



Class : 11

2023 - 24

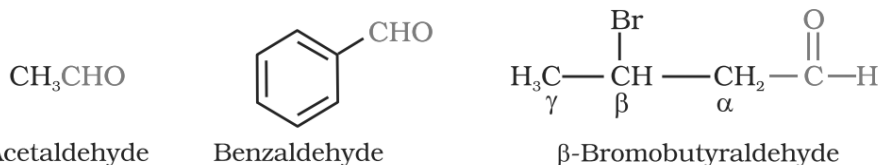
## ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

### Nomenclature and Structure of Carbonyl Group:

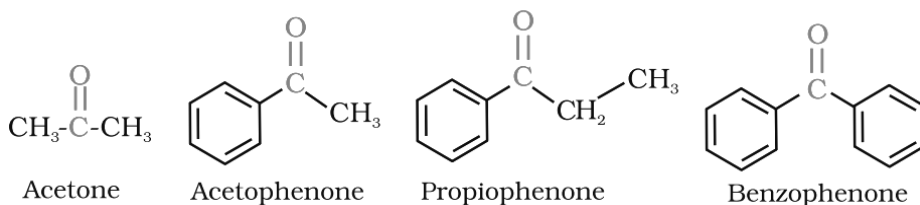
#### Nomenclature of Aldehydes and ketones

##### Common names:

- The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending *-ic* of acid with aldehyde.

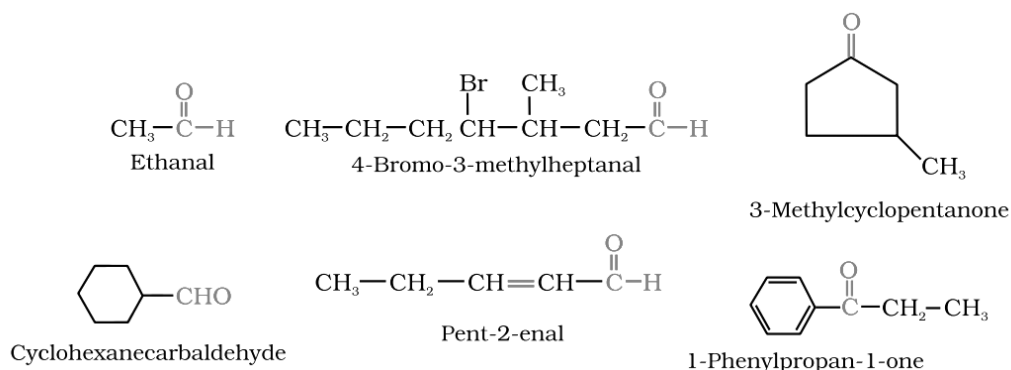


- The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group.
- Alkyl phenyl ketones are usually named by adding the name of acyl group as prefix to the word phenone.

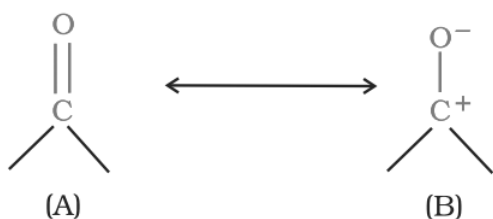


##### IUPAC names

- Aldehyde : Alkan(c) + al  $\rightarrow$  Alkanal (e.g. methanal)  
Ketone : Alkan (c) + one  $\rightarrow$  Alkanone  
(e.g. Propanone)
- In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group. When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cycloalkane.



**Structure of the Carbonyl Group:** The carbonyl carbon atom is  $sp^2$  hybridised and forms three sigma ( $\sigma$ ) bonds. The fourth valence electron of carbon remains in its  $p$ -orbital and forms a  $\pi$ -bond with oxygen by overlap with  $p$ -orbital of an oxygen.



The oxygen atom also has two non bonding electron pairs.

$\therefore$  The carbonyl carbon and the three atoms attached to it lie in the same plane and the  $\pi$ -electron cloud is above and below this plane.

The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. Hence, the carbon) carbon is an electrophilic (Lewis acid), and carbonyl oxygen. nucleophilic (Lewis base) centre.

Carbonyl compounds have substantial dipole moments and are polar than ethers.

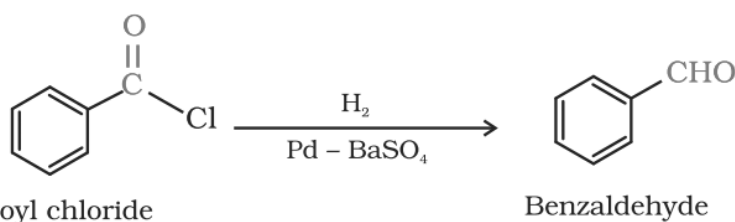
The high polarity of the carbonyl group is explained on the basis of resonance involving a neutral (A) and a dipolar (B) structures as shown.

### Preparation of Aldehydes and Ketones:

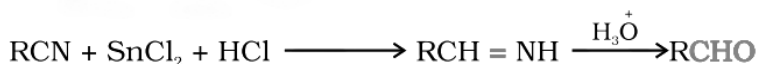
**By oxidation of alcohols:** Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.

