

ORGANIC CHEMISTRY BASED ON FUNCTIONAL GROUPS -II

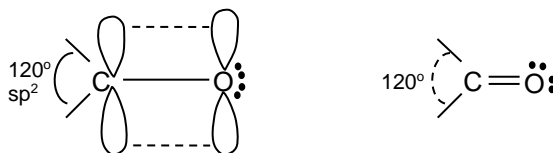
ALDEHYDES AND KETONES

Aldehydes and ketones are compounds containing a carbonyl (>C=O) functional group.

The general formula of aldehyde is $\text{R}-\text{CHO}$ and that of ketone is $\text{R}-\text{CO}-\text{R}'$. Where R and R' are alkyl or aryl groups.

Structure

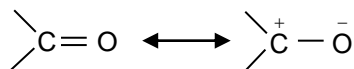
The carbon atom of the carbonyl group is sp^2 hybridised. Therefore it forms 3 sigma bonds at 120° to each other. The 4th unhybridised 'p' orbital overlaps with a 'p' orbital of oxygen to form a π bond. The carbonyl carbon atom and the three atoms bonded to it lie in one plane. The π electron cloud is above and below this plane.



Polarity of carbonyl group

The carbonyl group is polar in nature. This is due to the higher electro-negativity of oxygen relative to carbon. Hence the carbonyl carbon is an electrophilic (Lewis acid) and carbonyl oxygen is nucleophilic (Lewis base) centre.

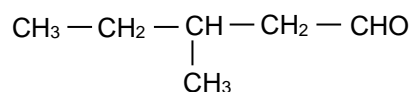
The high polarity of carbonyl group is also explained on the basis of the resonance involving neutral and dipolar structures.



The polar nature of aldehydes and ketones is confirmed by their large dipole moments. [*Acetaldehyde* (2.72D) and *acetone* (2.88D)]. The dipole moments of aldehydes and ketones are higher than that of ethers. [*Diethyl ether* (1.18D)]

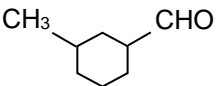
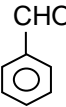
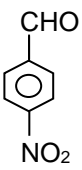
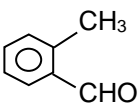
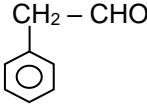
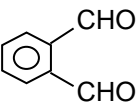
Nomenclature

The trivial names (common names) of aldehydes are derived from the names of corresponding acids by replacing "**ic acid**" by "**aldehyde**". The carbon atoms are indicated by Greek letters α , β , γ etc.

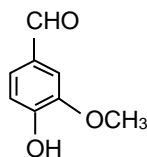


β - Methyl valeraldehyde (Common Name)
3 - methyl pentanal (IUPAC Name)

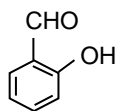
In IUPAC system, an aldehyde has the ending '**al**'. The longest carbon chain including the $-\text{CHO}$ group is selected as the parent hydrocarbon.

Compound	Trivial names	IUPAC names
H – CHO	Formaldehyde	Methanal
CH ₃ – CHO	Acetaldehyde	Ethanal
CH ₃ – CH ₂ – CHO	Propionaldehyde	Propanal
CH ₃ – CH ₂ – CH ₂ – CHO	n-Butyraldehyde	Butanal
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	Iso-Butyraldehyde	2-methyl propanal
	γ - methyl cyclohexane carbaldehyde	3-methyl cyclohexane carbaldehyde
	Benzaldehyde	Benzaldehyde
	p-Nitrobenzaldehyde	4-Nitrobenzaldehyde
	o-Tolualdehyde	2-Methyl benzaldehyde
	Phenyl acetaldehyde	2-phenyl ethanal
CH ₃ – CH = CH – CHO	Crotonaldehyde	But-2-enal
	Phthalaldehyde	Benzene-1,2-dicarbaldehyde
CH ₂ = CH – CHO	Acrolein	Prop-2-enal

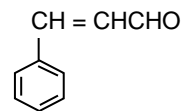
Vanillin (from vanilla beans), salicylaldehyde (from meadow sweet) and cinnamaldehyde (from cinnamon) have very pleasant fragrances.



Vanillin



Salicylaldehyde



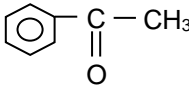
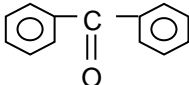
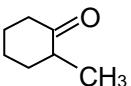
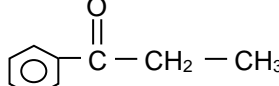
Cinnamaldehyde

They are used in many food products and pharmaceuticals to add flavours.

In common system ketones are named by using the names of alkyl groups attached to carbonyl group followed by the word '**ketone**'. Eg: CH₃ CO C₂H₅ Ethyl methyl ketone.

In IUPAC system the longest carbon chain containing the 'keto' group is selected as the parent hydrocarbon. The name of the ketone is obtained by replacing 'e' of the alkane by 'one'. The position of the keto group is indicated by a number.

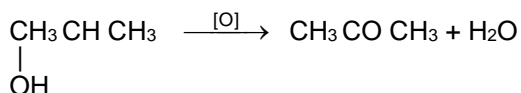
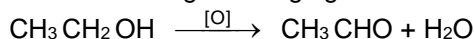
The common name and IUPAC names of the some ketones are given in the table.

Compound	Common name	IUPAC name
$\text{CH}_3 \text{CO CH}_3$	Acetone	Propanone
$\text{CH}_3 \text{CO C}_2\text{H}_5$	Ethyl methyl ketone	Butan-2-one
$\begin{array}{c} \text{CH}_3 \text{CO CH CH}_3 \\ \\ \text{CH}_3 \end{array}$	Methylisopropyl ketone	3-methylbutane-2-one
$\begin{array}{c} \text{CH}_3 \text{CH CO CH CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	Di-isopropyl ketone	2,4-Dimethylpentan-3-one
	Methyl phenyl ketone	Acetophenone
	Diphenyl ketone	Benzophenone
	α -methyl cyclohexanone	2-methyl cyclohexanone
$\text{CH}_3 \text{CO CO CH}_3$	Diacetyl	Butane-2,3-dione
$(\text{CH}_3)_2\text{C} = \text{CH} - \text{CO} - \text{CH}_3$	Mesityl oxide	4-methyl pent-3-en-2-one
	Ethyl phenyl ketone (Propiophenone)	1- Phenyl propan-1-one

METHODS OF PREPARATION

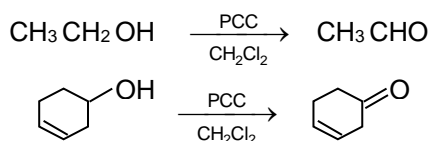
(1) FROM ALCOHOLS

(a) **By oxidation** – Aldehydes and ketones can be prepared by the oxidation of primary and secondary alcohols respectively. The commonly used oxidizing agents are $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 or CrO_3 . However these are strong oxidizing agents and further oxidize aldehydes to carboxylic acids.



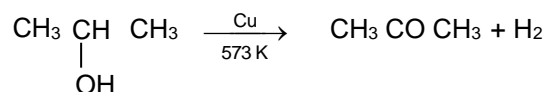
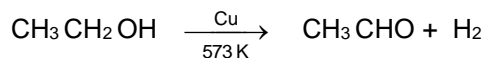
(b) By using Pyridinium chloro chromate(PCC) [$\text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}^-$]

PCC is a milder oxidizing agent. It oxidizes primary alcohols to aldehydes and secondary alcohols to ketones in dichloromethane solvent. The aldehydes are not further oxidized to carboxylic acids. The carbon - carbon double bonds also remain unaffected.



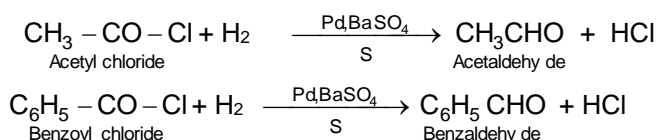
(c) By dehydrogenation (By using Ag or Cu)

Aldehydes and ketones can also be prepared by passing vapours of alcohols over heated copper gauze at 573 K. Primary alcohols give aldehydes while secondary alcohols give ketones.



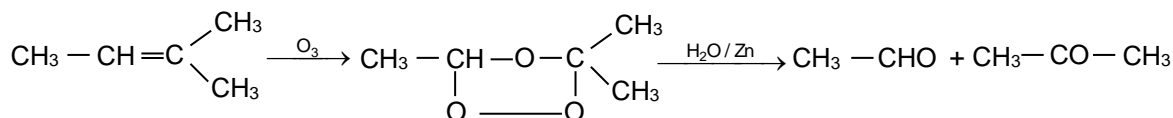
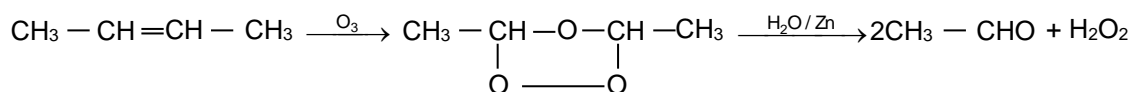
(2) From acid chlorides [Rosenmund reduction]

Aldehydes are prepared from acid chloride by reaction with hydrogen in the presence of palladium catalyst spread over barium sulphate. The catalyst is partially deactivated by addition of sulphur or quinoline. This is to prevent further reduction of aldehydes to alcohols. This reaction is called *Rosenmund's reaction*.



