OH$$

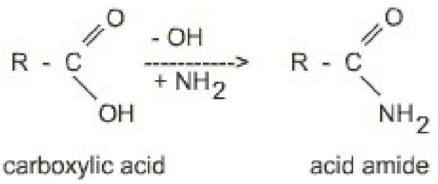
**The reaction is known as trans-esterification.**

### Uses of esters

- Esters are used as artificial fruit flavours for making essences.
- They are used as a solvent.

### Acid amides ($RCONH_2$)

Acid amides are derivatives of carboxylic acid in which -OH groups of acid is replaced by $-NH_2$ group.



### Nomenclature

According to IUPAC system these are named as alkanamides. The names are derived by replacing the ending e of the parent hydrocarbon by amide.

**For exampl**

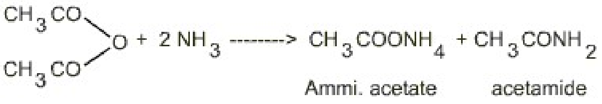
| | $CH_3COOH$ | $CH_3CONH_2$ |
|---|---|---|
| Common name | Acetic acid | Acetamide |
| IUPAC name | Ehtanaoic acid | Ethanamide |

| **Formula** | **Common name** | **IUPAC name** |
|---|---|---|
| $HCOHN_2$ | Formamide | Methanamide |
| $CH_3CONH_2$ | Acetamide | Ethanamide |
| $CH_3CONH\text{-}CH_3$ | N-methyl acetamide | N-methyl ethanamide |
| $CH_3CH_2CONH_2$ | Propionamide | Propanamide |

### Preparation

### From acid chlorides or acid anhydrides

$$CH_3COCl + NH_3 \longrightarrow \underset{\text{acetamide}}{CH_3CONH_2} + HCl$$



$$CH_3COONH_4 \xrightarrow{\Delta} \underset{\text{acetamide}}{CH_3CONH_2} + H_2O$$

$$C_6H_5COCl + NH_3 \longrightarrow \underset{\text{benzamide}}{C_6H_5CONH_2} + HCl$$

$$CH_3COCl + 2CH_3NH_2 \longrightarrow \underset{\text{n-methyl acetamide}}{CH_3CONHCH_3} + CH_3NH_3{}^+Cl^-$$

### From ammonium salts of carboxylic acids

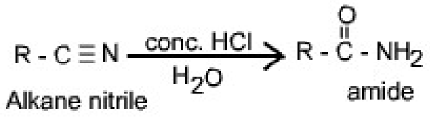
Amides can be prepared by heating ammonium salts of carboxylic acids.

$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$$

ammonium acetate aetamide

### From nitriles

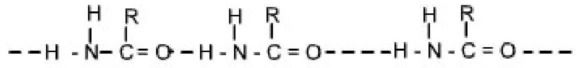
Alkane nitriles on partial hydrolysis produce amides



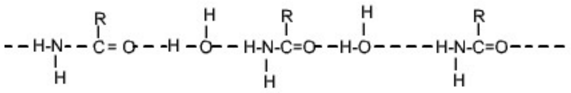
### Properties

### Physical properties

All amides except formamide are crystalline solids at room temperature. Formamide is liquid. They have high boiling points than the corresponding acids. The higher boiling points of amides is because of intermolecular hydrogen bonding as shown below.



Lower members are soluble in water due to formation of H bonding with water.



### Chemical properties of amides Amides undego hydrolysis when treated with aqueous acid or bases

$$CH_3CONH_2 + HOH \xrightarrow{\text{dil. HCl}} CH_3COOH + NH_4Cl$$

$$CH_3CONH_2 + H_2O \xrightarrow{\text{dil. NaOH}} CH_3COONa + NH$$

$$C_6H_5CONH_2 + H_2O \xrightarrow{\text{dil.NaOH}} C_6H_5COONa + NH_3$$

### Reaction with HCl

$$CH_3CONH_2 + HCl \longrightarrow CH_3CONH_2HCl$$

acetamide hydrogen chloride

### Reaciton with Na

$$2CH_3CONH_2 + 2Na \longrightarrow 2CH_3CONHNa + H_2$$

### Reduction

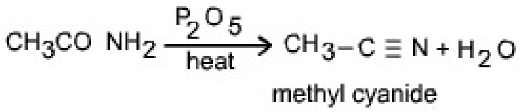
Amides can be easily reduced with Na/$C_2H_5OH$ or by $4AlH_4$

$$CH_3CONH_2 + 4(H) \xrightarrow[H_2O]{Na/C_2H_5OH} CH_3\text{-}CH_2\text{-}CH_2 +$$

ethylamine

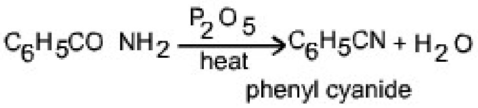
### Dehydration

Amides on heating with dehydrating agents like $P_2O_5$ or $SOCl_2$ get dehydrated to from cyanides