- **By dehydrogenation of alcohols :** In this method alcohol vapours are passed over heavy metal catalysts ( Ag or Cu). Primary and secondary alcohols give aldehydes and ketones, respectively.
- **From hydrocarbons:**
- **By ozonolysis of alkenes:** Ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes, ketones or a mixture of both depending on the substitution pattern of the alkene.
- **By hydration of alkynes:** Addition of water to ethyne in the presence of  $H_2SO_4$  and  $HgSO_4$  gives acetaldehyde.
- Preparation of Aldehydes:

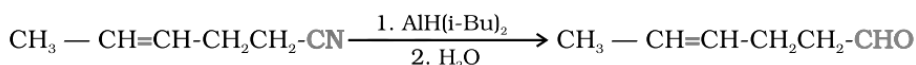
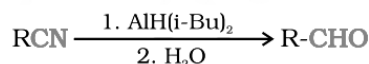
From acyl chloride (acid chloride) Rosenmund reduction



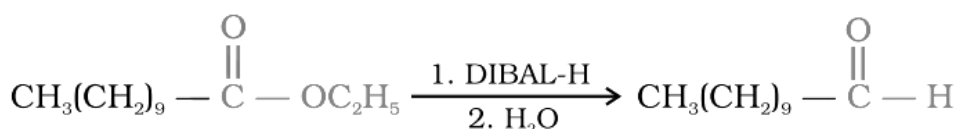
From nitriles and esters Stephen reaction



Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:

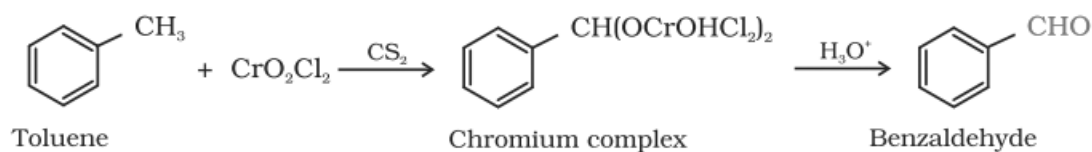
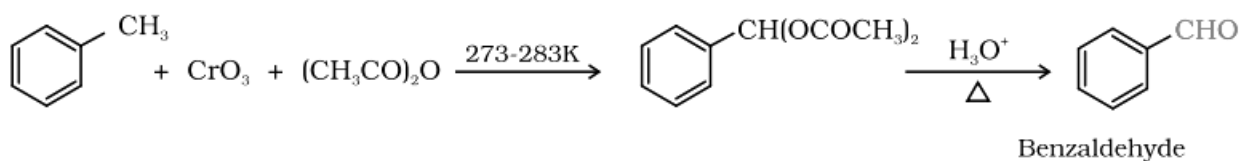


Similarly, esters are also reduced to aldehydes with DIBAL-H.



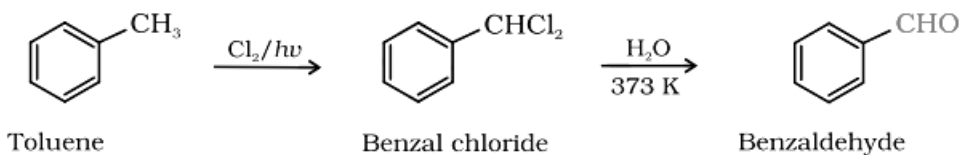


### Use of Chromic Oxide(CrO<sub>3</sub>):

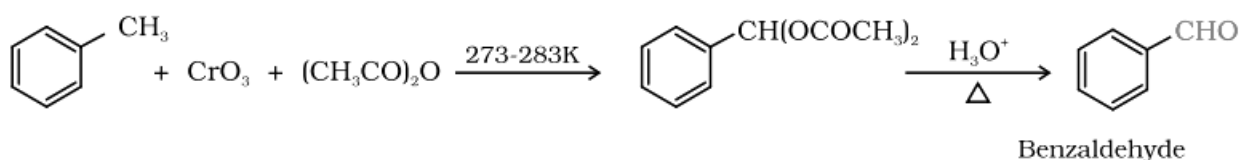
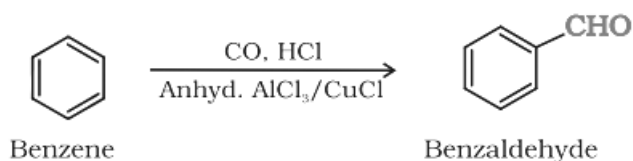


### By side chain chlorination followed by hydrolysis:

This is a commercial method of manufacture of benzaldehyde.

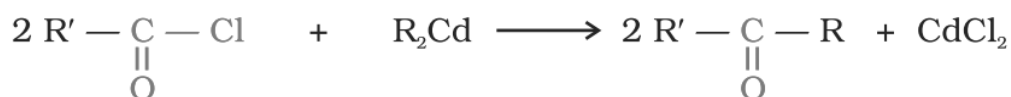
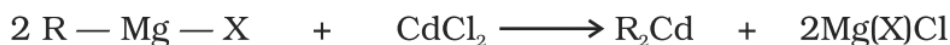