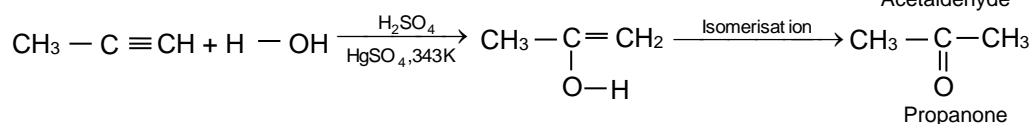
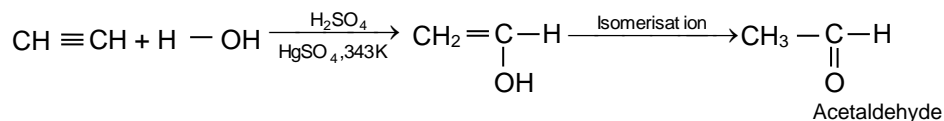
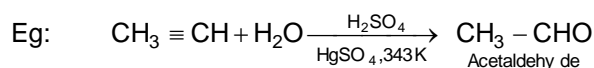
(3) By Ozonolysis of alkenes

Alkenes react with ozone to form ozonides which on decomposition with water in the presence of zinc dust give aldehydes and ketones. This process is called **ozonolysis**



(4) From Alkynes

Aldehydes and ketones can be prepared by the hydration of alkynes



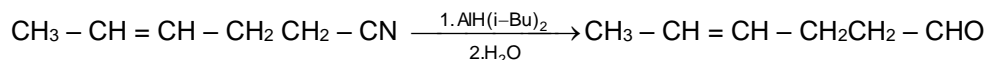
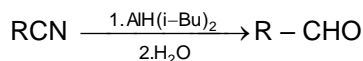
(5) From Nitriles and esters

Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

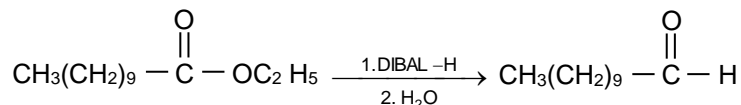


This reaction is called **Stephen reaction**.

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.

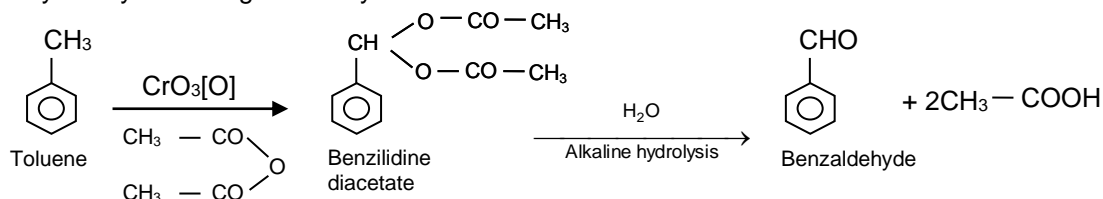


Preparation of Aromatic aldehydes and Ketones

Oxidation of toluene and its derivatives using strong oxidizing agents give benzoic acid. But under special conditions toluene can be oxidized to benzaldehyde.

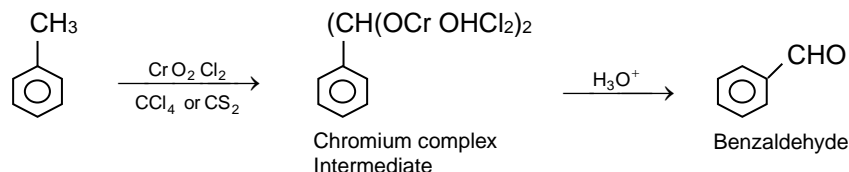
(i) Using CrO₃:

Aromatic aldehydes are obtained by the oxidation of side chain in an aromatic ring using chromium trioxide (CrO₃) in acetic anhydride. Acetic anhydride converts the aldehydes formed into non oxidisable product [**benzylidene diacetate**] and prevents further oxidation into acids. It is then hydrolysed by alkali to give aldehyde.

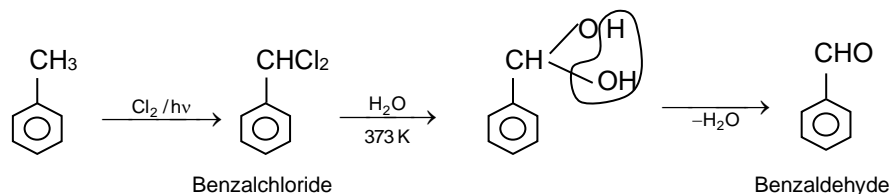


(ii) Etard's reaction

When toluene is oxidized with chromyl chloride, benzaldehyde is formed. This reaction is called Etard's reaction.

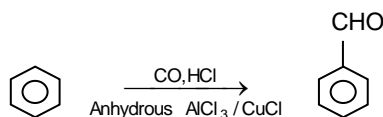


(iii) By side chain chlorination followed by hydrolysis



(iv) By Gatterman - Koch reaction

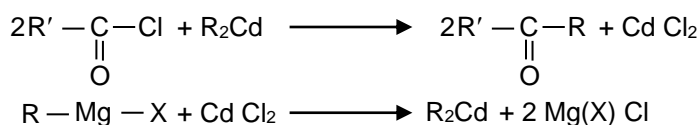
Benzene or its derivatives when treated with CO + HCl in presence of anhydrous aluminium chloride or cuprous chloride give benzaldehyde or its derivatives



Preparation of ketones

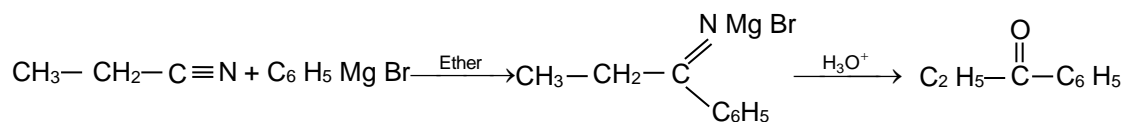
(1) From acid chlorides

Treatment of acid chlorides with dialkyl cadmium give ketones. The dialkyl cadmium is prepared by the reaction of cadmium chloride with Grignard reagent.



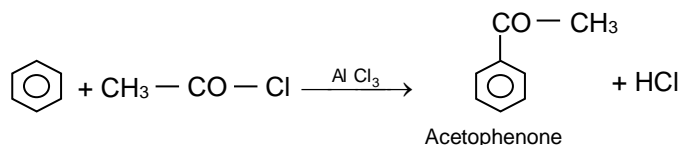
(2) From nitriles

Treatment of nitrile with Grignard reagent followed by hydrolysis give ketones.



(3) By Friedel Craft's reaction

Aromatic ketones can be prepared by treating an aromatic hydrocarbon with an acid chloride in presence of anhydrous AlCl_3 .



This reaction is called Friedel Craft's acylation. This reaction is an example of electrophilic substitution reaction.

Physical properties

Most of the aldehydes are liquids of room temperature (except formaldehyde which is a gas). The lower aldehydes have a sharp pungent smell.

Lower ketones are colourless liquids but higher members are colourless solids. Ketones have a pleasant smell.

Boiling point:

Aldehydes and ketones have higher boiling point than hydrocarbons of comparable molecular masses. This is because aldehydes and ketones contain polar carbonyl groups and therefore they have intermolecular dipole-dipole interactions.

This dipole-dipole interaction is weaker than intermolecular H-bonding in alcohols. Therefore B.P of aldehydes and ketones are relatively lower than the alcohols of comparable molecular masses.

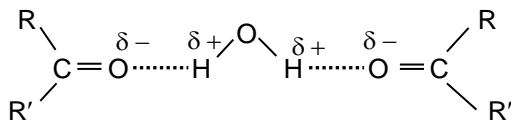
Eg: $\text{CH}_3-\text{CH}_2-\text{CHO}$
M.W = 58 B.P = 322 K

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$
M.W = 60, B.P = 371 K

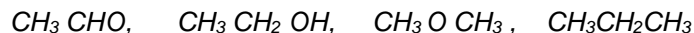
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$
M.W = 58 BP = 309K

Solubility:

The lower members of aldehydes and ketones are soluble in H_2O . It is due to their capability of forming hydrogen bonds with water. As the size of the alkyl group increases, the solubility in water decreases.