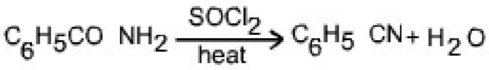
$$CH_3CO\ NH_2 \xrightarrow[heat]{P_2O_5} CH_3-C\equiv N + H_2O$$

methyl cyanide



$$C_6H_5CO\ NH_2 \xrightarrow[heat]{P_2O_5} C_6H_5CN + H_2O$$

phenyl cyanide



$$C_6H_5CO\ NH_2 \xrightarrow[heat]{SOCl_2} C_6H_5\ CN + H_2O$$

### Reduction with nitrous acid (HONO)

$$CH_3CONH_2 + HONO \xrightarrow[+\ H_2O]{NaNO_2/HCl} CH_3COOH + N_2$$

$$C_6H_5CONH_2 + HONO \xrightarrow[+\ H_2O]{NaNO_2/HCl} C_6H_5COOH + N_2$$

### Hofman bromamide reaciton

When a primary amide is treated with bromine in the presence of an alkali, a primary amine containing one carbon atom less than the starting material is formed.

$$CH_3CONH_2 + Br_2 + 4KOH \xrightarrow{heat} CH_3NH_2 + K_2CO_3 + 2KBr + 02H_2O$$

$$C_6H_5CONH_2 + Br_2 + 4KOH \xrightarrow{heat} C_6H_5CONH_2 + K_2CO_3 + 2KBr + 2H_2O$$

analine

### Uses of amides

- Primary amides are used for the preparation of primary amines.They are used as solvent.

## SOLVED PROBLEMS

**Q.1 What is meant by the following terms ? Give an example in each case.**

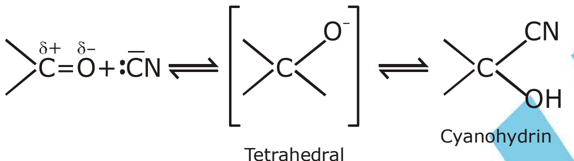
**(i) Cyanohydrin (ii) Acetal (iii) Semicar bazone**

**(iv) Aldol (v) Hemiacetal (vi) Oxime (vii) Ketal (viii) Imine**

**(ix) 2,4-DNP derivative (x) Schiff's base.**

**Ans.** (i) Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. It is catalysed by a base and the generated cyanide ion ($CN^-$)being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.

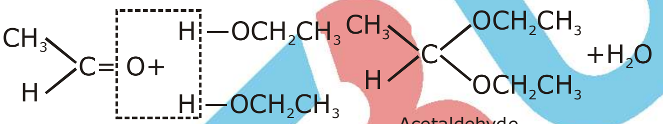
$$HCN + OH^- \rightleftharpoons :\overline{C}N + H_2O$$



Tetrahedral intermediate

Cyanohydrin

(ii) gem-Dialkoxy compounds in which the two alkoxy groups are present on the terminal carbon atom are called acetals. These are produced by the action of an aldehyde with two equivalents of a monohydric alcohol in the presence of dry HCl gas.

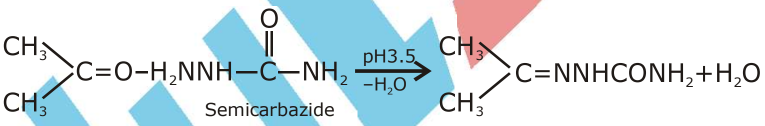


Acetaldehyde

Ethyl alcohol

Acetaldehyde diethyl acetal

(iii) Semicarbazones are derivatives of aldehydes and ketones and are produced by the action of semicarbazide on them in weak acidic medium.