### By Gattermann- Koch reaction:

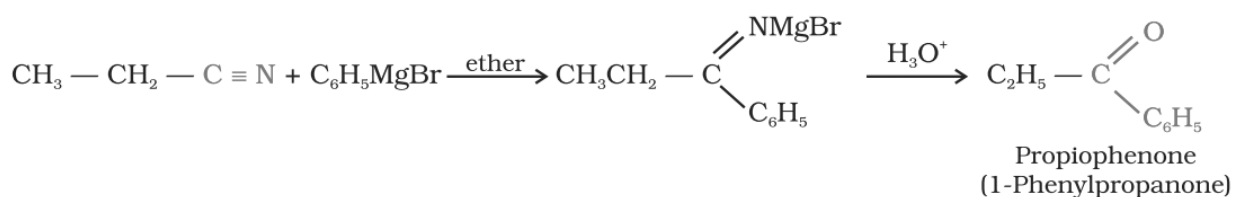


### Preparation of Ketones:

#### From acyl chlorides:



#### From nitriles:

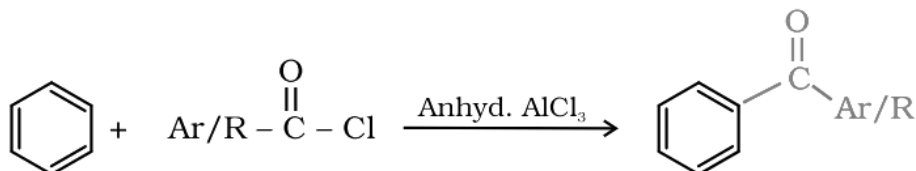




### By oxidation of methylbenzene :

- Use of chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) Etard reaction: Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.  
Aldehydes, Ketones and Carboxylic Acids

### From benzene or substituted benzenes Friedel Craft acyl reaction:



### Physical properties:

Methanal is a gas at room temperature, ethanal is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature. The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

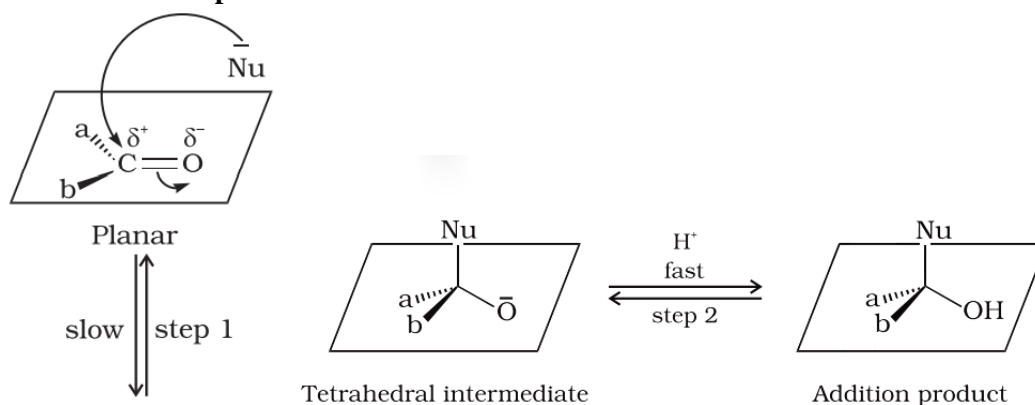
The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions, because they form hydrogen bond with water. However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

- As the size of the molecule increases, the odour becomes less pungent and more fragrant.

### Chemical Reactions:

#### Nucleophilic addition reactions :

- Mechanism of nucleophilic addition reactions :

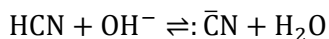


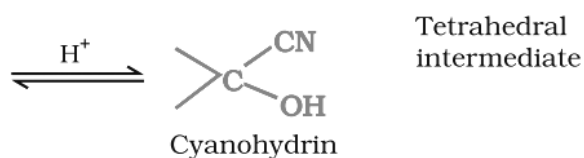
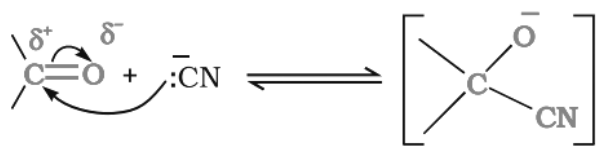
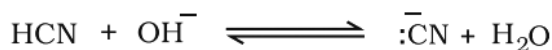
### Reactivity

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons,

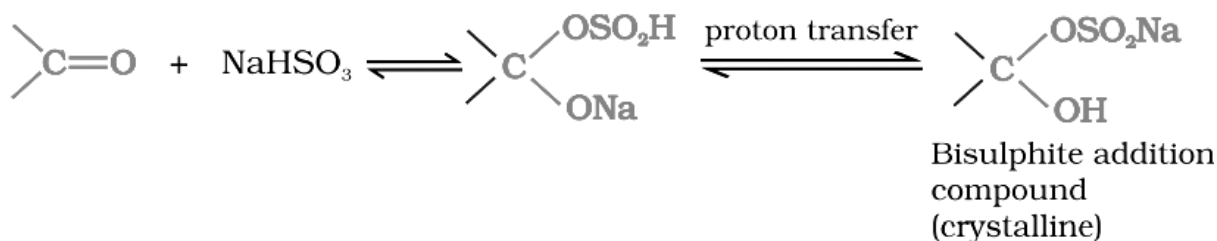
### Examples of nucleophilic addition and nucleophilic addition. elimination reactions:

- Addition of hydrogen cyanide (HCN):** It is catalysed by a base and the generated cyanide ion ( $\text{CN}^-$ ) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.





