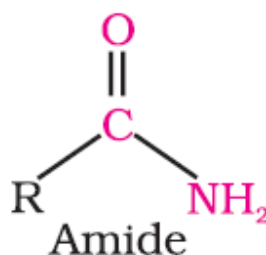
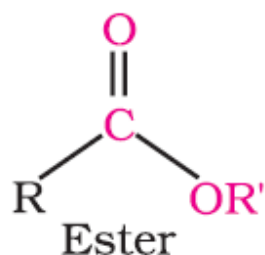
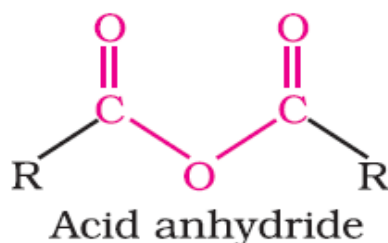
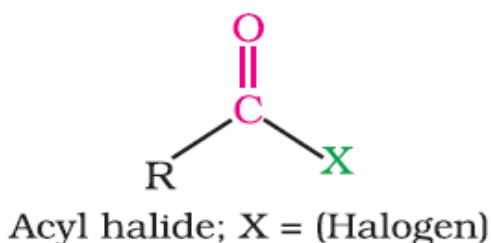
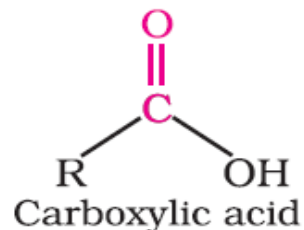
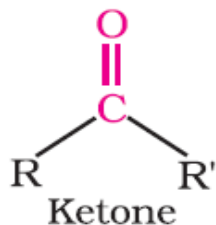
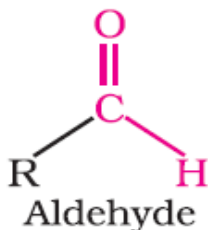


## 12. ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

These are compounds containing carbon-oxygen double bond ( $>C=O$ ) called carbonyl group. In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in ketones, it is bonded to two carbon atoms. The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides) while in compounds where carbon is attached to nitrogen and to halogens are called amides and acyl halides respectively. The general formulas of these compounds are:



### Aldehydes and Ketones

#### Nomenclature:

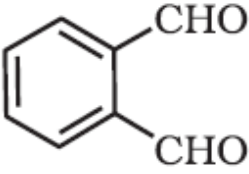
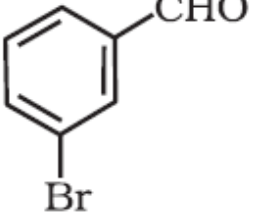
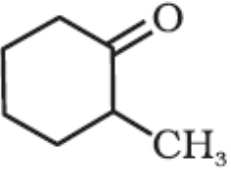
The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending -ic acid with aldehyde. The position of the substituent in the carbon chain is indicated by Greek letters  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , etc.

The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group and by suffixing ketone. The positions of the substituents are indicated by Greek letters,  $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\beta'$  and so on.

The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending -e with '-al' and '-one' respectively. 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.

Some examples are:

Compound	Common name	IUPAC name
<b>ALDEHYDES</b>		
HCHO	Formaldehyde	Methanal
CH <sub>3</sub> CHO	Acetaldehyde	Ethanal
(CH <sub>3</sub> ) <sub>2</sub> CHCHO	Isobutyraldehyde	2-Methylpropanal
CH <sub>3</sub> CH(OCH <sub>3</sub> )CHO	$\alpha$ -Methoxypropionaldehyde	2-Methoxypropanal

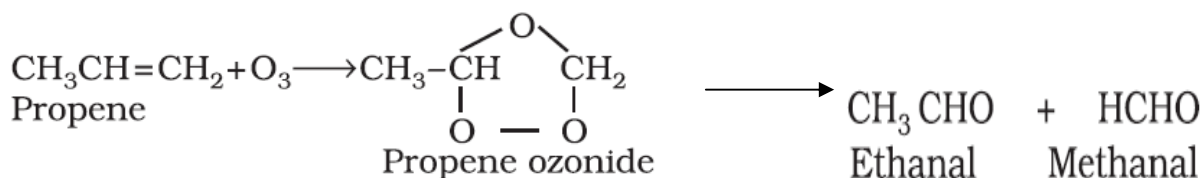
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	Valeraldehyde	Pentanal
$\text{CH}_2=\text{CHCHO}$	Acrolein	Prop-2-enal
	Phthalaldehyde	Benzene-1,2-dicarbaldehyde
	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde Or 3-Bromobenzaldehyde
<b>KETONES</b>		
$\text{CH}_3\text{COCH}_3$	Acetone	Propanone
$\text{CH}_3\text{COCH}_2\text{CH}_3$	Ethyl methyl ketone	Butanone
$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ketone	Pentan-2-one
$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	Diethyl ketone	Pentan-3-one
$(\text{CH}_3)_2\text{CHCOCH}(\text{CH}_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$	Mesityl oxide	4-Methylpent-3-en-2-one
	$\alpha$ -Methylcyclohexanone	2-Methylcyclohexanone

### Preparation of Aldehydes and Ketones

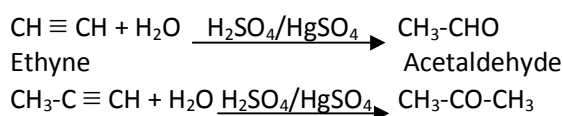
- By oxidation of alcohols:** Primary alcohols on oxidation with mild oxidising agents like  $\text{CrO}_3$  to give aldehydes while secondary alcohols give ketones.  

$$\begin{array}{l} \text{R-CH}_2\text{OH} \xrightarrow{[\text{O}]} \text{R-CHO} \\ \text{R}_2\text{CHOH} \xrightarrow{[\text{O}]} \text{R}_2\text{CO} \end{array}$$
- By dehydrogenation of alcohols:** Alcohols when heated with Cu or Silver catalyst at 573K, we get carbonyl compounds. Primary alcohols give aldehydes, while secondary alcohols give ketones.  

$$\begin{array}{l} \text{R-CH}_2\text{OH} \xrightarrow{\text{Cu/573 K}} \text{R-CHO} \\ \text{R}_2\text{CHOH} \xrightarrow{\text{Cu/573 K}} \text{R}_2\text{CO} \end{array}$$
- By ozonolysis of alkenes:** Alkenes add ozone followed by hydrolysis with zinc dust and water, we get aldehydes or ketones.



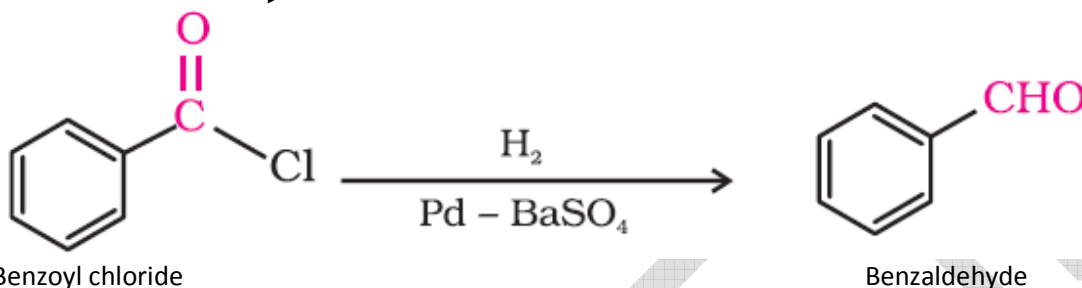
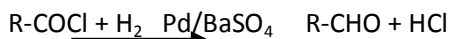
- By hydration of alkynes:** Alkynes add water in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$  to give carbonyl compounds. Ethyne (acetylene) gives acetaldehyde and all other alkynes give ketones.



## Preparation of Aldehydes

### 1. From acyl chloride (Acid chloride) [*Rosenmund's Reduction*]:

Acid chlorides react with hydrogen in presence of Pd supported on  $\text{BaSO}_4$ , we get aldehydes. This reaction is called Rosenmund's reduction.