Q. Arrange the following compounds in the increasing order of their boiling points.



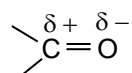
Ans: $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{CH}_3\text{CHO} < \text{CH}_3\text{CH}_2\text{OH}$

CHEMICAL PROPERTIES:

Aldehydes and ketones are highly reactive compounds. Most of the reaction of aldehydes and ketones are similar due to the presence of common carbonyl group.

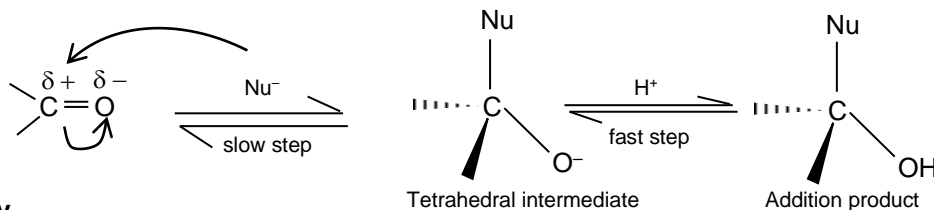
Nucleophilic addition reactions

The carbonyl group is polarized due to the higher electronegativity of oxygen than carbon. Therefore aldehydes and ketones undergo attack by nucleophiles at the carbonyl carbon.



Mechanism

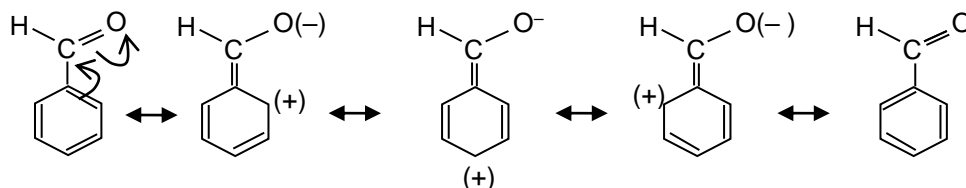
The nucleophile (Nu) will attack the carbonyl carbon from above or below the plane of the carbonyl group to form the C – Nu bond. It is accompanied by heterolytic cleavage of the carbon-oxygen pi bond. The pi bond electrons are transferred to the oxygen atom. During this process the hybridization of carbonyl carbon changes from sp^2 to sp^3 . The negatively charged oxygen then captures a proton from the medium to give the final product.



Reactivity

Aldehydes are more reactive than ketones towards nucleophilic reactions. This is due to the electron-repelling (+ I) inductive effect of alkyl groups. The presence of two alkyl groups at the carbonyl carbon atom in ketones decreases the positive charge over it. Therefore the tendency of attack by a nucleophile decreases. In ketones, the presence of bulky alkyl groups also hinders the approach of the nucleophile to the carbonyl carbon. This factor is called the *steric factor*.

Benzaldehyde is less reactive than aliphatic aldehydes. This is due to the electron releasing resonance effect of benzene ring.



Due to this electron releasing resonance effect (+R effect) the magnitude of positive charge decreases and becomes less susceptible to the nucleophilic attack.

Q. Arrange the following compounds in the increasing order of reactivity

1. Ethanal, Propanal, Propanone, Butanone
2. Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone

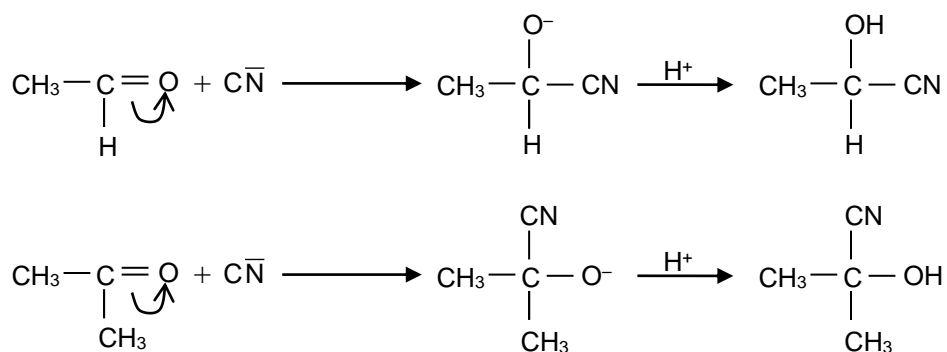
Ans:

1. Butanone < Propanone < Propanal < Ethanal.
2. Acetophenone < *p*-Tolualdehyde < Benzaldehyde < *p*-Nitrobenzaldehyde

I. Addition Reactions

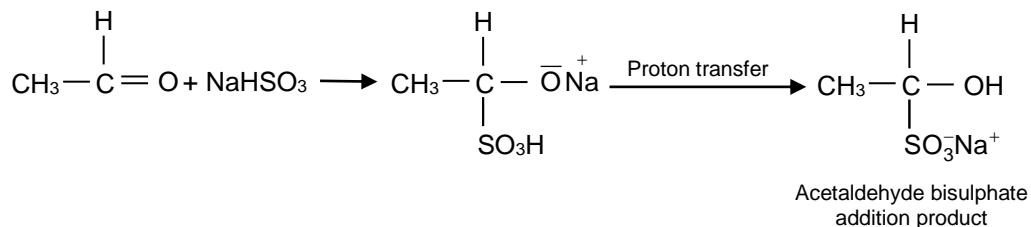
(a) Addition of hydrogen cyanide:

Both aldehydes and ketones form addition products called **cyanohydrins** with HCN. This reaction is slow with pure HCN. Therefore it is catalysed by a base ($HCN + NaOH \rightarrow CN^- + H_2O$)

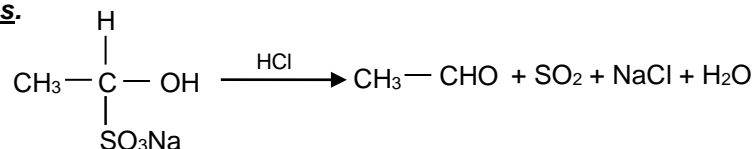


(b) Addition of sodium bisulphite

Sodium hydrogen sulphite adds to carbonyl compounds to form crystalline addition products. Most of the aldehydes and a few ketones like methyl ketones form bisulphite addition products.

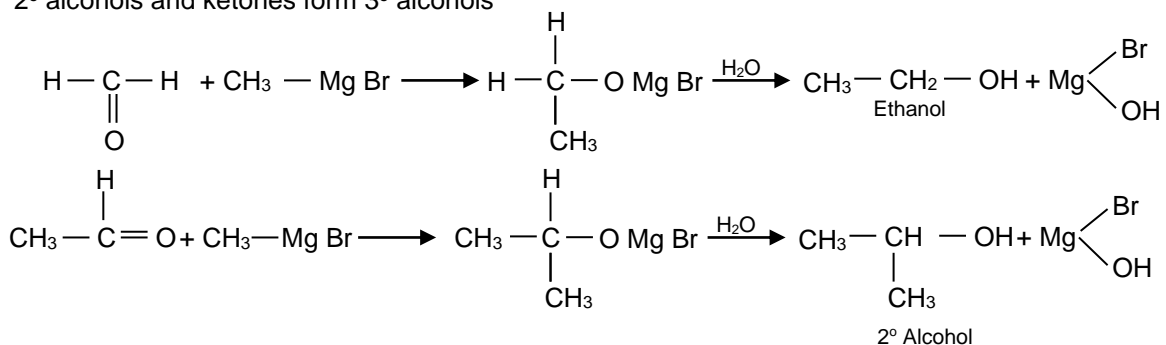


The bisulphate addition compound can be converted back into aldehydes and ketones by treating it with dil acid or alkali. **Hence this reaction can be used for the separation and purification of aldehydes and ketones.**



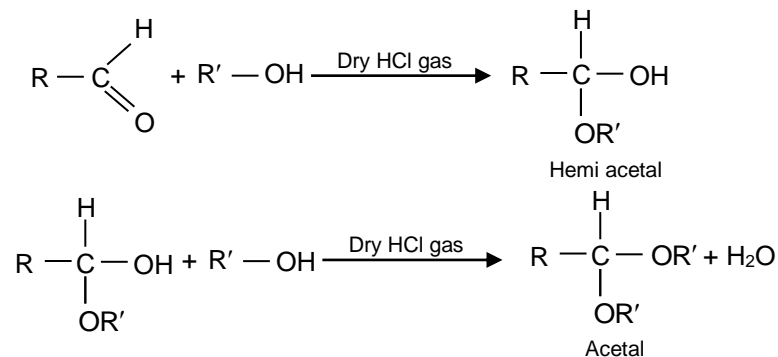
(c) Addition of Grignard reagent:

Aldehydes and ketones form addition compounds with Grignard reagent which on hydrolysis give alcohols. Here formaldehyde form primary alcohol, all other aldehydes form 2° alcohols and ketones form 3° alcohols

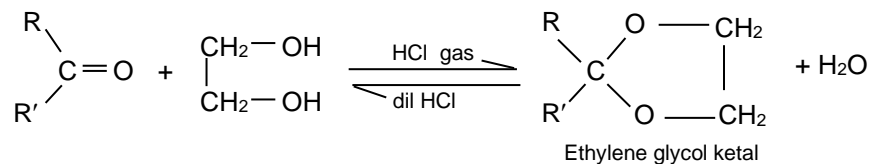


(d) Addition of alcohols

Aldehydes react with monohydric alcohols in the presence of dry HCl gas to form *gem-dialkoxy* compounds called **acetals**. In this reaction addition of one molecule of alcohol results in the formation of a **hemiacetal**. It is an unstable compound and reacts with another alcohol molecule to form stable **acetal**.