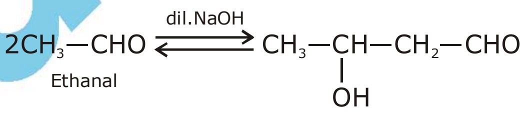


Acetaldehyde diethyl acetal

Semicarbazide

Acetone semicarbazone

(iv) Aldehydes and ketones having at least one $\alpha$–hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form $\beta$–hydroxy aldehydes (aldol) or $\beta$–hydrogen ketones (ketol). respectively. This is known as Aldol reaction.



$$2CH_3-CHO \xrightleftharpoons{\text{dil.NaOH}} CH_3-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2-CHO$$

Ethanal

3-Hydroxybutanal (Aldol)

**Q.2 How will you convert ethanal into the following compounds ?**

**(i) Butane-1, 3-diol (ii) But-2-enal (iii) But-2-enoic acid**

**Ans.** (i)

$$\underset{\text{Ethanal}}{2CH_3-CHO} \xrightarrow[\text{Aldol condensation}]{\text{Dil.NaOH}} \underset{\text{3-Hydroxybutanal}}{\overset{4}{C}H_3\overset{3}{C}HOH-\overset{2}{C}H_2-\overset{1}{C}HO}$$

$$\xrightarrow[\text{(Reduction)}]{NaBH_4} \underset{\text{Butane-1,3-diol}}{\overset{4}{C}H_3-\overset{3}{C}HOH-\overset{2}{C}H_2\overset{1}{C}H_2OH}$$

(ii)

$$\underset{\text{Ethanal}}{2CH_3-CHO} \xrightarrow[\text{(Aldol condensation)}]{\text{Dil.NaOH}} \underset{\text{3-Hydroxybutanal}}{\overset{4}{C}H_3-\overset{3}{C}HOH-\overset{2}{C}H_2-\overset{1}{C}HO}$$

$$\xrightarrow[(-H_2O)]{H_3O^+/\text{Heat}} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$$

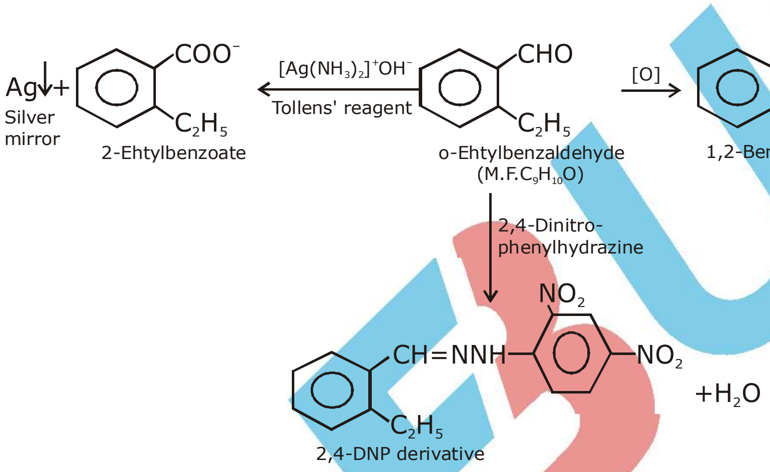
(iii) $\underset{\text{Ethanal}}{2CH_3{-}CHO} \xrightarrow[\text{(ii) } H^+,\ \Delta]{\text{(i) dil.NaOH}} \underset{\text{But-2-enal}}{CH_3CH{=}CHCHO} \xrightarrow[\text{Tollen's reagent}]{[Ag(NH_3)_2]^+OH^-} \underset{\text{But-2-enoic acid}}{CH_3CH{=}CHCO_2H}$

**Q.3 An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identity the compound.**

**Ans.** (i) The given compound with molecular formula $C_9H_{10}O$ forms a 2, 4-DNP derivative and reduces Toilens' reagent, it must be an aldehyde.

(ii) As it undergoes Cannizzaro reaction, therefore, CHO group is directly attached to the benzene ring.

(iii) On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid, therefore, it must be an ortho subsitututed benzaldehyde. The only o-substituted aromatic aldehyde having molecular formula $C_9H_{10}O$ is o-ethylbenzaldehyde. ALI the reactions can be explained on the basis of this structure.