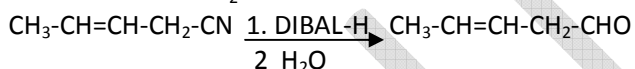
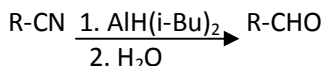


### 2. From nitriles and esters:

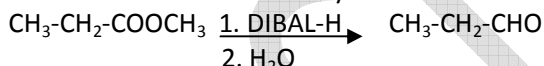
Nitriles when reduced with stannous chloride in the presence of hydrochloric acid, we get imines, which on hydrolysis give corresponding aldehyde. This reaction is called **Stephen reaction**.



Nitriles can also be selectively reduced by *diisobutylaluminium hydride* (DIBAL-H) to imines followed by hydrolysis to aldehydes. DIBAL-H does not affect other reducible groups like double bonds.



Esters are also reduced to aldehydes with DIBAL-H.

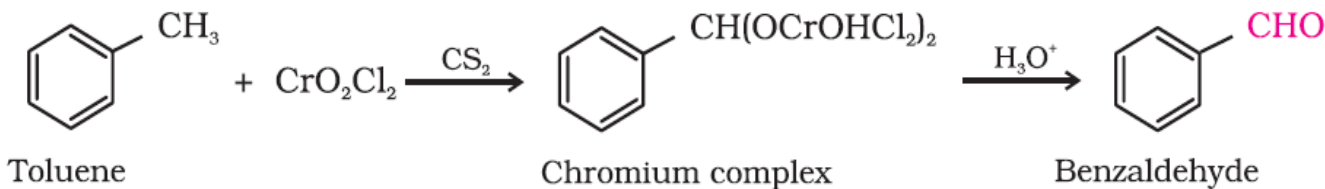


## Preparation of Aromatic aldehydes:

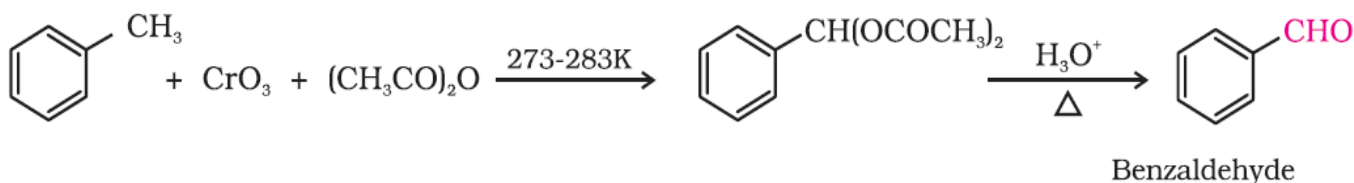
### 1. By oxidation of methylbenzene:

Methyl benzenes when oxidised by using mild oxidising agents like chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) or chromic oxide ( $\text{CrO}_3$ ) in acetic anhydride, we get benzaldehyde.

Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde. This reaction is called **Etard reaction**.

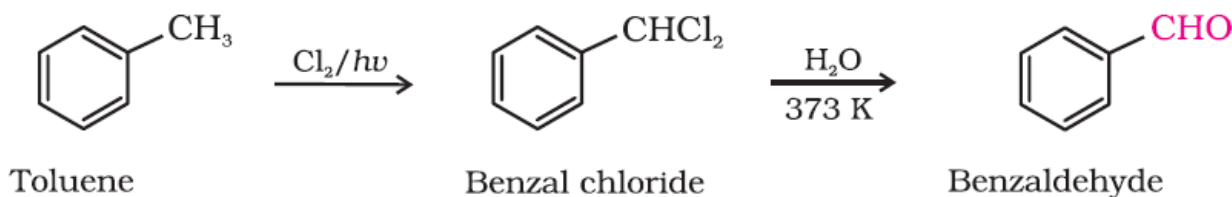


On treating with chromic oxide in acetic anhydride, methyl benzene is converted to benzylidene diacetate which on acidification gives benzaldehyde.



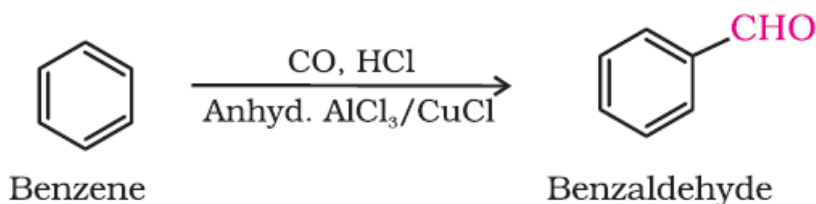
### 2. By side chain chlorination followed by hydrolysis:

Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This method is used for the manufacture of benzaldehyde.



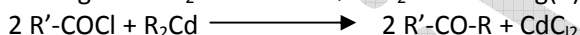
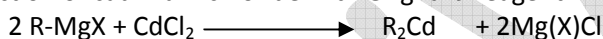
### 3. By Gatterman – Koch reaction:

When benzene is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, we get benzaldehyde. This reaction is known as Gatterman-Koch reaction.

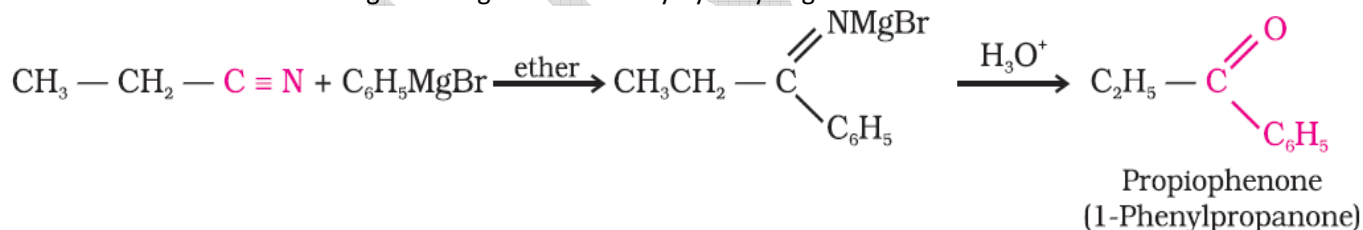


### Preparation of Ketones

1. **From acyl chlorides:** Acid chlorides react with dialkylcadmium, we get ketones. Dialkyl cadmium is prepared by the reaction of cadmium chloride with Grignard reagent.

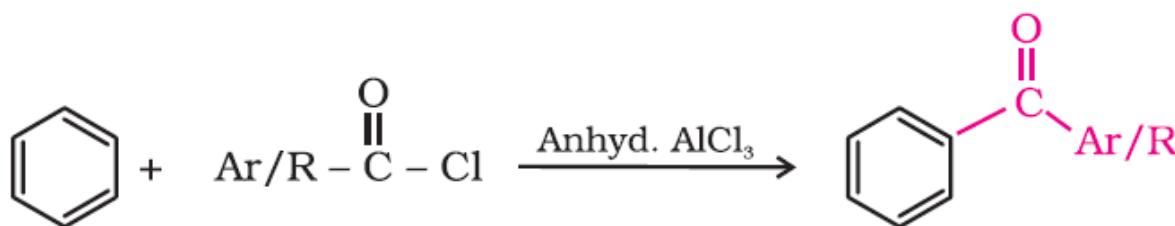


2. **From nitriles:** Nitriles add Grignard reagent followed by hydrolysis gives ketones.



### 3. From benzene or substituted benzenes [*Friedel – Crafts acylation reaction*]

When benzene or substituted benzene is treated with acid chloride ( $\text{R-COCl}$ ) in the presence of anhydrous aluminium chloride, we get a ketone. This reaction is known as **Friedel-Crafts acylation reaction**.



### Physical Properties of Aldehydes and Ketones

#### 1. Boiling Point:

The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to dipole-dipole interactions which results in weak molecular association. But their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

#### 2. Solubility:

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

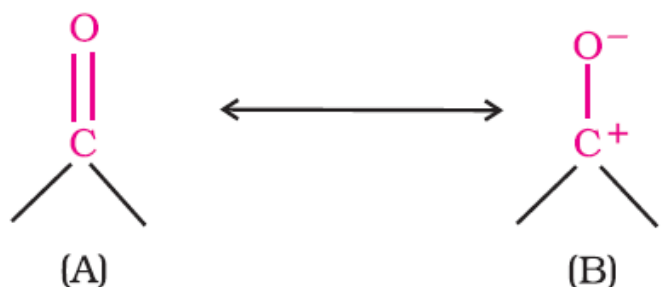
### 3. Physical state:

Methanal is a gas at room temperature, ethanal and acetone are volatile liquids and other aldehydes and ketones are liquid or solid at room temperature.