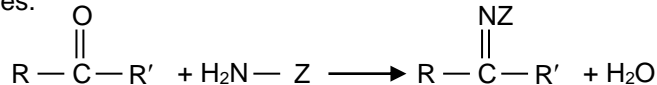


Ketones usually do not react with monohydric alcohols. But ketones react with ethylene glycol to form cyclic products known as **ethylene glycol ketals**

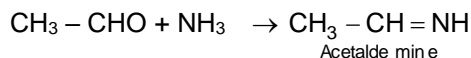


(e) Addition of ammonia and its derivatives

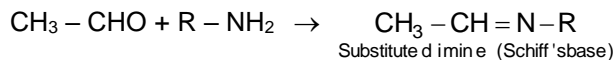
Aldehydes and ketones react with ammonia and its derivatives to give compounds containing $>C=N-Z$ group. These are crystalline compounds and are used for the characterization of aldehydes and ketones.



(1) With ammonia: Aldehydes react with ammonia to imines

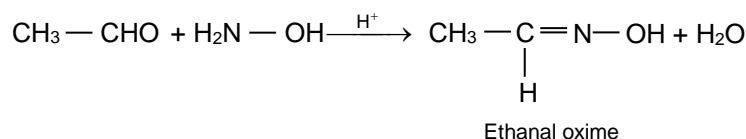


(2) With amine ($R-NH_2$)



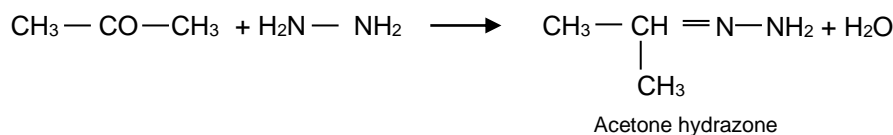
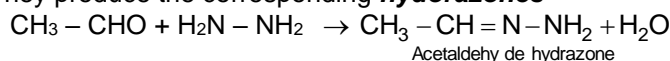
(3) With hydroxylamine:

Aldehydes and ketones react with hydroxylamines to form **oximes**.

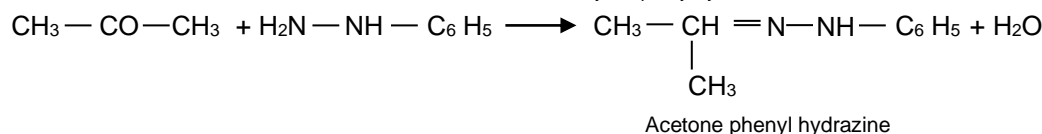
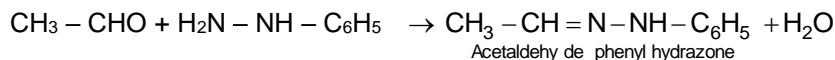


(4) With hydrazine:

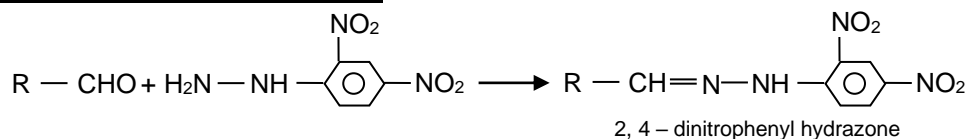
They produce the corresponding **hydrazones**



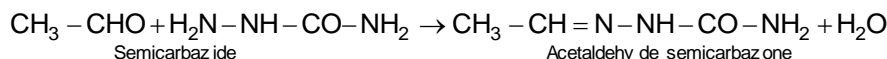
(5) With Phenyl hydrazine: They produce the respective **phenyl hydrazones**



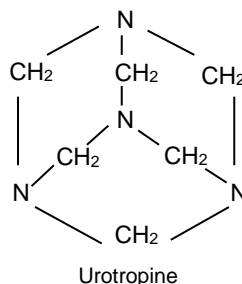
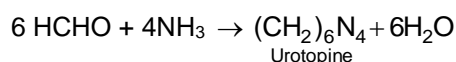
(6) With 2,4-dinitro phenyl hydrazine



(7) With semicarbazide: They give the respective **semicarbazones**.



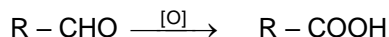
Formaldehyde reacts with ammonia to form **hexamethylene tetraamine**. It is known as **urotropine**. It is used as a medicine to treat urinary infections.



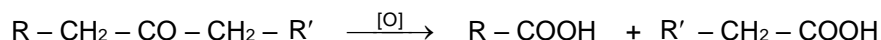
Controlled nitration of urotropine produces an explosive **RDX (Research and development explosive)**

II Oxidation

Aldehydes are easily oxidized to carboxylic acids when treated with common oxidizing agents like nitric acid, KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$. They are even oxidized by mild oxidizing agents such as Ag^+ and Cu^{2+} ions in alkaline medium.

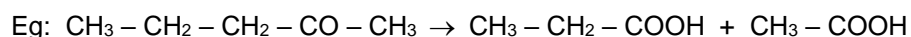


Ketones are not oxidized easily. Under vigorous conditions, the cleavage of carbon-carbon bond takes place yielding a mixture of acids having less number of carbon atoms.



The easy oxidation of aldehyde is due to the presence of a hydrogen atom on the carbonyl group which can be converted into $-\text{OH}$ group. Ketones do not contain any hydrogen attached to the $>\text{C}=\text{O}$ group. Hence they are resistant to oxidation.

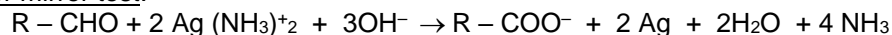
In the case of unsymmetrical ketones, the cleavage occurs in such a way that keto group stays with the smaller alkyl group. This is known as **Popoff's rule**.



Since aldehydes are readily oxidized they behave as good reducing agents

(i) Tollen's test

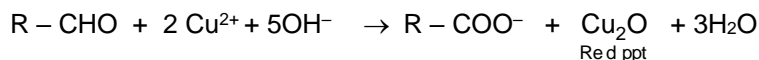
Tollen's reagent is ammoniacal silver nitrate solution. Tollen's reagent contains Ag^+ ions complexed with ammonia, $\text{Ag}(\text{NH}_3)_2^+$, which prevents precipitation of silver oxide in basic solution. In the oxidation of aldehydes with Tollen's reagent, silver ions are reduced to metallic silver and a silver mirror is produced on the inner sides of the test tube. Hence this test is known as silver mirror test.



(ii) Fehling's test

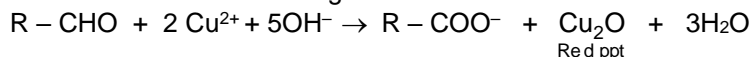
Fehling solution is an alkaline solution of CuSO_4 containing sodium potassium tartrate (Rochelle salt). Fehling's solution comprises of two solutions. **Solution A** \rightarrow Aqueous CuSO_4 . **Solution B** \rightarrow Alkaline sodium potassium tartarate. These two solutions are mixed in equal amounts before the test.

Aldehydes reduce copper (II) to Cu(I) and a red precipitate of cuprous oxide (Cu_2O) is formed.



(iii) Benedict's test

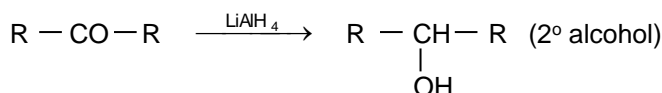
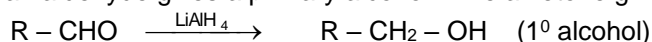
Benedict's solution is alkaline solution of cupric $[\text{Cu(II)}]$ ion complexed with citrate ions. The reaction is same as that of Fehling's solution.



Ketones do not give the above tests. Therefore the above tests are used to distinguish between aldehydes and ketones

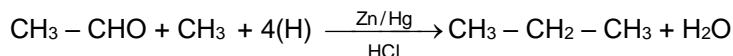
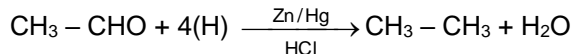
3. Reduction

On reduction using reducing agents like LiAlH_4 , sodium borohydride (NaBH_4) or H_2 in the presence of Ni, an aldehyde gives a primary alcohol while a ketone gives a secondary alcohol.