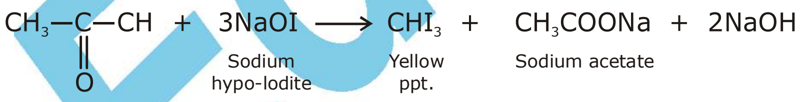


**Q.4 Give simple chemical tests to distinguish between the following pairs of compound :**
**(i) Propanal and Propanone**
**(ii) Phenol and Benoic acid**
**(iii) Benzoic acid and Ethyl Benzoate**

**Ans.** (i) Propanal and Propanone :

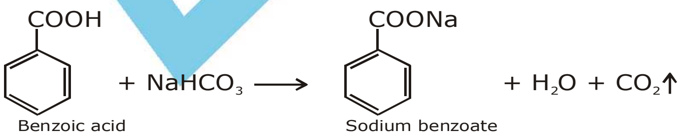
Iodoform Test : This test is given by propanone and not by propanal. Propanone on reacting with hot NaOH/$I_2$ gives a yellow precipitate of $CHI_3$ while propanal does not.

$2NaOH + I_2 \rightarrow NaI + NaOI + H_2O$

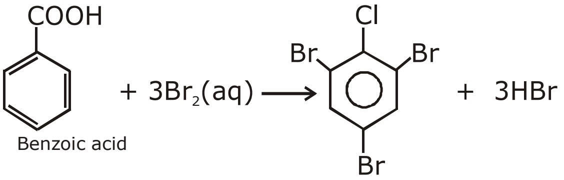


$$\underset{\underset{O}{\|}}{CH_3{-}C{-}CH} + \underset{\text{Sodium hypo-lodite}}{3NaOI} \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3} + \underset{\text{Sodium acetate}}{CH_3COONa} + 2NaOH$$

(ii) Phenol and Benzoic acid : Benzoic acid reacts with $NaHCO_3$ giving $CO_2$ gas with effervescence, whereas phenol does not.

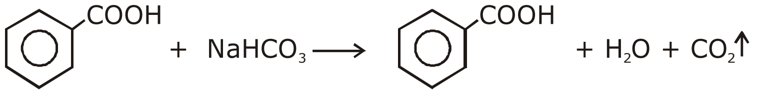


Phenol decolourises $Br_2$ water giving white ppt, benzoic acid does not.



2, 4, 6-Tribromophenol (white ppt.)

(iv) Benzoic acid and ethyl benzoate : Benzoic acid on reaction with sodium hydrogenecarbonate gives out $CO_2$ gas with effervescence, while ethyl benzoate does not.



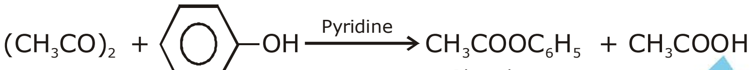
**Q.5** **Describe the following :**

**(i) Acetylation** **(ii) Cannizzaro reaction**

**(iii) Cross aldol condensation** **(iv) Decarboxylation**

**Ans.** (i) Acetylation : The replacement of an active hydrogen of alcohols, phenols or amines with an acyl (RCO) group to form the corresponding esters or amides is called acetylation. This replacement is carried out by using acid chloride or an acid anhydride in the presence of a base like pyridine or dimethylaniline.-

$$CH_3COCl + C_2H_5OH \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$



Phenyl acetate

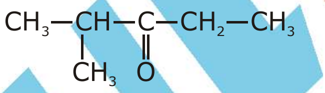
$$CH_3COCl + C_2H_5NH_2 \longrightarrow \underset{\text{N-Ethylacetamide}}{CH_3CONHC_2H_5} + HCl$$

(ii) Decarboxylation: Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratoi of 3:1). The reaction is known as decarboxylation.

$$R-COONa \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} R-H + Na_2CO_3$$

Alkali metal salts of carboxylic acids also undergo decarboxdylation on electrolysis of their aqueous solutions and form hydrocarbon having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as Kolbe electrolysis.

**Q.6** **Write the IUPAC name of**

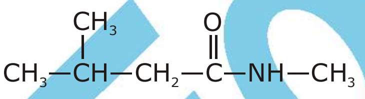


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle O}{\underset{\|}{C}}-CH_2-CH_3$$

**Ans.** 2-Methylpentan-3-one.

**Q.7** **Write the IUPAC name of : $CH_3CH(Br)CH_2CONHCH_3$**

**Ans.**

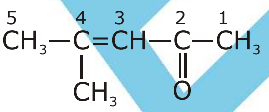


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-NH-CH_3$$

n-Methyl-3-bromo butanamide

**Q.8** **Draw the structure of 4-methylpent-3-en-2-one.**

**Ans.**



$$\overset{5}{CH_3}-\underset{\displaystyle CH_3}{\underset{|}{\overset{4}{C}}}=\overset{3}{CH}-\underset{\displaystyle O}{\underset{\|}{\overset{2}{C}}}-\overset{1}{CH_3}$$

4-Methylpent-3-en-2-one

## EXERCISE-I UNSOLVED PROBLEMS

Q.1 What is PCC ? What is its use in synthetic organic chemistry ? Illustrate with a suitable example.