#### 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 forms a  $\pi$ -bond with oxygen. In addition, the oxygen atom also has two non bonding electron pairs. Thus, 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 bond angles are approximately  $120^\circ$ .

The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a nucleophilic (Lewis base) centre. The high polarity of the carbonyl group is explained on the basis of resonance as follows:

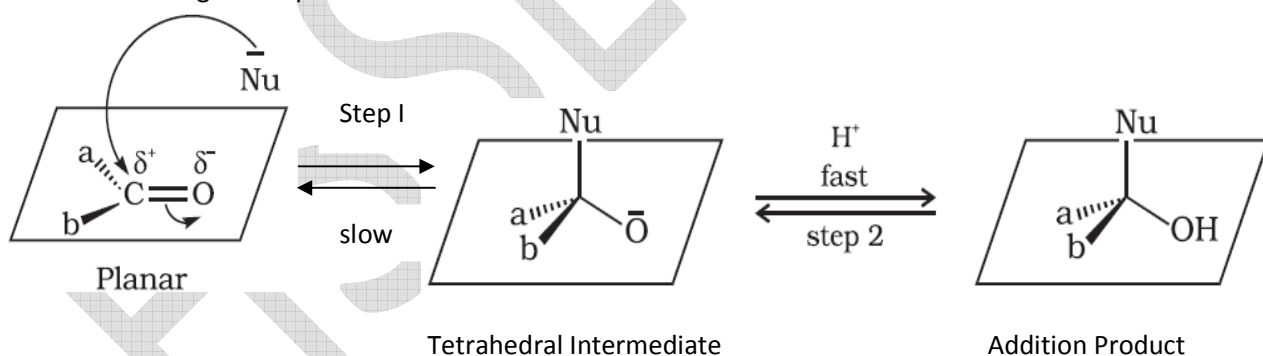


## Chemical Reactions of Aldehydes and Ketones

Since aldehydes and ketones contain a carbonyl group, they undergo similar chemical reactions. The important reactions of aldehydes and ketones are:

### 1. Nucleophilic addition reactions:

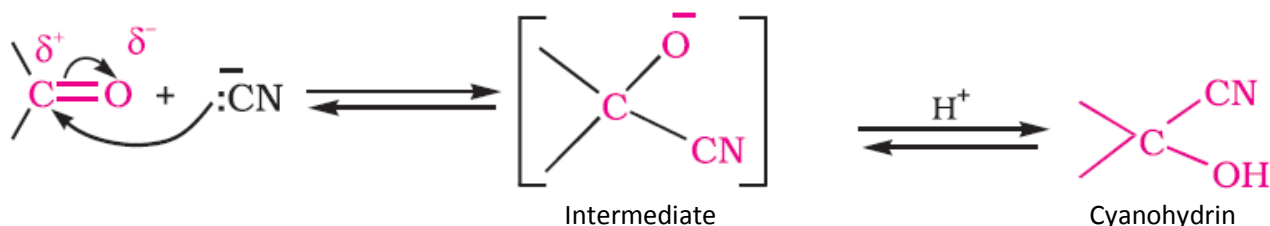
A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of  $sp^2$  hybridised orbitals of carbonyl carbon. As a result, the hybridisation of carbon changes from  $sp^2$  to  $sp^3$  and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the product.



Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two bulky alkyl groups in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes. Electronically, ketones are less reactive because of the electron releasing nature of the two alkyl groups reduces the electrophilicity of the carbonyl carbon.

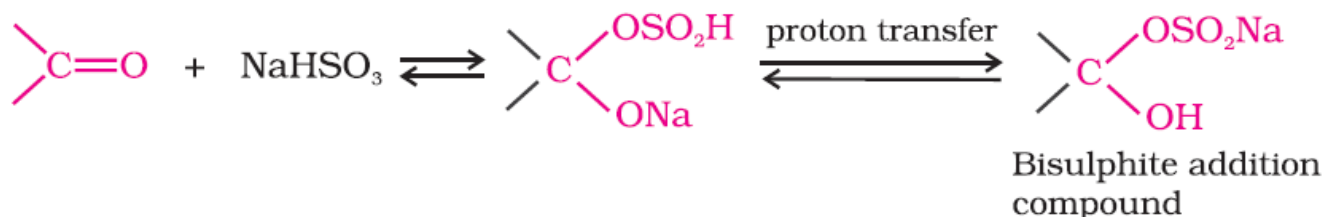
Some important nucleophilic addition reactions of aldehydes and ketones are:

- a) **Addition of hydrogen cyanide (HCN):** Aldehydes and ketones react with hydrogen cyanide (HCN) in presence of a base to give cyanohydrins.



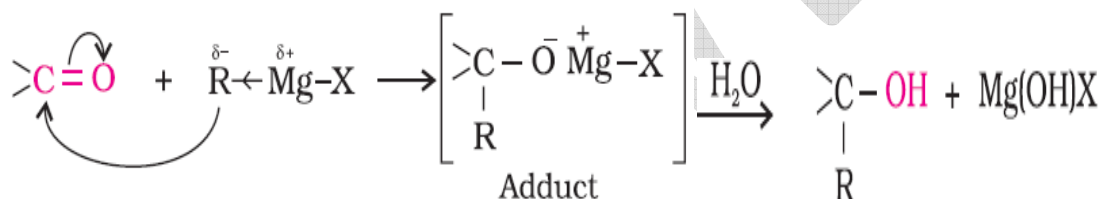
Aldehydes give aldehyde cyanohydrins and ketones give ketone cyanohydrins. The cyanohydrins are useful synthetic intermediates since it can be converted to carboxylic acids, amines, amides etc.

- b) **Addition of sodium hydrogensulphite:** Aldehydes and ketones add sodium hydrogensulphite to form the addition products (bisulphite adduct).

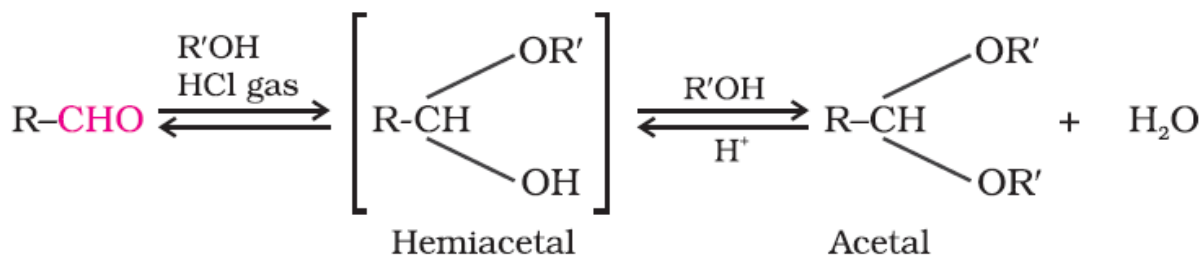


The bisulphate adduct are water soluble and can be converted back to the original aldehyde or ketone by treating it with dilute mineral acid or alkali. Therefore, this reaction is used for the separation and purification of aldehydes and ketones.

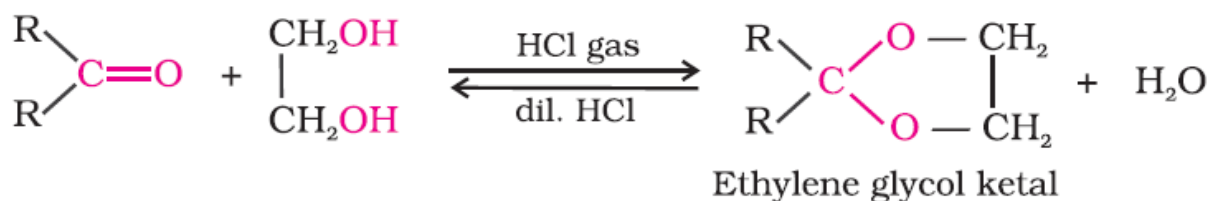
- c) **Addition of Grignard reagents:** Carbonyl compounds add Grignard reagent followed by hydrolysis, alcohols are formed. Formaldehyde gives primary alcohols, other aldehydes give secondary alcohols and ketones give tertiary alcohols.



- d) **Addition of alcohols:** Aldehydes react with monohydric alcohol in the presence of dry HCl to give alkoxyalcohol intermediate (known as hemiacetals), which further react with one molecule of alcohol to give a gem-dialkoxy compound known as acetal.