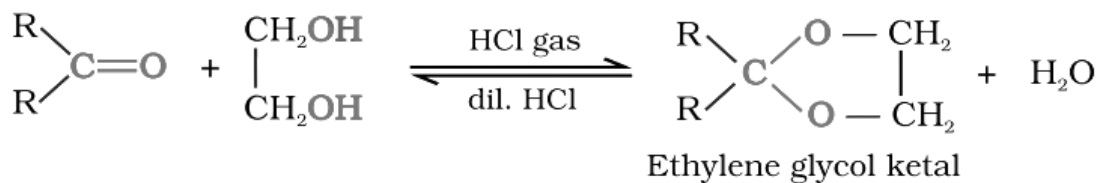
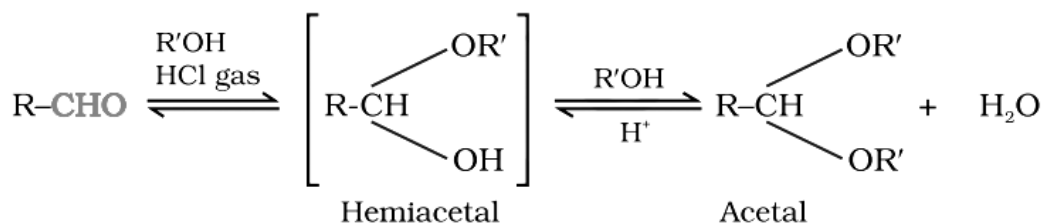
- **Addition of sodium hydrogensulphite:**



The hydrogensulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali. Therefore, these are useful for separation and purification of aldehydes.

- **Addition of Grignard reagents :** Addition of Grignard reagents to aldehydes yields alcohol.

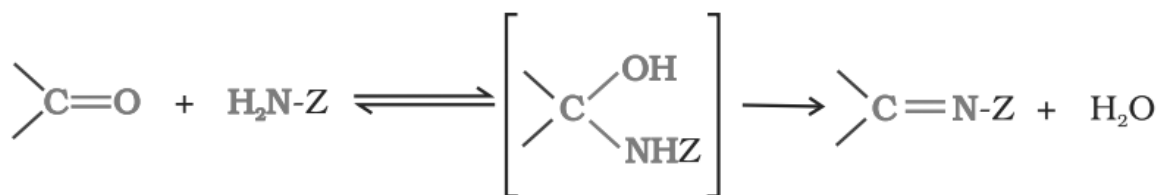
- **Addition of alcohols:**



- Dry hydrogen chloride protonates the oxygen of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon facilitating the nucleophilic attack of ethylene glycol.
- Acetals and ketals are hydrolysed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.
- **Addition of ammonia and its derivatives:** Nucleophiles, such as ammonia and its derivatives  $\text{H}_2\text{N} - \text{Z}$  add to the carbonyl group of aldehydes and ketones.

The reaction is reversible and catalysed by acid.

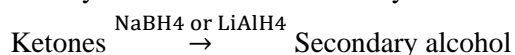
The equilibrium favours the product formation due to rapid dehydration of the intermediate to form  $> \text{C} = \text{N} - \text{Z}$ .



Z = Alkyl, aryl, OH, NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>NH, NHCONH<sub>2</sub>, etc.

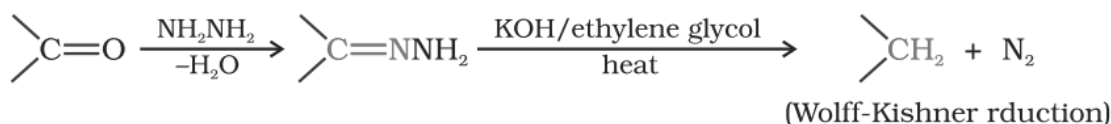
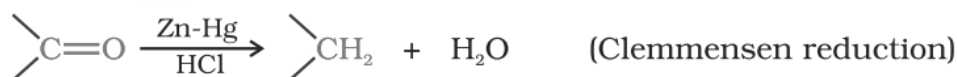
- **Reduction :**

- **Reduction to alcohols:**



∴ **Reduction to hydrocarbons:**

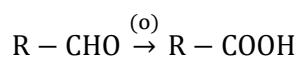
**Clemmensen reduction**



**Wolff-Kishner reduction**

**Oxidation :**

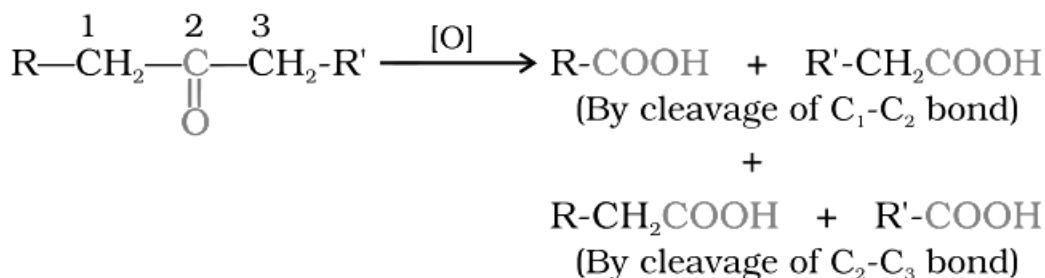
Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate potassium dichromate, etc.



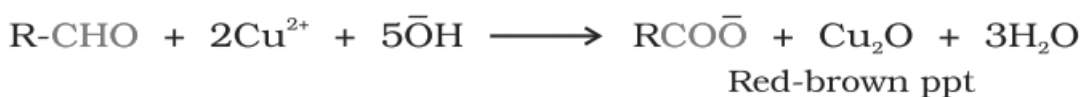
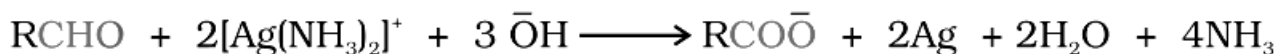
- Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage.