Q.2 What is DIBAL-H ? What is its use in synthetic organic chemistry ? Illustrate with a suitable example.

Q.3 How can you convert allyl alcohol into propenal

Q.4 How can you convert hex-4-enenitrille into hex-4-enal ?

Q.5 Give names of the reagents used to bring about following conversion :
(a) Hexan-1-ol $\longrightarrow$ Hexanal
(b) Cyclohexanol $\longrightarrow$ Cyclohexanone
(c) p-Fluorotoluene $\longrightarrow$ p-Fluorobenzaldelhyde.

Q.6 Name the reagents you will use to bring about the following conversions :
(a) Ethane nitrile to ethanal
(b) Alkyl alcohoo to propenal
(c) But -2-ene to ethanal.

Q.7 Arrange the following compound in the increasing order of their boiling points :
$CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2CH_2OH$, $H_5C_2—O—C_2H_5$, $CH_3CH_2CH_2CH_2CH_3$.

Q.8 How does a carbonyl group differ from an ethylenic bond ?

Q.9 Explain why
(i) Di-tert-butyl ketone does not give a precipitate with $NaHSO_3$ whereas acetone does
(ii) Diakyl cadmium is considered superior to Grignard's reagent for the preparation of a ketone from an acid chloride.

Q.10 An unknown aldehyde 'A' on reacting with alkali gives a β-hydroxyaldehyde, which loses water to form an unsaturated aldehyde 2-butenal. Another aldehyde 'B' undergoes disproportionation on reaction in the presence of conc. alkali to form products 'C' and 'D'. 'C' is an aryl alcohol with formula $C_7H_8O$.
(i) Identify A and B
(ii) Write the sequence of the reactions involved
(iii) Name the product, when 'B' reacts with zinc amalgam and hydrochloric acid.

Q.11 A compound $X(C_2H_4O)$ on oxidation gives Y $(C_2H_4O_2)$. X undergoes haloform reaction. On treatment with HCN 'X' forms product 'Z', which on hydrolysis gives 2-hydroxy-propanoic acid.
(i) Write down structures of X and Y.
(ii) Name two products when X reacts with dil NaOH.
(iii) Write down the equations for the reaction involved.

Q.12 An organic compound (A) having molecular formula $C_9H_{10}O$ forms an orange red precipitate (B) with 2,4-DNP reagent Compounde (A) give yellow precipitate (C) when heated in the presence of iodine and NaOH along with a colourless compound (D). (A) does not reduce Tollen's reagent or Fehling's solution nor does it doecolourise bromine water. On drastic oxidation of (A) with chromine acid, a carboxylic acid (E) of molecular formula $C_7H_6O_2$ is formed. Deduce the structure of the organic compound (A) to (E).

Q.13 (a) An organic compound 'A' with molecular formula $C_5H_8O_2$, is reduced to n-pentane on treatment with Zn-Hg/HCl. 'A' forms a dioxime with hydroxylamine and gives a positive Iodoform test and Tollen's test. Identify compound 'A' and deduce its structure.
(b) Write the chemical equations for the following conversions (not more than 2 steps)
  (i) Ethyl benzene to benzene
  (ii) Acetaldehyde to butane-1, 3-diol
  (iii) Acetone to propene.

Q.14 (a) Why carboxylic acids have higher boiling points than alcohols of comparable molecular masses.
(b) Write chemical reactions to affect the following transformations :
  (i) Butan-1-ol to butanoic acid
  (ii) Benzyl alcohol to phehylethanoic acid
  (iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid.

Q.15 (a) Two molecules of organic compound 'A' on treatment with a strong solution of NaOH gives two compounds B and C. Compound 'B' on dehydrogenation with Cu gives 'A' while acidification of 'C' yields carboxylic acid 'D' having molecular formula of $CH_2O_2$ Identify the compounds A, B, C and D.
(b) Explain why aldehydes are more reactive than ketones.

## EXERCISE-II BOARD PROBLEMS

Q.1 Draw the structure of 4-methylpent-3-en-2-one.