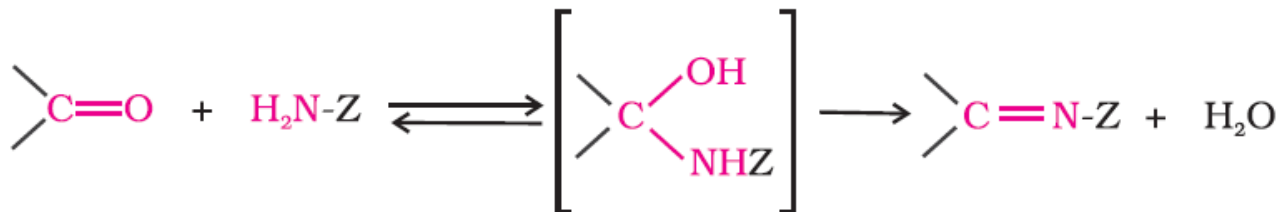


Ketones react with ethylene glycol in presence of dry HCl to form cyclic products known as ethylene glycol ketals. Acetals and ketals are hydrolysed with aqueous mineral acids to give corresponding aldehydes and ketones respectively.

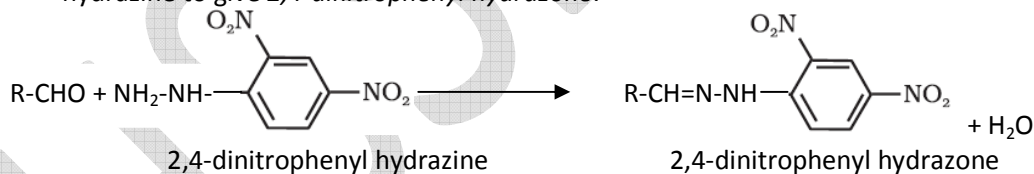




- e) **Addition of ammonia and its derivatives:** Nucleophiles like ammonia and its derivatives  $\text{H}_2\text{N-Z}$  are added to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid.



- i) **Addition of ammonia:** Aldehydes and ketones add ammonia followed by elimination of a water molecule to give *imines*.  
 $\text{R-CHO} + \text{NH}_3 \rightarrow \text{R-CH(OH)NH}_2 \rightarrow \text{R-CH=NH} + \text{H}_2\text{O}$   
 (imines)  
 $\text{R}_2\text{CO} + \text{NH}_3 \rightarrow \text{R}_2\text{C(OH)NH}_2 \rightarrow \text{R}_2\text{C=NH} + \text{H}_2\text{O}$
- ii) **Addition of Amine:** Carbonyl compounds add amines to give *substituted imines (Schiff's bases)*.  
 $\text{R-CHO} + \text{R}'\text{-NH}_2 \rightarrow \text{R-CH(OH)NHR}' \rightarrow \text{R-CH=NR}' + \text{H}_2\text{O}$   
 $\text{R}_2\text{CO} + \text{R}'\text{-NH}_2 \rightarrow \text{R}_2\text{C(OH)NHR}' \rightarrow \text{R}_2\text{C=NR}' + \text{H}_2\text{O}$
- iii) **Addition of hydroxyl amine ( $\text{NH}_2\text{-OH}$ ):** Carbonyl compounds condensed with hydroxyl amine to give *oximes*.  
 $\text{R-CHO} + \text{NH}_2\text{OH} \rightarrow \text{R-CH=N-OH} + \text{H}_2\text{O}$   
 (aldoxime)  
 $\text{R}_2\text{CO} + \text{NH}_2\text{OH} \rightarrow \text{R}_2\text{C=N-OH} + \text{H}_2\text{O}$
- iv) **Addition of hydrazine ( $\text{NH}_2\text{-NH}_2$ ):** Carbonyl compounds condensed with hydrazine to give *hydrazone*.  
 $\text{R-CHO} + \text{NH}_2\text{-NH}_2 \rightarrow \text{R-CH=N-NH}_2 + \text{H}_2\text{O}$   
 (hydrazone)  
 $\text{R}_2\text{CO} + \text{NH}_2\text{-NH}_2 \rightarrow \text{R}_2\text{C=N-NH}_2 + \text{H}_2\text{O}$
- v) **Addition of phenyl hydrazine ( $\text{NH}_2\text{-NH-C}_6\text{H}_5$ ):** Carbonyl compounds condensed with phenyl hydrazine to give *phenyl hydrazone*.  
 $\text{R-CHO} + \text{NH}_2\text{-NH-C}_6\text{H}_5 \rightarrow \text{R-CH=N-NH-C}_6\text{H}_5 + \text{H}_2\text{O}$   
 (phenyl hydrazone)  
 $\text{R}_2\text{CO} + \text{NH}_2\text{-NH-C}_6\text{H}_5 \rightarrow \text{R}_2\text{C=N-NH-C}_6\text{H}_5 + \text{H}_2\text{O}$
- vi) **Addition of 2,4-dinitrophenyl hydrazine (2,4-DNP):** Carbonyl compounds condensed with 2,4-dinitrophenyl hydrazine to give *2,4-dinitrophenyl hydrazone*.

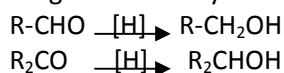


2,4-dinitrophenyl hydrazine is also known as *Borches reagent*. 2,4-DNP-derivatives are yellow, orange or red solids and hence this reaction is used for the characterisation of aldehydes and ketones.

- vii) **Addition of Semicarbazide ( $\text{NH}_2\text{-NH-CO-NH}_2$ ):** Carbonyl compounds condensed with semicarbazide to yield *samcarbazon*.  
 $\text{R-CHO} + \text{NH}_2\text{-NH-CO-NH}_2 \rightarrow \text{R-CH=N-NH-CO-NH}_2 + \text{H}_2\text{O}$   
 (semicarbazone)  
 $\text{R}_2\text{CO} + \text{NH}_2\text{-NH-CO-NH}_2 \rightarrow \text{R}_2\text{C=N-NH-CO-NH}_2 + \text{H}_2\text{O}$

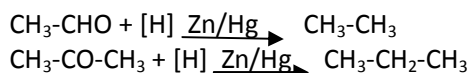
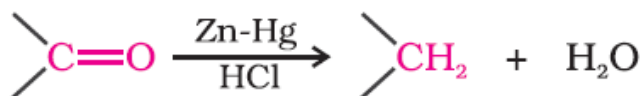
## 2. Reduction:

- i) **Reduction to alcohols:** When reduced using sodium borohydride ( $\text{NaBH}_4$ ) or lithium aluminium hydride ( $\text{LiAlH}_4$ ) or  $\text{H}_2$  in presence of Ni, Pd or Pt catalyst (Catalytic hydrogenation), aldehydes give primary alcohols, while ketones give secondary alcohols.

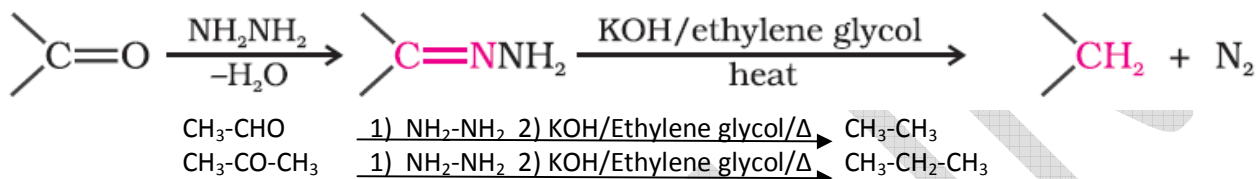


ii) *Reduction to Hydrocarbons:*

**Clemmensen reduction:** Aldehydes and ketones can be reduced to alkanes on treatment with zinc amalgam and concentrated hydrochloric acid. During this reaction, the carbonyl group is reduced to CH<sub>2</sub> (methylene) group.

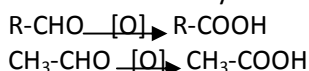


**Wolff-Kishner reduction:** Carbonyl group can also be reduced to methylene group, by treating with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol.