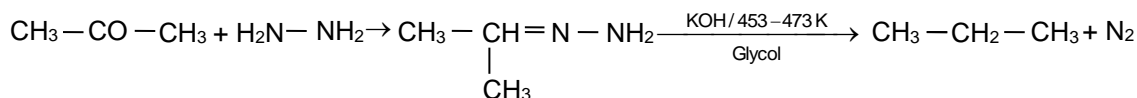
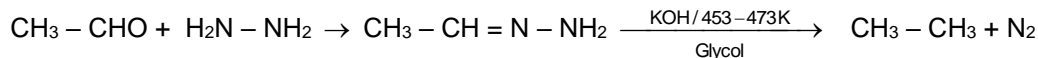
Clemmensen's Reduction

Aldehydes and ketones on reduction with zinc amalgam and con.HCl, give the corresponding hydrocarbons. This reaction is known as **Clemmensen's reduction**.



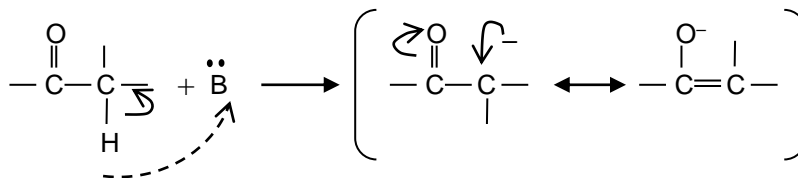
Wolf-kishner Reduction

Aldehydes and ketones can be converted into corresponding hydrocarbons by wolf-kishner reduction. In this method, aldehyde and ketone is heated with hydrazine and KOH in ethylene glycol as solvent.



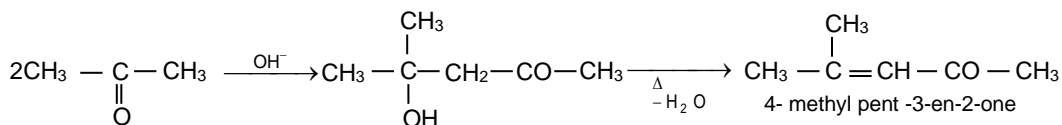
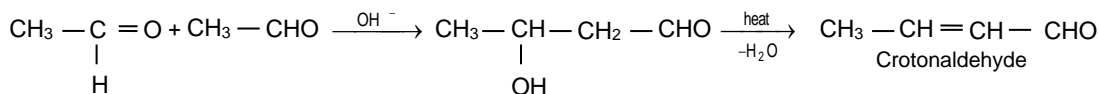
Acidity of α -hydrogen of aldehydes and ketones

The α -hydrogen of aldehydes and ketones are acidic in nature. The acidity of hydrogen is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilization of the conjugate base.



5. Aldol Condensation

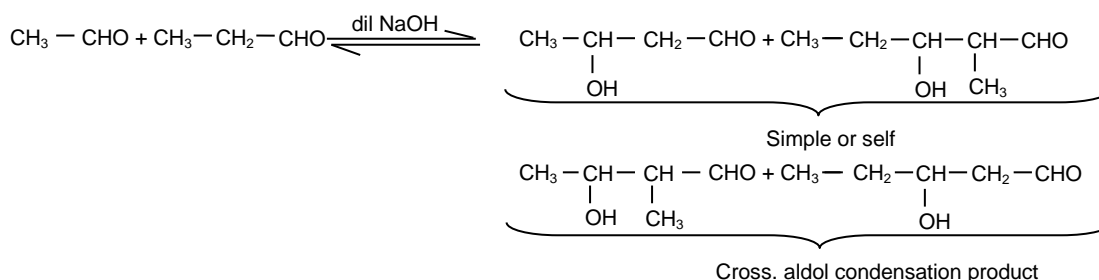
Aldehydes and Ketones **having atleast one α -hydrogen atom**, when treated with dil alkali undergo condensation reaction to form β -hydroxy aldehydes or β - hydroxy ketones. They undergo dehydration very easily to form unsaturated carbonyl compounds. This reaction is known as **aldol condensation**.



The name aldol condensation is derived from the names of two functional groups- aldehyde and alcohol. But ketones on condensation give ketols.

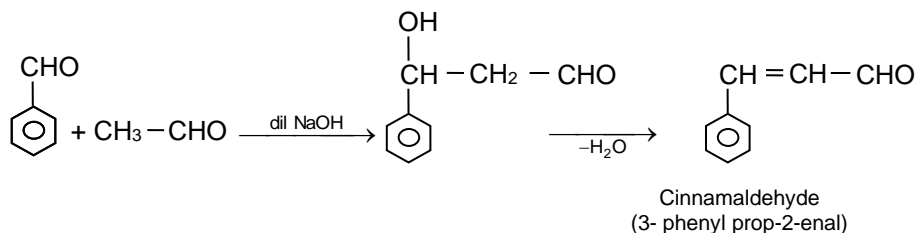
Cross aldol condensation

Aldol condensation of a mixture of two different aldehydes (or ketones) having α -hydrogen gives a mixture of four products. Two of the products are made up of the same carbonyl compound and are called **self or simple aldol condensation products**. The other two products are formed between two different carbonyl compounds. These are called **cross aldol condensation products**.



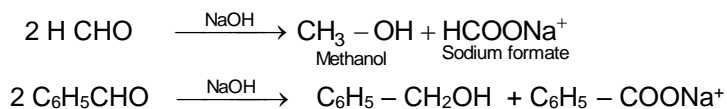
Cinnamaldehyde

Cross aldol condensation between benzaldehyde and acetaldehyde give cinnamaldehyde



(6) Cannizzaro reaction

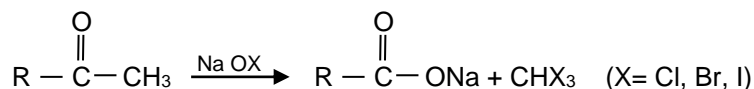
On treating with concentrated NaOH or KOH, aldehydes having no α -hydrogen atoms undergo self-oxidation and reduction reaction to give a mixture of acids and alcohols. Here one molecule of the aldehyde is oxidized to an acid while another molecule is reduced to an alcohol. This reaction is known as **Cannizzaro reaction**



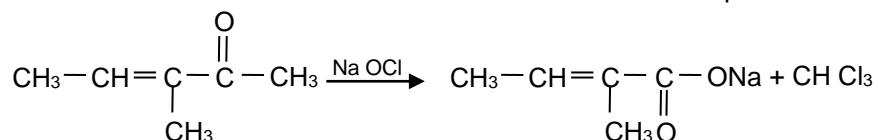
Benzaldehyde, formaldehyde, trimethyl acetaldehyde etc undergo Cannizzaro reaction.

(7) Haloform reaction

Aldehydes and ketones having at least one methyl group linked to the carbonyl group react with sodium hypohalite to give haloform.

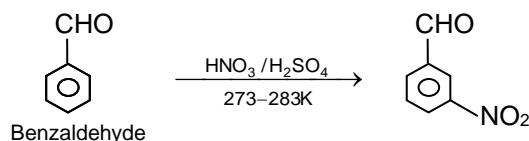


This reaction does not affect a carbon – carbon double bond if present in the molecule.



8. Electrophilic substitution

The carbonyl group acts as a deactivating group and meta directing. Therefore electrophilic substitutions will take place at meta position.

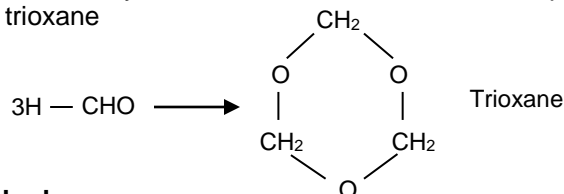


Formalin

40% solution of formaldehyde (8% methanol and 52% water) is known as formalin. Formalin is a disinfectant and a preservative for biological samples.

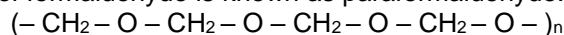
Metaformaldehyde or trioxane.

When formaldehyde is allowed to stand at room temperature, it polymerizes to a trimer called trioxane



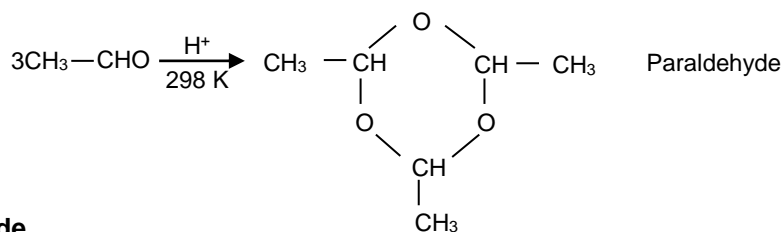
Paraformaldehyde

Polymer of formaldehyde is known as paraformaldehyde.