Q.2 (a) How would you account for the following

(i) Aldehydes are more reactive than ketones towards nucleophiles.

(ii) The boiling points of aldehydes and ketones are lower than of the corresponding acids.

(iii) The aldehydes and ketones undergoe a number of addition reactions.

(b) Give chemical tests to distinguish between

(i) Acetaldehyde and benzaldehyde

(ii) Propanone and propanol.

Q.3 (a) State tests to distinguish between the following pairs of compounds.

(i) Propanal and propanone

(ii) Phenol and benzoic acid

(b) How will you bring about the following conversions ?

(i) Propanone to propene

(ii) Benzaldehyde to benzophenone

(iii) Ethanol to 3-hydroxybutanal

Q.4 (a) Write chemical equations to illustrate the following name bearing reactions :

(i) Cannizzaro's reaction

(ii) Hell - Volhard-Zelinsky reaction

(b) Give chemical tests to distinguish between the following pairs of compounds :

(i) Propanal and Propanone

(ii) Acetophenone and Benzophenone

(iii) Phenol and Benzoic acid

Q.5 (a) How will you bring about the following conversions ?

(i) Ethanol to 3-hydroybutanal

(ii) Benzaldehyde to Benzophenone.

(b) An organic compound A has the molecular formula $C_8H_{16}O_2$. It gets hydrolysed with dilute sulphuric acid and gives a carboxylic acid B and an alcohol C. Oxidation of C with chromic acid also produced B. C on dehydration reaction gives but -1-ene. Write equations for the reactions involved.

Q.6 (a) Give chemical te4sts to distinguish between compounds in the following pairs of substances

(i) Ethanal and Propanal

(ii) Benzoic acid and Ethyl benzoate

(b) An organic compound contains 69.77 % carbon, 11.63 % hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and gives positive iodoform test. On vigorous addition, it gives ethanoc and propanoic acids. Derive the structure of the compound.

Q.7 (a) Give chemical tests to distinguish between

(i) Propanal and propanone.

(ii) Benzaldehye and acetophenone.

(b) How would you obtain.

(i) But-2-enal from ethanal

(ii) Butanoic acid from butanol

(iii) Benzoic acid from ethylbenzene ?

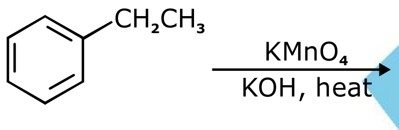
Q.8 (a) Describe the following giving linked chemical equations :

(i) Cannizzaro reaction

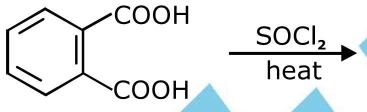
(ii) Decarboxylation

(b) Completel the following chemical equations

(i)



(ii)



(iii) $C_6H_5CONH \xrightarrow[\text{heat}]{H_3O^+}$

Q.9 Rearrange the following compounds in the increasing order of their boiling points :

$CH_3 - CHO, CH_3 - CH_2 - OH, CH_3 - CH_2 - CH_3$

Q.10 (a) How will you convert the following :

(i) Propanone to Propan-2-ol

(ii) Ethanol to 2-hydroxy propanoic acid

(iii) Toluene to benzoic acid

(b) Give simple chemical test to distinguish between

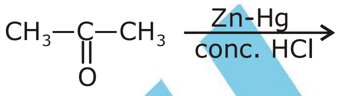
(i) Pentan-2-one and Pentan -3-one

(ii) Ethanol and Propanal

**OR**

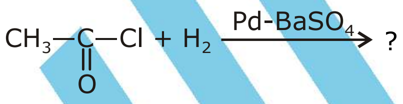
(a) Write the products of the following reactions :

(i)



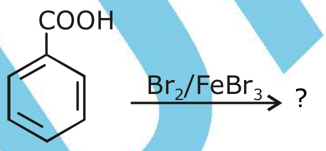
$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\text{conc. HCl}]{\text{Zn-Hg}}$

(ii)



$CH_3-\underset{\underset{O}{\|}}{C}-Cl + H_2 \xrightarrow{\text{Pd-BaSO}_4} ?$

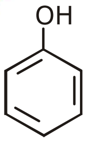
(iii)



(b) Which acid of each pair shown here would you expect to be stronger ?

(i) $Fe - CH_2 - COOH$ or $Cl - CH_2 - COOH$

(ii)



or $CH_3COOH$

Q.11 Write the IUPAC names of the following compound :