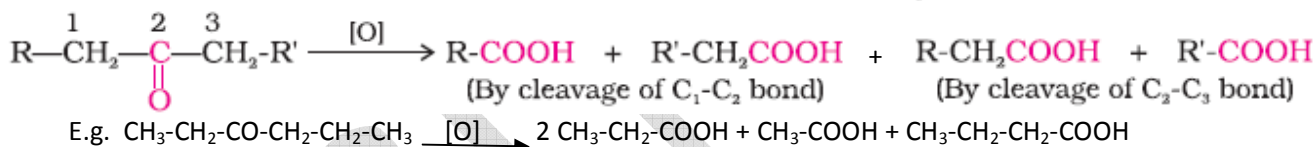


3. **Oxidation:**

Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate etc. Mild oxidising agents like CrO<sub>3</sub>, Tollens' reagent and Fehlings' reagent can also oxidise aldehydes.

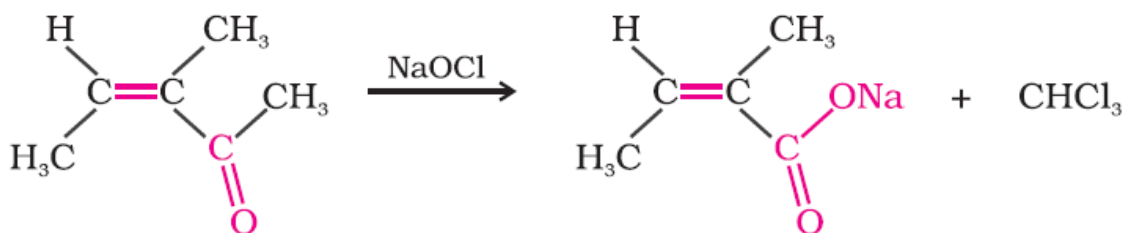


Ketones when oxidised using strong oxidising agents and at high temperatures, we get a mixture of carboxylic acids having lesser number of carbon atoms. During this reaction carbon-carbon bond cleavage occurs.



4. **Haloform Reaction:**

Aldehydes or ketones having CH<sub>3</sub>-CO- group or CH<sub>3</sub>-CHOH- group, when treated with sodium hypohalite or halogen in presence of NaOH, we get a haloform (CHX<sub>3</sub>). This reaction is called haloform reaction. During this reaction, the methyl group is converted to haloform. This reaction does not affect a carbon-carbon double bond, if present in the molecule.



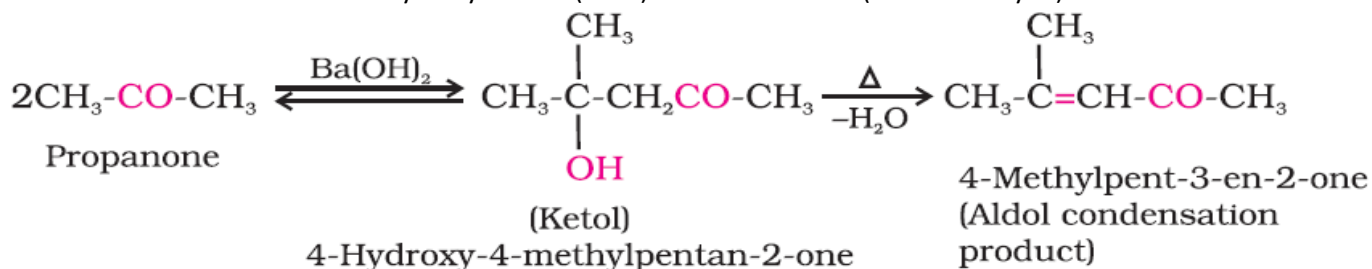
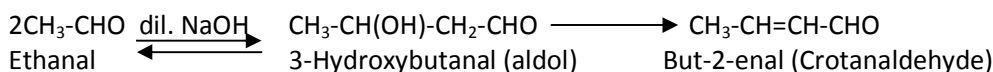
The reaction with sodium hypoiodite gives a yellow precipitate of iodoform and this reaction is used for the detection of CH<sub>3</sub>-CO- group or CH<sub>3</sub>-CHOH- group in a compound. For example 2-pentanone and 3-pentanone can be distinguished by iodoform reaction. 2-pentanone gives this reaction.

5. **Aldol condensation Reaction:**

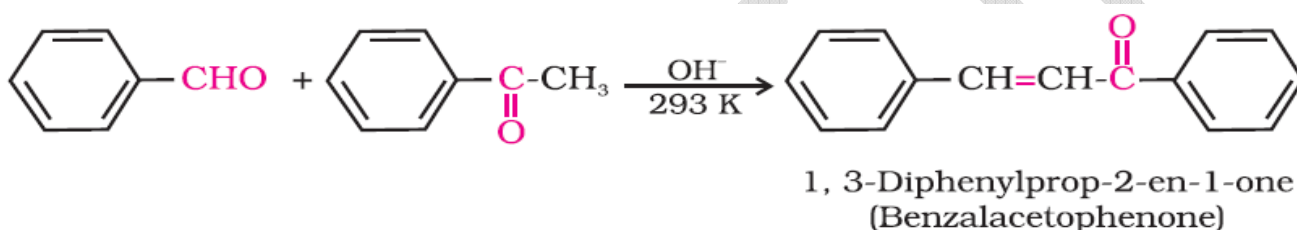
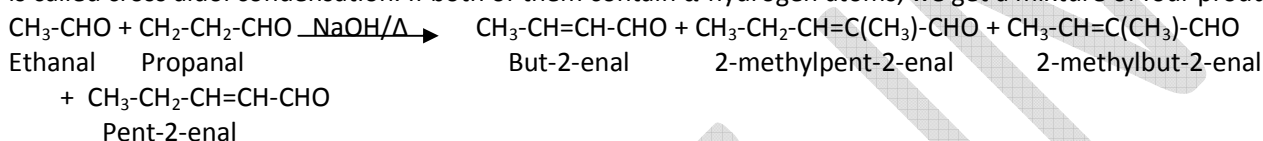
Aldehydes and ketones having at least one α-hydrogen atom when treated with dilute alkali, we get β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol) respectively. This is known as Aldol reaction. The product formed contains both aldehydic (ketonic) and alcoholic group. So the name aldol or ketol is used.

The aldol or ketol on heated undergo dehydration to give α,β-unsaturated aldehyde or ketone. This reaction is called Aldol condensation.



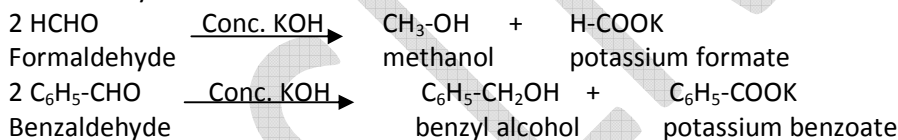


6. **Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes or ketones, it is called cross aldol condensation. If both of them contain  $\alpha$ -hydrogen atoms, we get a mixture of four products.



7. **Cannizzaro Reaction:**

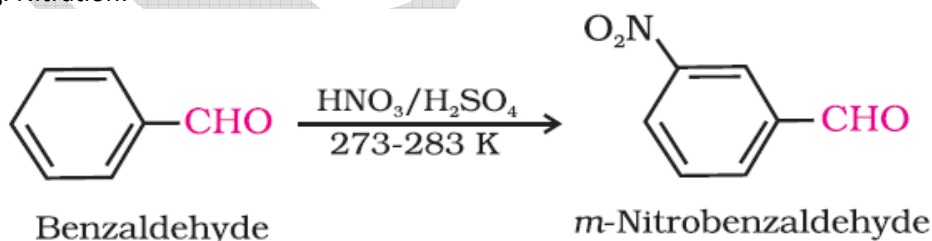
Aldehydes having no  $\alpha$ -hydrogen atom (e.g.  $\text{HCHO}$ ,  $\text{C}_6\text{H}_5\text{-CHO}$ ,  $\text{CCl}_3\text{-CHO}$  etc), when treated with Conc. alkali ( $\text{NaOH}$  or  $\text{KOH}$ ) undergo self oxidation and reduction (disproportionation) to form one molecule of the alcohol and one molecule of carboxylic acid salt. This reaction is called Cannizzaro reaction.



8. **Electrophilic Substitution Reactions:**

Aldehydic and ketonic groups are meta directing and deactivating. So on electrophilic substitution reactions, they give meta-derivatives.