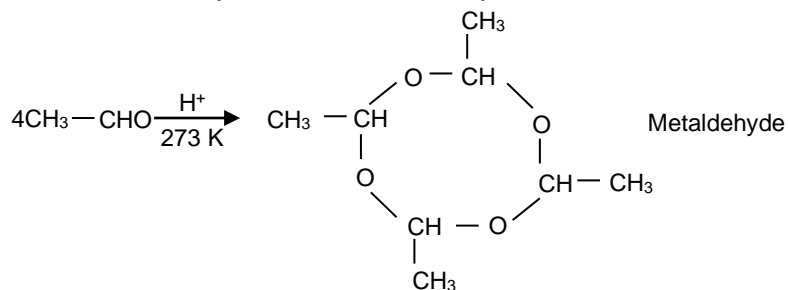
Paraldehyde

A trimer of acetaldehyde is called paraldehyde. Paraldehyde is used in medicine as hypnotic.

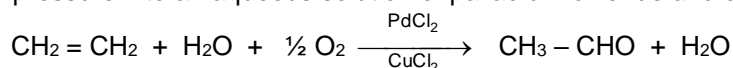


Metaldehyde

A tetramer of acetaldehyde is called metaldehyde.



Wacker's process Acetaldehyde is also manufactured by passing a mixture ethene and O_2 under pressure into an aqueous solution of palladium chloride and cupric chloride catalysts.



Uses of aldehyde

1. Formaldehyde is used for the manufacture of formalin which is used for preserving biological specimens
2. Formaldehyde is also used in the manufacture of bakelite, urea-formaldehyde glue and other polymers.
3. Acetaldehyde is used in the manufacture of acetic acid, ethyl acetate, polymers etc.
4. Acetaldehyde is also used for the production of paraldehyde and metaldehyde. Paraldehyde is used as a hypnotic.
5. Benzaldehyde is used in the manufacture of perfumes and dyes.
6. Acetone and ethyl methyl ketone are common industrial solvents.
7. Many aldehydes and ketones are obtained from nature. Vanillin (from vanilla beans), salicylaldehyde (from meadow sweet) and cinnamaldehyde (from cinnamon) etc. These are used as flavouring agents.

CARBOXYLIC ACIDS


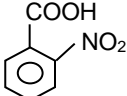
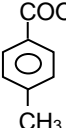
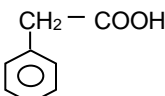
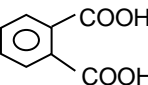
Organic compounds containing carboxyl group $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$ are termed **carboxylic acids**. The carboxyl group contains a carbonyl group attached to a hydroxyl group.

Some higher members of aliphatic carboxylic acids ($\text{C}_{12} - \text{C}_{18}$) occur in natural fats as esters. Hence these are also known as **fatty acids**.

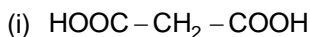
Nomenclature

The trivial names of carboxylic acids are based on their source or origin. Eg: Formic acid – It is obtained from red ants (Latin: *Formica* means ants).

In IUPAC system, the name of an acid is obtained by replacing the terminal 'e' of the corresponding alkane with "**oic acid**".

Formula	Common name	IUPAC name
H—COOH	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
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—COOH}$	n-Butyric acid	Butanoic acid
$\begin{array}{c} \text{CH}_3\text{—CH—COOH} \\ \\ \text{CH}_3 \end{array}$	Isobutyric acid	2-methyl propanoic acid
$\begin{array}{c} \text{CH}_3\text{—CH}_2\text{—CH—COOH} \\ \\ \text{Br} \end{array}$	α -Bromobutyric acid	2-Bromobutanoic acid
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—COOH}$	n- Valeric acid	Pentanoic acid
	Benzoic acid	Benzoic acid
	O-nitro benzoic acid	2-nitrobenzoic acid
	p-Toluic acid	4-methyl benzoic acid
	Phenyl acetic acid	2-phenyl ethanoic acid
	Phthalic acid	Benzene-1,2-dicarboxylic acid

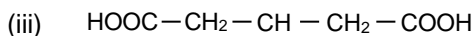
Polycarboxylic acids



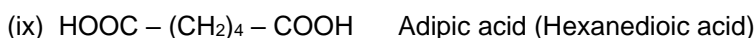
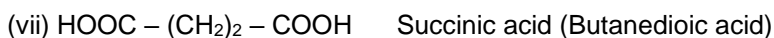
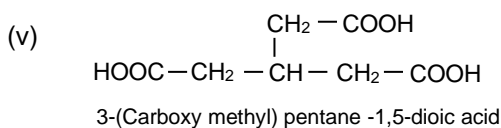
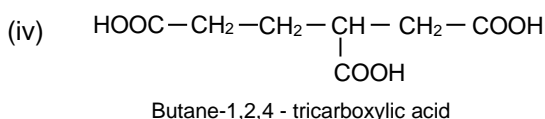
Propanedioic acid
(Malonic acid)



$\begin{array}{c} | \\ \text{CH}_3 \end{array}$
[2 - methyl butanedioic acid]

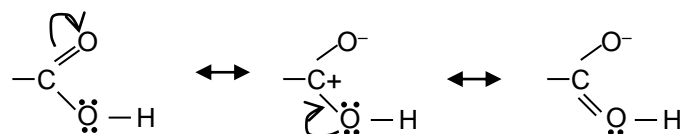


$\begin{array}{c} | \\ \text{COOH} \end{array}$
Propane-1,2,3 - tri carboxylic acid



Structure of carboxyl group

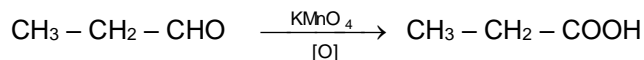
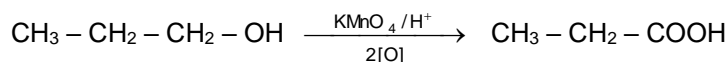
In carboxylic acid, the bonds to the carboxyl carbon lie in one plane. The bond angle is 120° . The carboxyl carbon is less electrophilic due to the possible resonance structures.



Methods of Preparation

(i) By the oxidation of primary alcohols and aldehydes.

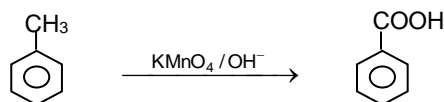
Primary alcohols and aldehydes are readily oxidized to the corresponding carboxylic acids by oxidizing agents like KMnO_4 in acidic, neutral or alkaline medium or $\text{K}_2\text{Cr}_2\text{O}_7$ and CrO_3 in acidic medium.



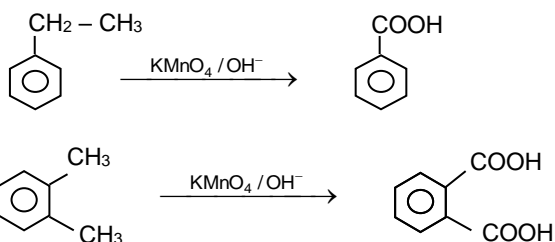
Oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ or CrO_3 in acidic media often gives some esters. Therefore oxidation with KMnO_4 in neutral or alkaline medium is preferred.

(ii) From Alkyl benzenes

Alkyl benzenes on oxidation with alkaline KMnO_4 give aromatic acids.

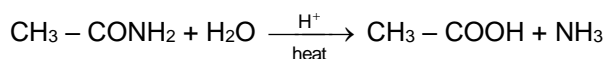
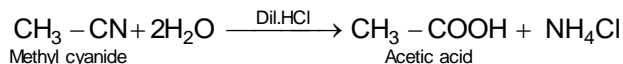


The alkyl side chain gets oxidized to $-\text{COOH}$ group irrespective of the size of the chain.



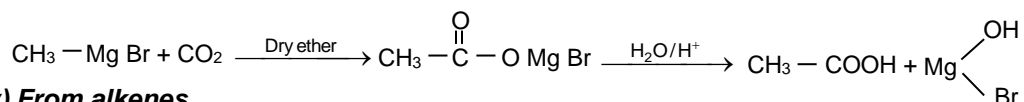
(iii) From nitriles and amides

Alkyl cyanides on hydrolysis with dilute acids or alkalis give carboxylic acids.



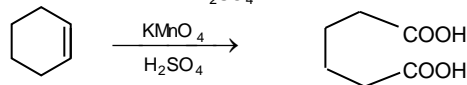
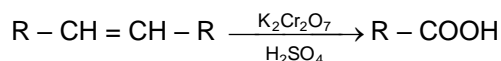
(iv) From Grignard reagents

Grignard reagents when treated with carbon dioxide give carboxylic acids.