The mild oxidising agents given below are used to distinguish aldehydes from ketones:

- **Tollens' test:** On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal.

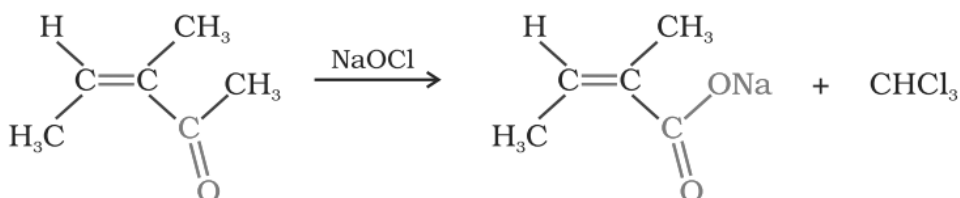
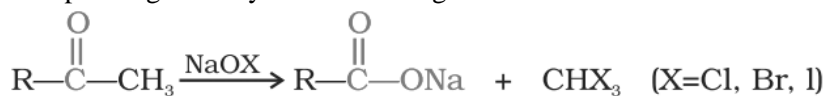


- **Fehling's test:** Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). Aromatic aldehydes do not respond to this test.



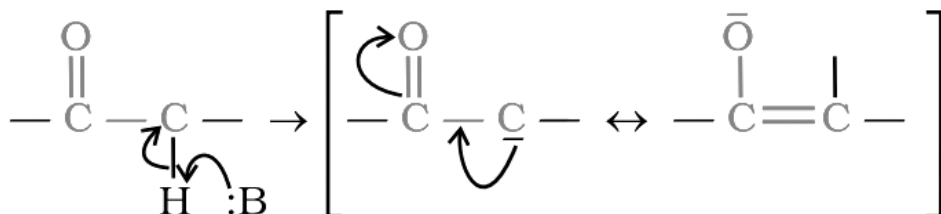


- Oxidation of methyl ketones by haloform reaction:** Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalide to sodium salts of corresponding carboxylic acids having one carbon atom less than that of the carbonyl compound.

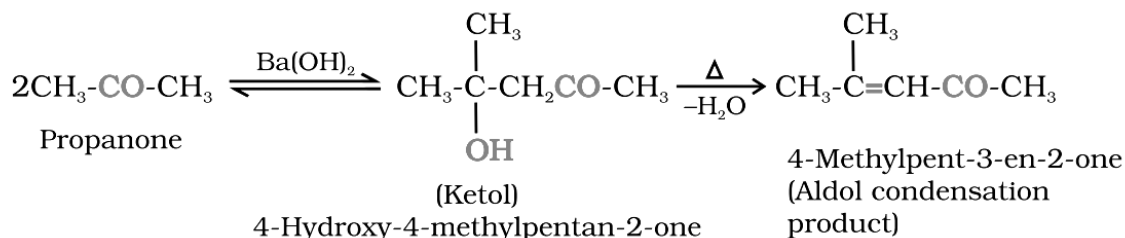
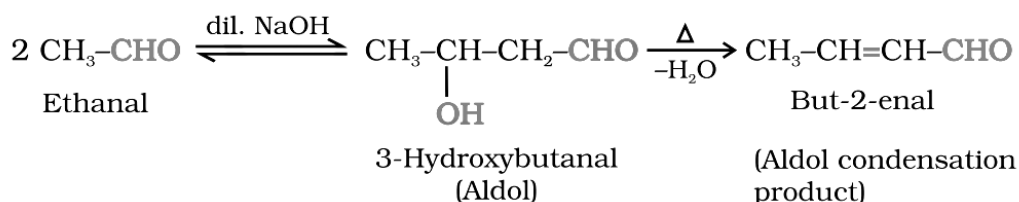


The methyl group is converted to haloform. This oxidation does not affect a carbon-carbon double bond, if present in the molecule. Iodoform reaction with sodium hypoiodite is also used for detection of  $\text{CH}_3\text{CO}$  group or  $\text{CH}_3\text{CH}(\text{OH})$  group which produces  $\text{CH}_3\text{CO}$  group on oxidation.

**Reactions due to  $\alpha$ -hydrogen :** The acidity of  $\alpha$ -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



**Aldol condensation:** 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  $\beta$ -hydroxy ketones (ketol), respectively. This is known as Aldol reaction.

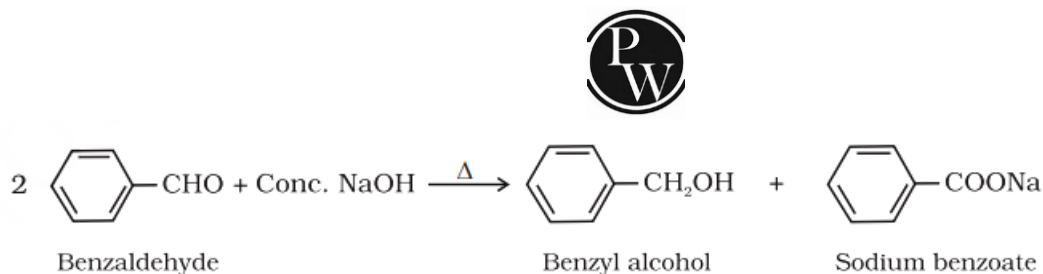


The aldol and ketol readily lose water to give  $\alpha, \beta$ -unsaturated carbonyl compounds which are aldol condensation products and the reaction is called Aldol condensation.

**Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain  $\alpha$ -hydrogen atoms, it gives a mixture of four products.

Ketones can also be used as one component in the cross aldol reactions.

**Cannizzaro reaction:** Aldehydes which do not have an  $\alpha$ -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on heating with concentrated alkali.



**Electrophilic substitution reaction:** Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.

### Uses of Aldehydes and Ketones:

Formaldehyde is well known as formalin (40%) solution used to preserve biological specimens and to prepare bakelite (a phenol-formaldehyde resin), urea-formaldehyde glues and other polymeric products.

- Acetaldehyde is used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.
- Benzaldehyde is used in perfumery and in dye industries.
- Acetone and ethyl methyl ketone are common industrial solvents.

### Carboxylic Acid :

- Carbon compounds containing a carboxyl functional group,  $-\text{COOH}$  are called carboxylic acids. The carboxyl group, consists of a carbonyl group attached to a hydroxyl group, hence its name carboxyl.
- Some higher members of aliphatic carboxylic acids ( $\text{C}_{12} - \text{C}_{18}$ ) known as fatty acids, occur in natural fats as esters of glycerol.
- Carboxylic acids serve as starting material for several other important organic compounds such as anhydrides, esters, acid chlorides, amides, etc.

### Nomenclature and Structure of Carboxyl Group

#### Nomenclature :

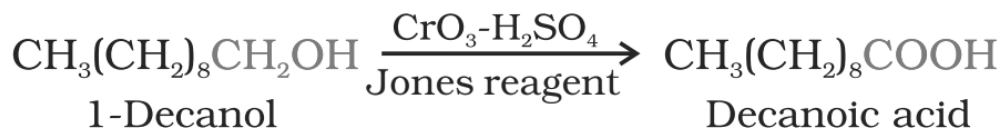
- A large number of them are known by their common names.
- The common names end with the suffix -ic acid and have been derived from Latin or Greek names of their natural sources. For example, formic acid ( $\text{HCOOH}$ ) was first obtained from red ants (Latin: formica means ant), acetic acid ( $\text{CH}_3\text{COOH}$ ) from vinegar (Latin: acetum, means vinegar), butyric acid ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ ) from rancid butter (Latin: butyrum, means butter).
- In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending  $-e$  in the name of the corresponding alkane with -oic acid. Methane + oic acid  $\rightarrow$  Methanoic acid
- For naming compounds containing more than one carboxyl group, the alkyl chain leaving carboxyl groups is numbered and the number of carboxyl groups is indicated by adding the multiplicative prefix, dicarboxylic acid, tricarboxylic acid, etc. to the name of parent alkyl chain.
- The position of  $-\text{COOH}$  groups are indicated by the arabic numeral before the multiplicative prefix.

#### Structure of Carboxyl Group :

- In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about  $120^\circ$ .
- The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:

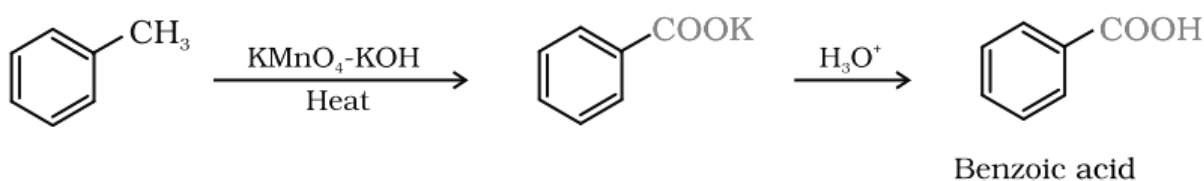
### Methods of Preparation of Carboxylic Acids

From primary alcohols and aldehydes :

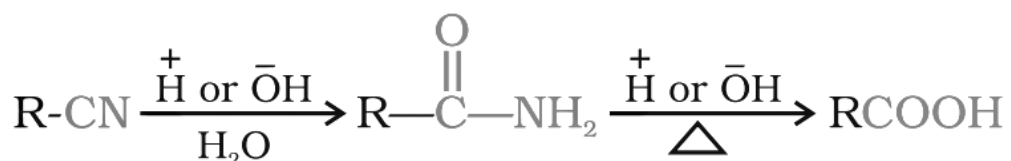


From alkylbenzenes by oxidation with chromic acid or acidic or alkaline potassium permanganate. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected.