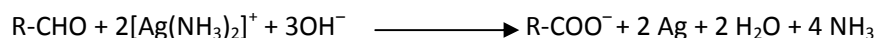
e.g. Nitration:



**Tests to distinguish Aldehydes and Ketones**

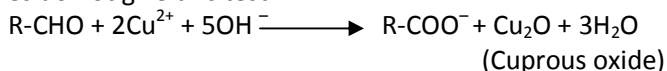
1. **Tollens' test:**

Tollen's reagent is freshly prepared *ammoniacal Silver nitrate*. On warming Tollens' reagent, aldehydes give a bright silver mirror. During this reaction, the aldehyde is oxidised to corresponding carboxylate ion and silver nitrate is reduced to silver metal.



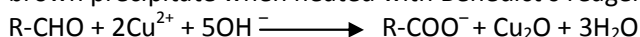
2. **Fehling's test:**

Fehling reagent is a mixture 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)*. On heating with Fehling's reagent, aldehyde gives a reddish brown precipitate of cuprous oxide ( $\text{Cu}_2\text{O}$ ). Aromatic aldehydes do not give this test.



### 3. **Benedict's test:**

Benedict's solution is a mixture of  $\text{CuSO}_4$ , *sodium citrate* and *sodium carbonate*. Aliphatic aldehydes give reddish brown precipitate when heated with Benedict's reagent.



The above tests are not answered by ketones.

### **CARBOXYLIC ACIDS**

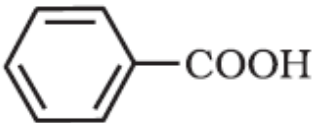
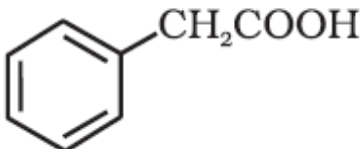
Carbon compounds containing a carboxyl functional group ( $-\text{COOH}$ ) are called carboxylic acids. The carboxyl group consists of a carbonyl group attached to a hydroxyl group, hence its name carboxyl. Aliphatic carboxylic acids containing 12 to 18 C atoms are called fatty acids. They occur in natural fats as esters of glycerol.

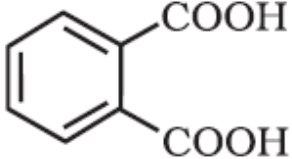
**Nomenclature**

The common names of carboxylic acids 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*. In numbering the carbon chain, the carboxylic carbon is numbered one. For naming compounds containing more than one carboxyl group, the ending *-e* of the alkane is retained. The number of carboxyl groups is indicated by adding the prefixes *di*, *tri*, etc. to the term *oic*.

Some examples are:

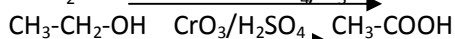
Compound	Common name	IUPAC name
$\text{HCOOH}$	Formic acid	Methanoic acid
$\text{CH}_3\text{COOH}$	Acetic acid	Ethanoic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid	Propanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butyric acid	Butanoic acid
$(\text{CH}_3)_2\text{CHCOOH}$	Isobutyric acid	2-Methylpropanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	Valeric acid	Pentanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	Caproic acid	Hexanoic acid
$\text{HOOC-COOH}$	Oxalic acid	Ethanedioic acid
$\text{HOOC-CH}_2\text{-COOH}$	Malonic acid	Propanedioic acid
$\text{HOOC-(CH}_2)_2\text{-COOH}$	Succinic acid	Butanedioic acid
$\text{HOOC-(CH}_2)_3\text{-COOH}$	Glutaric acid	Pentanedioic acid
$\text{HOOC-(CH}_2)_4\text{-COOH}$	Adipic acid	Hexanedioic acid
$\text{HOOC-CH}_2\text{-CH(COOH)-CH}_2\text{-COOH}$		Propane-1, 2, 3-tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-Phenylethanoic acid

	Phthalic acid	Benzene-1, 2-dicarboxylic acid
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## Methods of Preparation of Carboxylic acids

### 1. From primary alcohols and aldehydes:

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ( $\text{KMnO}_4$ ) in neutral, acidic or alkaline media or by potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) and chromium trioxide ( $\text{CrO}_3$ ) in acidic media.

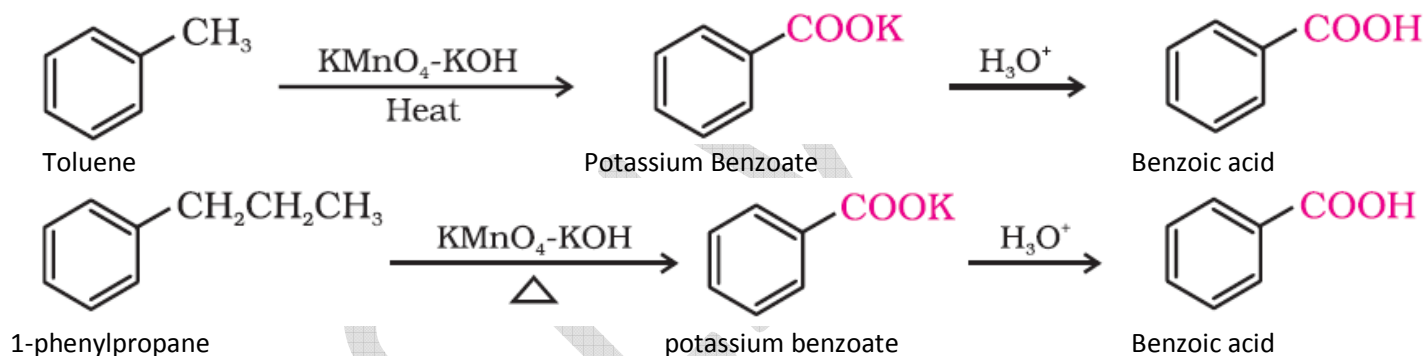


Aldehydes on oxidation with mild oxidising agents like  $\text{CrO}_3$  or Tollen's reagent to give carboxylic acids.



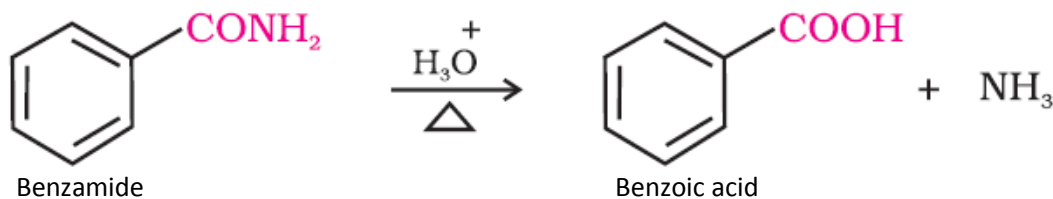
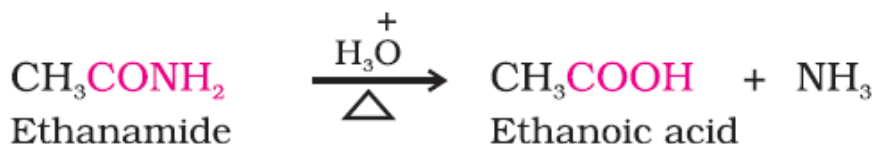
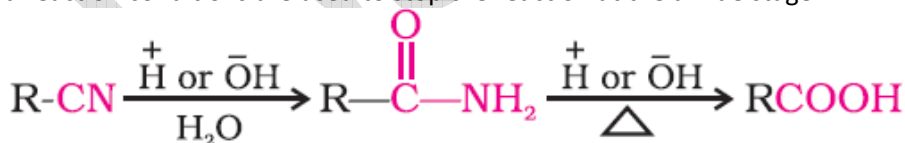
### 2. From alkylbenzenes:

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected.



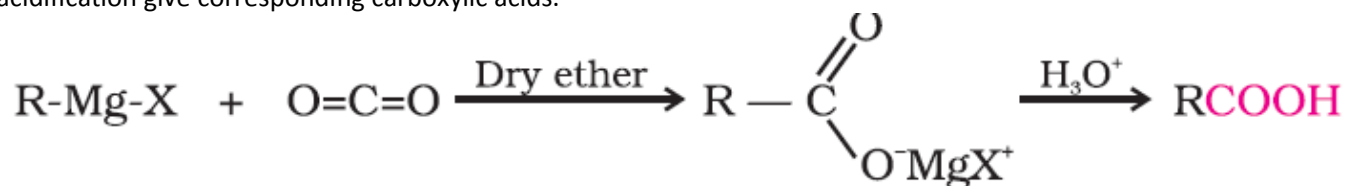
### 3. From nitriles and amides:

Hydrolysis of nitriles in presence of acid or alkali as catalyst first give amides, which on further give carboxylic acids. Mild reaction conditions are used to stop the reaction at the amide stage.