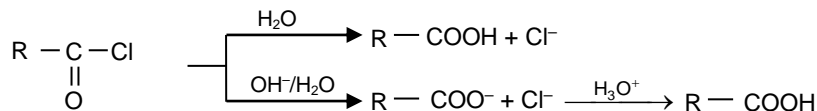
(v) From alkenes

Alkenes are oxidized to acids by oxidizing agents like chromic acid or acidic or alk. KMnO_4 or acidic $\text{K}_2\text{Cr}_2\text{O}_7$

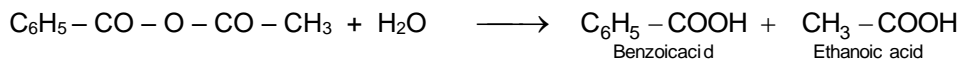


(vi) From acid halides, anhydrides and esters

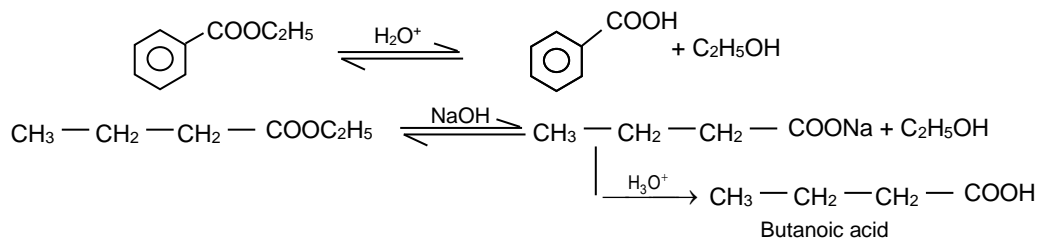
Acid halides give carboxylic acids when hydrolysed with water. They are more readily hydrolysed with aqueous base to give carboxylate ions. This on acidification give acids..



Anhydrides are hydrolysed by water to give acids



Acidic hydrolysis of esters directly give acids. But basic hydrolysis give carboxylates which on acidification give acids.



Physical Properties

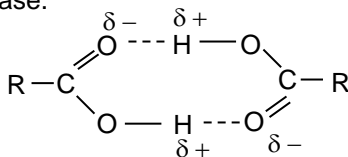
The first three aliphatic acids are colourless liquids with pungent smell. The next six are oily liquids. The higher members are colourless, odourless waxy solids. Benzoic acid is a crystalline solid.

Solubility:

They are soluble in water due to inter-molecular hydrogen bonding with water molecules. With increase in size of the alkyl group, solubility decreases. Higher members are practically insoluble in water.

Boiling Point

Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to the presence of intermolecular hydrogen bonding. Due to hydrogen bonding carboxylic acid exists as a dimer. The hydrogen bonds are not broken completely even in the vapour phase.



The O–H bond in carboxylic acids is more polar than O–H bond in alcohols. This is due to electron withdrawing effect of carbonyl group on O–H. Hence hydrogen bonding in carboxylic acids are more stronger than those in alcohols.

Due to dimeric structure the effective molecular mass of the acid becomes double the actual mass. This is evident from its colligative properties

The melting points and boiling points of aromatic acids are usually higher than those of aliphatic acids of comparable molecular mass.

Chemical Properties

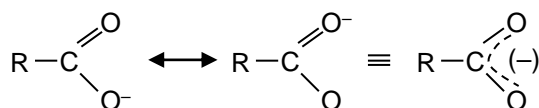
I. Acidic nature

Carboxylic acids are the most acidic amongst the organic compounds. However, they are less acidic than mineral acids (H_2SO_4 , HCl , HNO_3 etc)

Carboxylic acids are acidic due to the presence of polar O–H group. In aqueous solution, it ionizes to give carboxylate anion and the hydronium ion.



The carboxylate ions are stabilized by resonance.



At equilibrium, the equilibrium constant K_a is expressed as

$$K_a = \frac{[\text{R} - \text{COO}^-] [\text{H}_3\text{O}^+]}{[\text{R} - \text{COOH}]}$$

The equilibrium constant k_a is called **acidity or dissociation constant**. Larger the value of K_a , the stronger is the acid. But it is more convenient to express the acidic strength in terms of its $\text{p}K_a$ value ($\text{p}K_a = -\log K_a$). Now, smaller the value of $\text{p}K_a$, stronger is the acid.

Carboxylic acids are more acidic than phenols. Why?

The conjugate base of carboxylic acid (carboxylate ion) is stabilized by two equivalent resonance structures. Here the negative charge is at the more electronegative oxygen atom. But the conjugate base of phenol (phenoxide ion) has non equivalent resonance structures. Moreover the negative charge is at the less electronegative carbon atom.

Effect of substituents on acidic strength

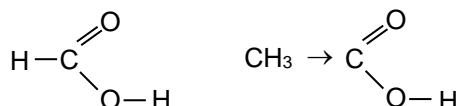
The substituents present on the aliphatic chain or aromatic ring affect the acidity of carboxylic acids.

The electron withdrawing groups stabilize the carboxylate ion by dispersal of the negative charge. Hence they increase the strength of the acid.

The electron releasing groups cause concentration of negative charge and thus destabilize the carboxylate anion. Hence they decrease the strength of the acid.

Electron withdrawing groups like halo group, $-\text{NO}_2$, $-\text{CN}$ etc increase the acidity. Electron donating groups like alkyl groups decrease the acidity of carboxylic acids.

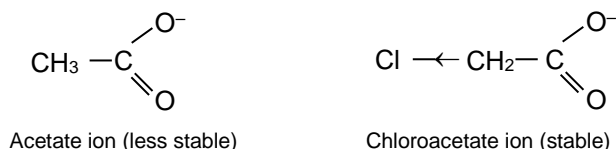
(i) $\text{H} - \text{COOH}$ is more acidic than $\text{CH}_3 - \text{COOH}$



In acetic acid the electron donating effect (+I effect) of the methyl group destabilizes the anion. Hence it is weaker acid than formic acid.

(ii) $\text{CH}_3 - \text{COOH} < \text{ClCH}_2 - \text{COOH} < \text{Cl}_2\text{CH} - \text{COOH} < \text{Cl}_3\text{C} - \text{COOH}$

The acidic strength increase from acetic acid to trichloro acetic acid. Compared to the acetate ion, the electron withdrawing chlorine atom in chloro acetate ion tends to decrease the electron density over carboxylate ion. Hence chloroacetate ion is more stabilized.

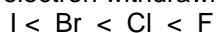


The increase in number of chlorine atoms increases the acidity of the acid.

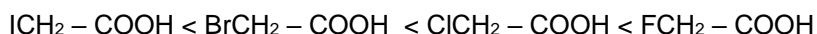
(iii) $\text{CH}_3 - \overset{\alpha}{\underset{\text{Cl}}{\text{CH}}} - \text{COOH} > \overset{\beta}{\underset{\text{Cl}}{\text{CH}_2}} - \text{CH}_2 - \text{COOH}$

The effect of substituent decreases as its distance from the $-\text{COOH}$ group increases.

(iv) The effect of electron withdrawing is different for different halogens

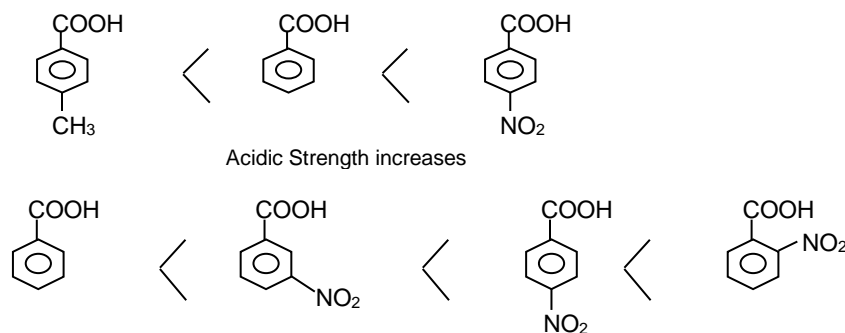


Hence the acidic strength of the acids increases in the order.



Acid strength of substituted benzoic acids

Electron withdrawing groups like $-\text{Cl}$, $-\text{NO}_2$, etc increase the acidic strength. The electron releasing groups such as $-\text{CH}_3$, $-\text{NH}_2$ etc decrease the acidic strength.

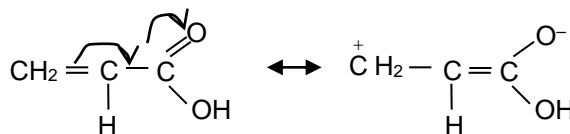


The effect is more pronounced at para position as compared to that at meta position.

The order of acidic strength

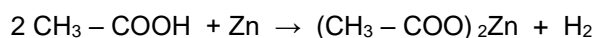
$\text{CF}_3\text{COOH} > \text{CCl}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{NO}_2\text{CH}_2\text{COOH} > \text{NC-CH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{HCOOH} > \text{ClCH}_2\text{CH}_2\text{COOH} > \text{C}_6\text{H}_5\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{COOH}$

The attachment of phenyl or vinyl group to carboxylic acid increases the acidity of carboxylic acids. This is because of greater electronegativity of sp^2 hybridised carbon. (But this is against the decrease expected due to resonance effect shown below.)



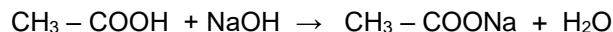
1. Reaction with metals

Carboxylic acids react with metals such as Na, K, Zn etc and liberate hydrogen gas.



2. Reaction with alkalies

Carboxylic acids react with alkalies (NaOH, KOH) to form salt and water.