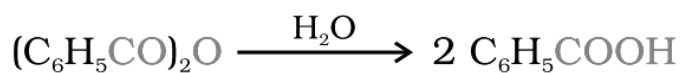
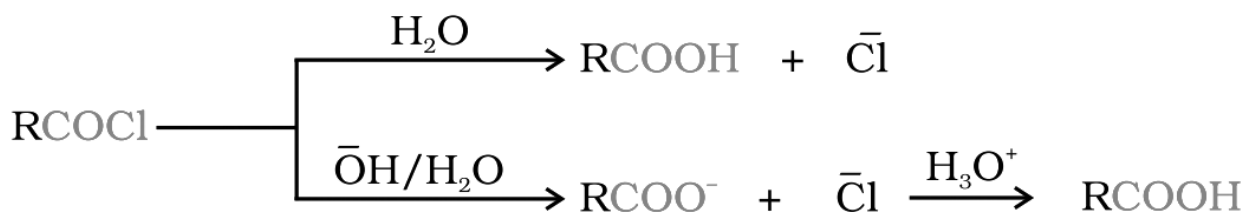
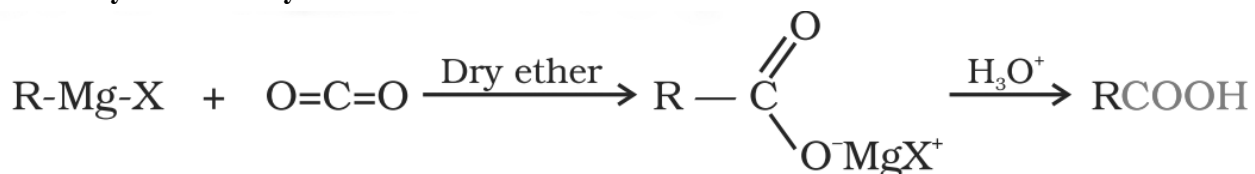
**From nitriles and amides:** Nitriles are hydrolysed to amides and then to acids in the presence of  $\text{H}^+$  or  $\bar{\text{O}}\text{H}$  as catalyst.



**From Grignard reagents:** Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid.

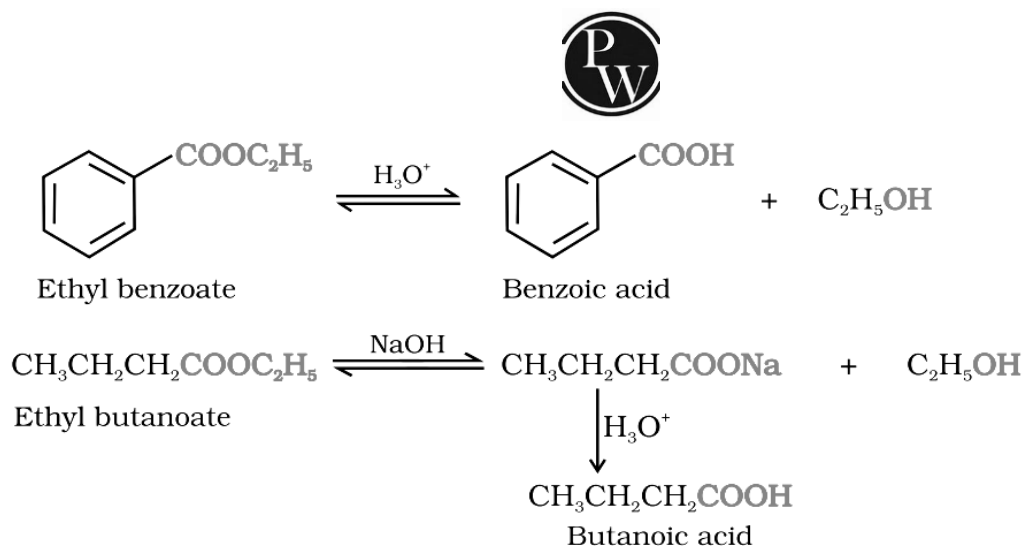


**From Acyl halides anhydrides:**



Benzoic anhydride Benzoic acid

**From Esters: acidic hydrolysis**



### Physical Properties

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours.

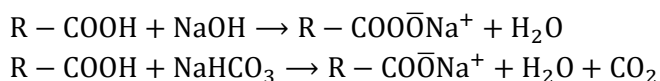
- The higher acids are wax like solids and are practically odourless due to their low volatility.
- Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.
- The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.
- Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.
- The solubility decreases with increasing number of carbon atoms.
- Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.

Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

### Chemical Reactions.

#### Reactions Involving Cleavage of O – H Bond :

**Reactions with metals and alkalines:** The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalies similar to phenols.



The strength of an acid is generally indicated by its  $pK_a$  value rather than its  $K_a$  value.

$$pK_a = -\log K_a$$

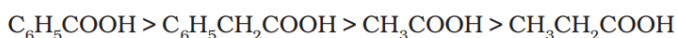
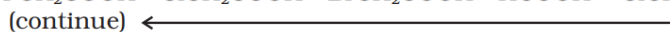
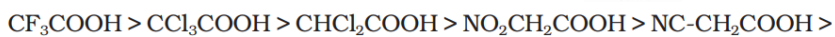
- Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols ( $pK_a$  is -16 for ethanol and 10 for phenol).
- Carboxylic acids are stronger acids than phenols because the carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols.

Effect of substituents on the acidity of carboxylic acids: Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects.

Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.