#### 4. From Grignard reagents:

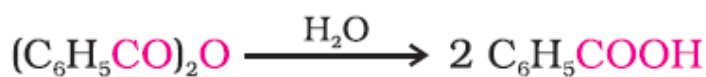
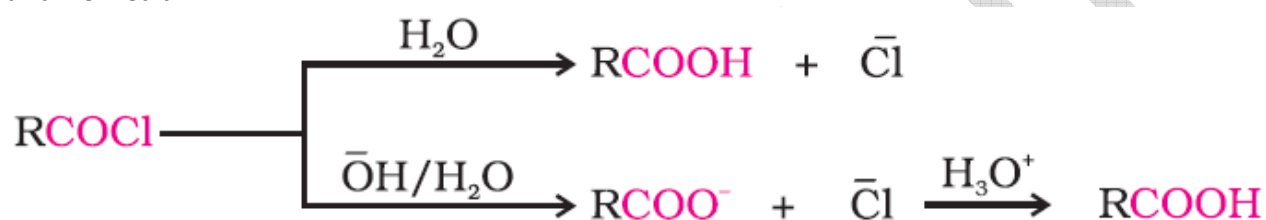
Grignard reagents react with carbon dioxide (dry ice) in dry ether to form salts of carboxylic acids which on acidification give corresponding carboxylic acids.



Grignard reagents and nitriles can be prepared from alkyl halides. So the above two reactions are used for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides.

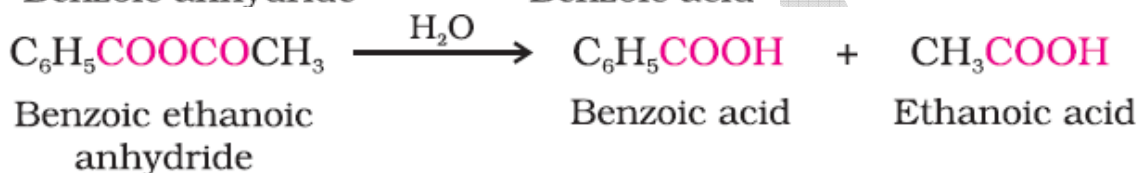
#### 5. From acyl halides and anhydrides:

Acid chlorides and anhydrides when hydrolysed with water give carboxylic acids. The rate of hydrolysis increases in alkaline medium.



Benzoic anhydride

Benzoic acid



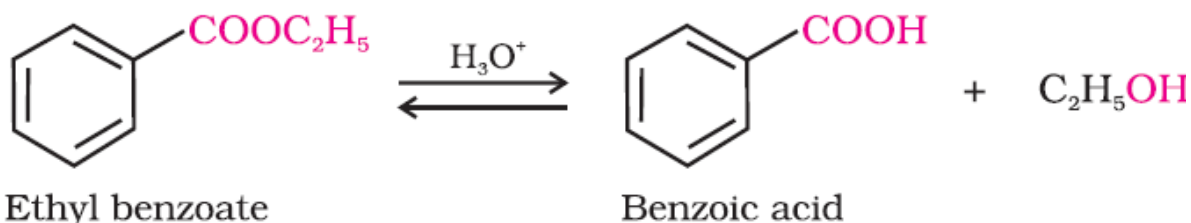
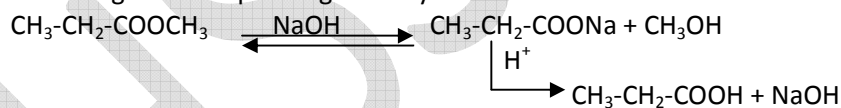
Benzoic ethanoic anhydride

Benzoic acid

Ethanoic acid

#### 6. From esters:

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives salt of carboxylic acids which on acidification give corresponding carboxylic acids.



Ethyl benzoate

Benzoic acid

#### Physical Properties

1. **Physical state:** 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.
2. **Boiling point:** Carboxylic acids are higher boiling liquids than aldehydes, ketones and alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. Most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.

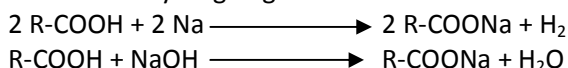
3. **Solubility:** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. The simplest aromatic carboxylic acid, benzoic acid, is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

## Chemical Reactions

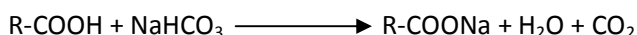
### A) Reactions Involving Cleavage of O–H Bond:

#### 1. Acidity:

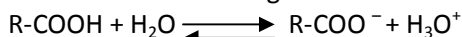
*Reactions with metals and alkalis:* Like alcohols and phenols, carboxylic acids react with electropositive metals and liberate hydrogen gas.



Unlike alcohols and phenols, carboxylic acids react with sodium carbonates and bicarbonates and give brisk effervescence of carbon dioxide.



Carboxylic acids dissociate in water to give resonance stabilized carboxylate anions and hydronium ion.



Due to the formation of hydronium ion in water, carboxylic acids are acidic in nature.

The acidity of a substance is expressed in terms of pKa value, which is the negative logarithm of Ka

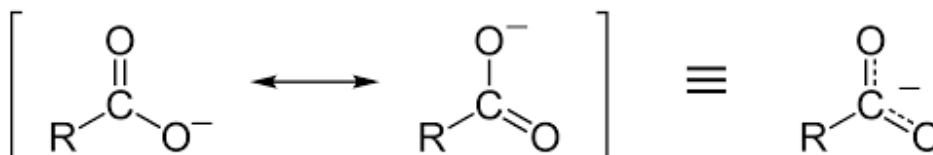
i.e.  $\text{pKa} = -\log K_a$

Greater the value of Ka, smaller will be pKa and stronger will be the acid.

#### Comparison of acidic character

Carboxylic acids are weaker than mineral acids, but they are stronger acids than other organic compounds like alcohols and many simple phenols. The higher acidity of carboxylic acids as compared to phenols can be explained as follows:

The carboxylate ion formed from the ionization of carboxylic acid is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. But the phenoxide ion formed from the ionization of phenol has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom.



Also the negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion, whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion. Therefore carboxylate ion is more stable than phenoxide ion and hence carboxylic acids easily donate  $\text{H}^+$  ion and form carboxylate ion. So it is more acidic.

#### Effect of substituents on the acidity of carboxylic acids:

Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the carboxylate ion through delocalisation of the negative charge by inductive and resonance effects. But electron donating groups decrease the acidity by destabilising the carboxylate ion.

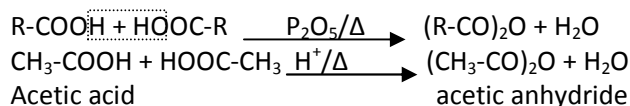


The effect of the following groups in increasing acidity order is  
 $\text{Ph} < \text{I} < \text{Br} < \text{Cl} < \text{F} < \text{CN} < \text{NO}_2 < \text{CF}_3$

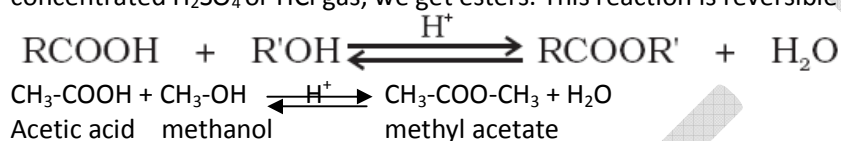
Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid. This is because of greater electronegativity of  $sp^2$  hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

### B) Reactions Involving Cleavage of C–OH Bond

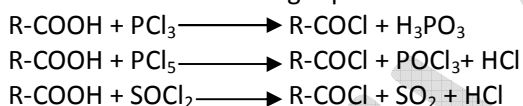
1. **Formation of anhydride:** Carboxylic acids on heating with mineral acids like  $H_2SO_4$  or with  $P_2O_5$  undergo dehydration to give acid anhydrides.