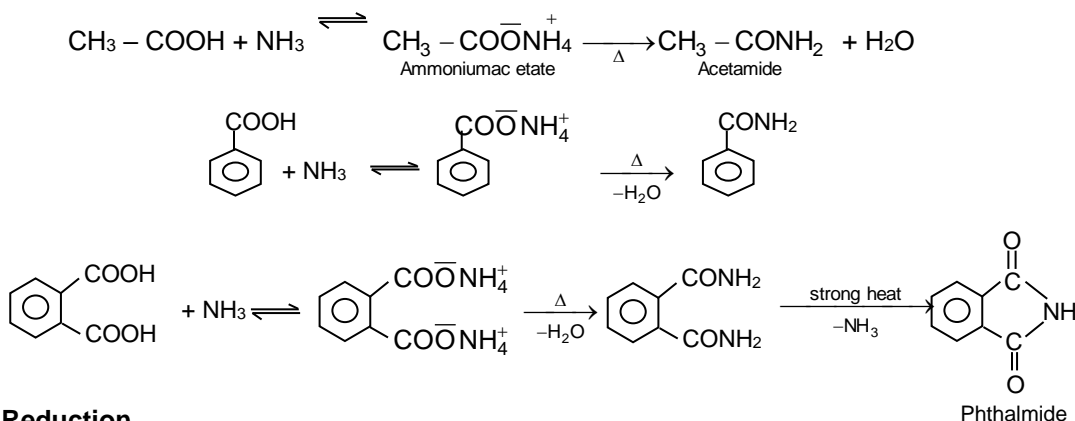


3. Reaction with bicarbonate (Test for true acids)



4. Reaction with ammonia

Carboxylic acids react with ammonia to form ammonium salts which on heating gives **amides**

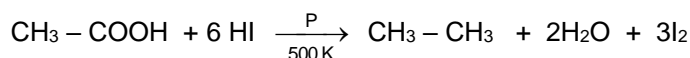


II. Reduction

Lithium aluminium hydride can reduce carboxylic acids to primary alcohols



Carboxylic acids can be reduced to alkanes on reaction with HI in the presence of phosphorus at 500K.

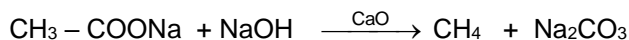


But **NaBH_4** (Sodium borohydride) does not reduce the carboxylic acid.

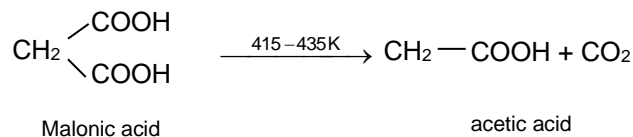
Decarboxylation

(i) Sodalime decarboxylation.

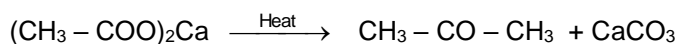
Sodium or potassium salts of carboxylic acids on heating with soda-lime (NaOH and CaO) give alkanes with one carbon less than the parent acids.



When two carboxyl groups are attached to the same carbon atom, decarboxylation takes place by simple heating.

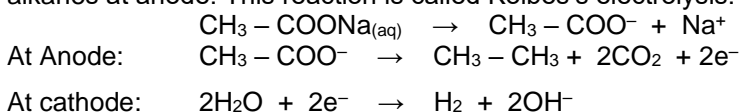


(ii) Calcium salts of carboxylic acids on heating gives aldehydes and ketones.



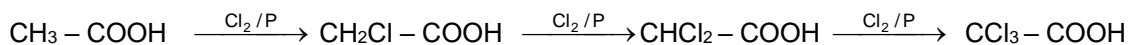
(iii) Kolbe's electrolysis:

Aqueous solutions of sodium or potassium salts of carboxylic acids on electrolysis give alkanes at anode. This reaction is called Kolbe's electrolysis.



HVZ- Reaction [Hell – Volhard – Zelinsky Reaction]

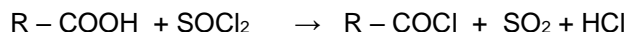
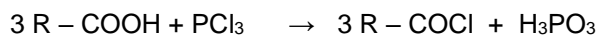
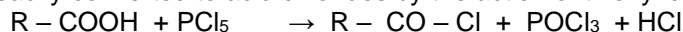
When carboxylic acids are treated with Cl_2 or Br_2 in the presence of red phosphorus, the α -hydrogen atoms of carboxylic acids are replaced by chlorine or bromine. This reaction continues till all the α -hydrogens are replaced



This reaction has great synthetic importance as the halogen atom can be replaced by a number of other groups giving useful products.

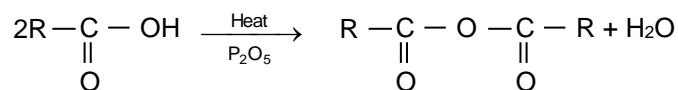
Reaction with PCl_5 , PCl_3 and SOCl_2

Acids can be readily converted to acid chlorides by the action of thionyl chloride, PCl_3 or PCl_5 .



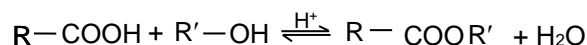
Formation of anhydride

Carboxylic acids on heating with mineral acids such as H_2SO_4 or P_2O_5 give corresponding acid anhydrides.

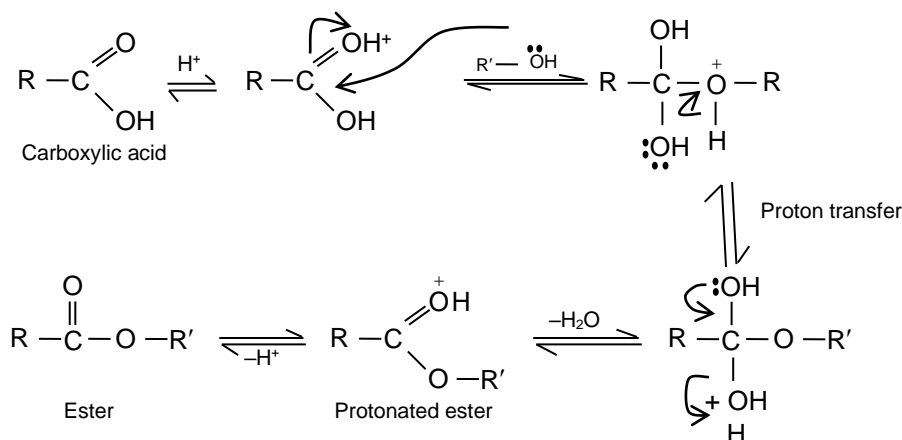


Esterification

Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated H_2SO_4 or HCl as catalyst.

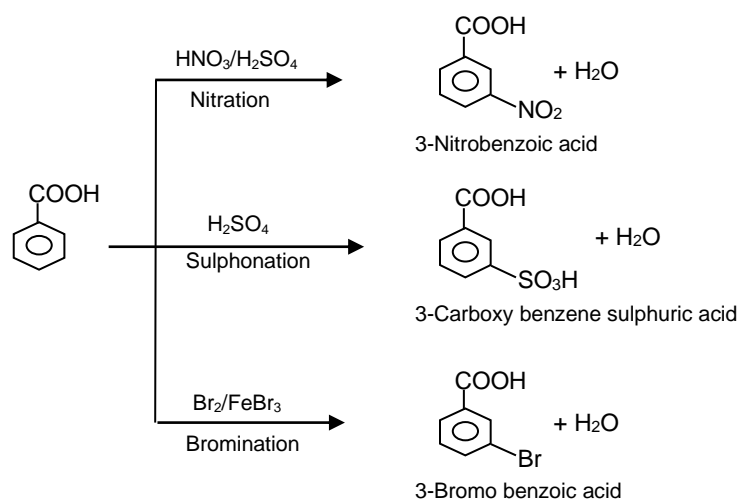


Mechanism: Esterification is a kind of **nucleophilic acyl substitution**



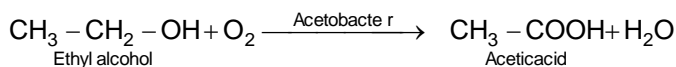
Ring substitution in aromatic acids

Carboxyl group is a meta directing group since it is electron withdrawing.



Vinegar

3 – 7% solution of $CH_3 - COOH$ is called **vinegar**. It is obtained by the fermentation of ethyl alcohol by the bacteria '**acetobacter**'.



Uses of acids:

Formic acid is used in rubber, leather and electroplating industries.

Acetic acid is used in the manufacture of rayon and in plastic, rubber and silk industries. It also finds use as a solvent. Vinegar is used in cooking.

Benzoic acid Esters of benzoic acid are used in perfume industry. The salts of benzoic acid such as **sodium benzoate** are used as food preservatives. 1,2- Benzene dicarboxylic acid (Phthalic acid) is used in the manufacture of plasticisers and resins. 1,4 – Benzene dicarboxylic acid (terephthalic acid) is the raw material for polyester production.

Glacial acetic acid

Water free acetic acid obtained by melting of the crystals is called glacial acetic acid.