The effect of the following groups in increasing acidity order is  $\text{Ph} < \text{I} < \text{Br} < \text{Cl} < \text{F} < \text{CN} < \text{NO}_2 < \text{CF}_3$

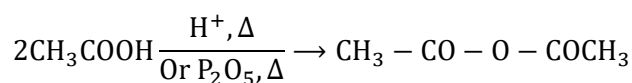
- Thus, the following acids are arranged in order of increasing acidity (based on  $pK_a$  values):



- Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect.
- The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

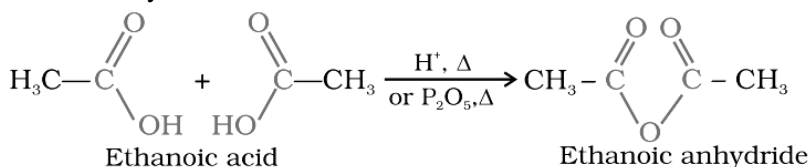
### Reactions Involving Cleavage of C – OH Bond:

Formation of anhydride :

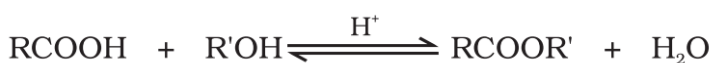


### Ethanoic acid

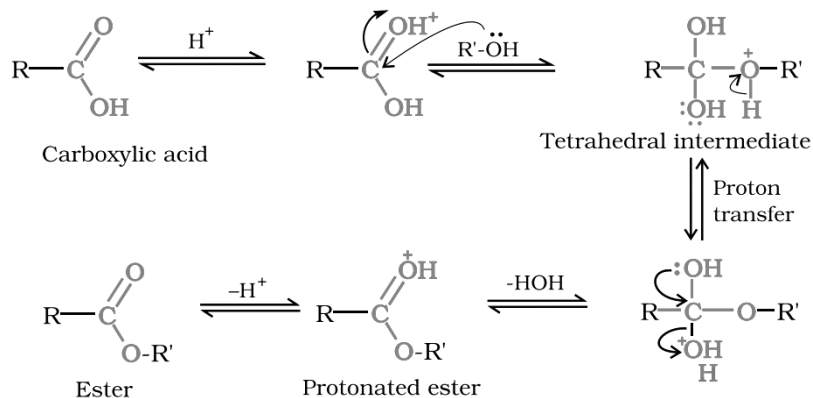
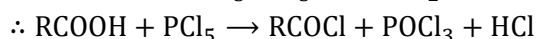
Ethanoic anhydride



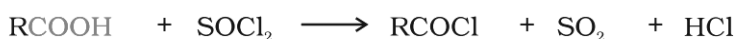
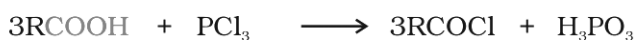
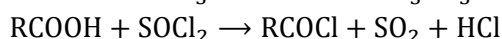
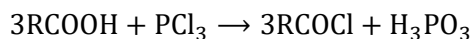
### Esterification :



- Reactions with  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{SOCl}_2$  :



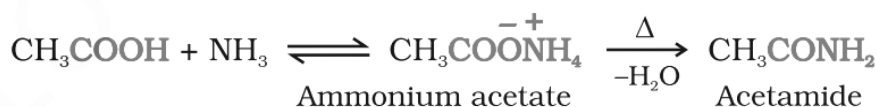
### Reactions with $\text{PCl}_5$ , $\text{PCl}_3$ and $\text{SOCl}_2$



Thionyl chloride ( $\text{SOCl}_2$ ) is preferred because the other two products are gaseous and escape the reaction mixture making the purification of the products easier.

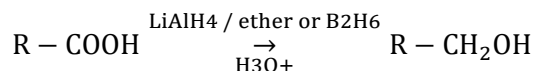


**Reaction with ammonia :**



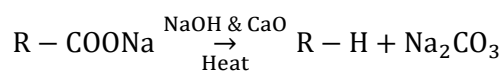
• **Reactions Involving-COOH Group:**

**Reduction:** Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane.



Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

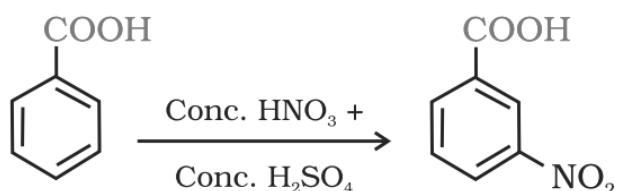
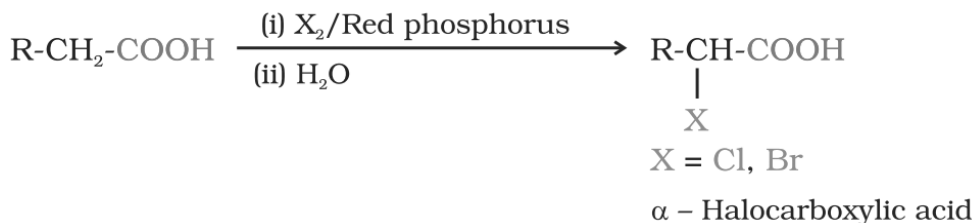
**Decarboxylation:**



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

**Substitution Reactions in the Hydrocarbon Part:**

**Halogenation (Hell Volhard-Zelinsky reaction):**



*m*-Nitrobenzoic acid

**Ring substitution:** Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group.

Carboxylic acid, do not undergo Friedel-Crafts reaction because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.

**Uses of Carboxylic Acids**

Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries.

Ethanoic acid is used as solvent and as vinegar in food industry.

Hexanedioic acid is used in the manufacture of nylon- 6,6 .

Esters of benzoic acid are used in perfumery. Sodium benzoate is used as a food preservative. Higher fatty acids are used for the manufacture of soaps and detergents.



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$\text{NaBH}_4$  acts as a selective reducing agent for carbonyl group and does not affect the ester group. Self condensation of aldehyde in presence of dil.  $\text{NaOH}$  is known as aldol condensation reaction and when different aldehydes or aldehydes and ketones are used as a reactant then this reaction is called cross aldol condensation reaction.

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**Library- <https://smart.link/sdfez8ejd80if>**