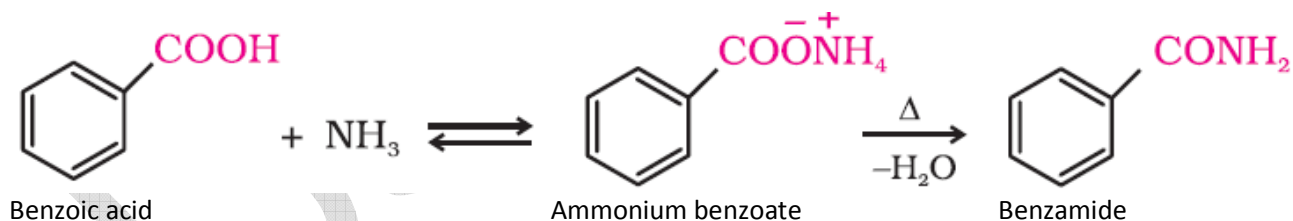
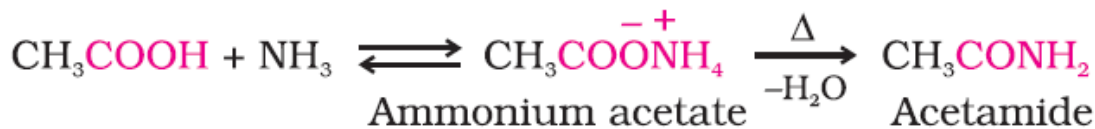
2. **Esterification:** Carboxylic acids when heated with alcohols or phenols in the presence of a mineral acid like concentrated  $H_2SO_4$  or  $HCl$  gas, we get esters. This reaction is reversible and is known as esterification.



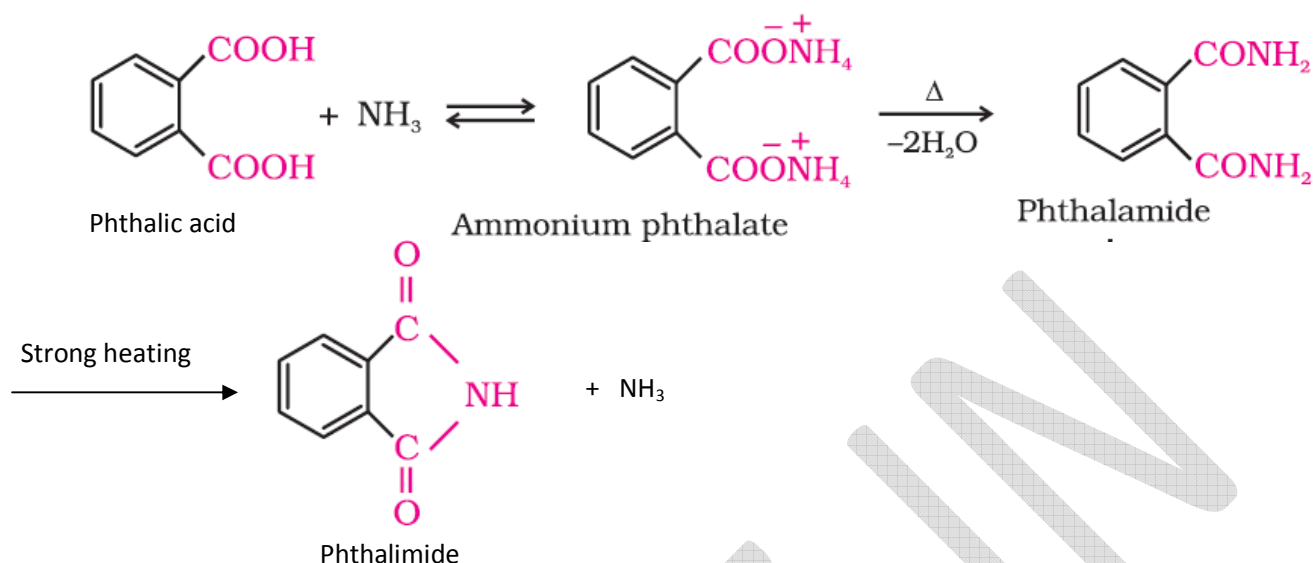
3. **Reactions with  $PCl_3$ ,  $PCl_5$  and  $SOCl_2$ :** Carboxylic acids on treating with  $PCl_3$ ,  $PCl_5$  or  $SOCl_2$ , we get acid chlorides. Reaction with thionyl chloride ( $SOCl_2$ ) is preferred because the byproducts are gases and are easily escaped from the reaction mixture so that we get pure acid chloride.



4. **Reaction with ammonia:** Carboxylic acids react with ammonia to give ammonium salts which on further heating at high temperature give amides.

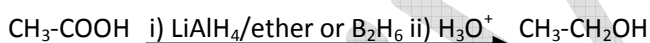
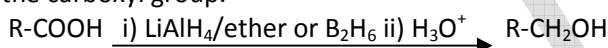






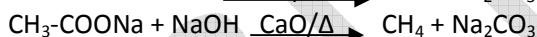
### C) Reactions Involving –COOH Group

- Reduction:** Carboxylic acids when reduced with lithium aluminium hydride or with diborane, primary alcohols are formed. Diborane does not reduce functional groups like ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

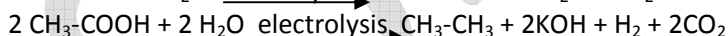
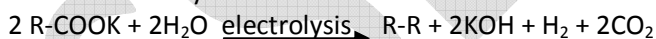


### 2. Decarboxylation:

- When sodium salts of carboxylic acid are heated with sodalime (a mixture of NaOH and CaO), they undergo decarboxylation (elimination of CO<sub>2</sub>) to form alkanes.



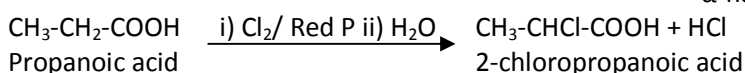
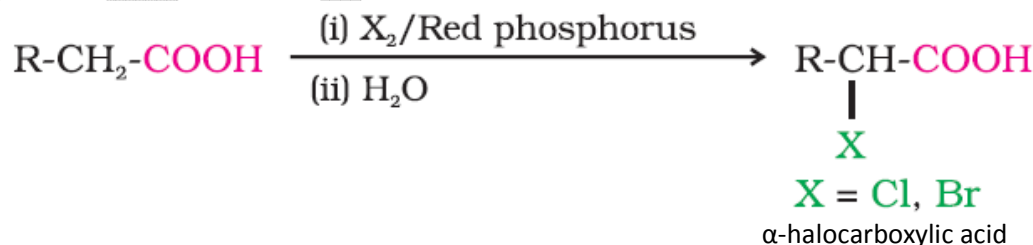
- Kolbe's electrolysis:** When an aqueous solution of sodium or potassium salt of carboxylic acid is electrolysed, we get alkanes having twice the number of carbon atoms that present in the alkyl group of the acid. This reaction is known as Kolbe electrolysis.



### D) Substitution Reactions in the Hydrocarbon Part:

#### 1. Halogenation [HVZ Reaction]

Carboxylic acids having an α-hydrogen atom, when treated with halogen (chlorine or bromine) in the presence of red phosphorus, we get α-halocarboxylic acids. This reaction is known as Hell-Volhard-Zelinsky (HVZ) reaction.

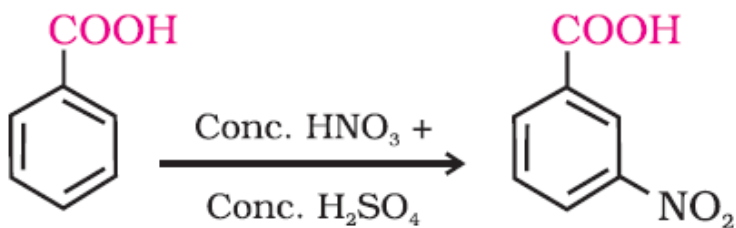


This reaction is synthetically important since the halogen atom can be replaced by other groups.

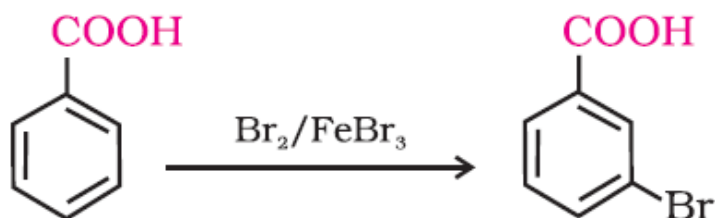
#### 2. Electrophilic substitution reactions:

The –COOH group is a deactivating group and meta-directing. So on electrophilic substitution reactions, we get meta derivatives.

e.g. 1. Nitration



2. Bromination



But carboxylic acids do not undergo Friedel-Crafts reactions because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group to form salts.

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