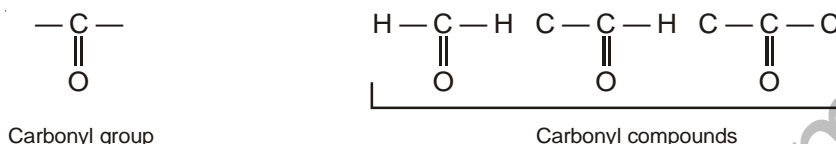


Aldehyde, Ketone & Benzaldehyde

1. CARBONYL COMPOUNDS

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



2. ALDEHYDE

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



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

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

3. KETONES

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



Where Z = Hydrocarbon radical (or substituted hydrocarbon radical)

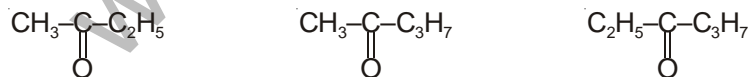
Ketonic group is represented by the condensed formula –CO– for convenience.

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

Simple or symmetrical ketones :



Mixed or unsymmetrical ketones :

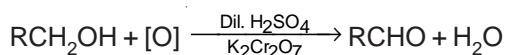


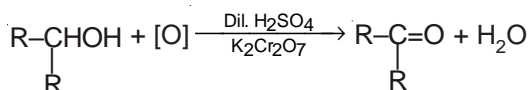
4. PREPARATION OF CARBONYL COMPOUNDS

Methods of Preparation of Both Alkanals and Alkanones

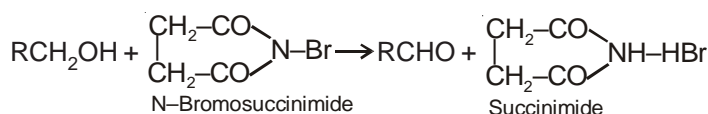
[a] **By Oxidation of Alkanols :**

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



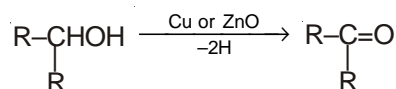
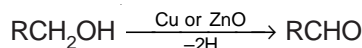


On using N-bromosuccinimide (NSB) as an oxidant, the reaction takes place as follows :



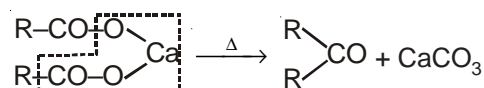
[b] By Dehydrogenation of Alkanols :

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

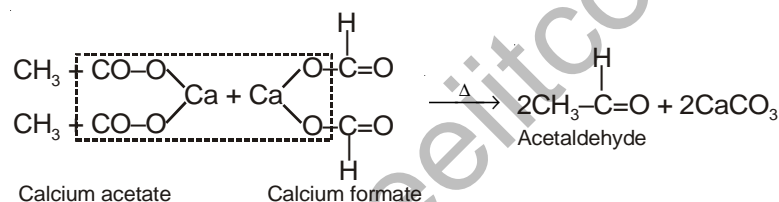


[c] By Dry Distillation of Calcium Alkanoates :

When calcium salts of alkanolic acids are subjected to dry distillation, then carbonyl compounds are formed. The yield increases on taking barium, manganese and thorium salts of alkanolic acids. Formaldehyde is formed on taking calcium formate (R = H) and acetone is formed on taking calcium acetate (R = CH₃).

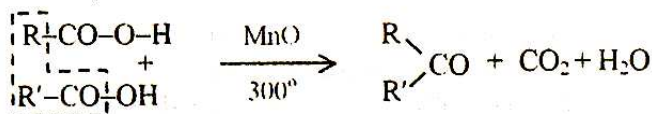


Acetaldehyde can be formed by taking a mixture of calcium formate and calcium acetate.



[d] By Action of MnO on Alkanoic Acids :

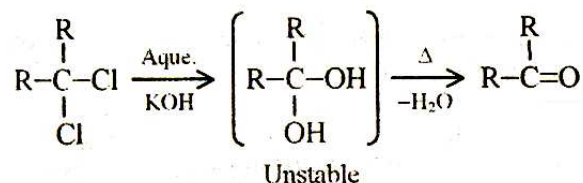
Alkanals and alkanones can be obtained by passing vapours of alkanolic acids over heated manganous oxide at 300°.



Formaldehyde is prepared from formic acid (R = R' = H), acetone from (R = R' = CH₃), and acetaldehyde from a mixture of acetic acid (R' = CH₃) and formic acid (R = H).

[e] By Alkaline Hydrolysis of gem-Dihalides :

Carbonyl compounds are formed on heating alkylidene dihalides with aqueous caustic alkali solution.

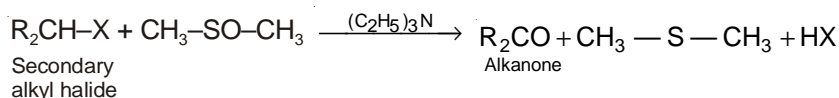
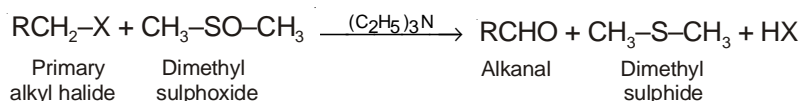


Methanal is formed (in very low yield) from methylene dichloride (CH_2Cl_2), ethanal from ethylidene dichloride (CH_3CHCl_2) and propanone from isopropylidene dichloride ($\text{CH}_3\text{CCl}_2\text{CH}_3$).

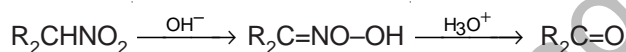
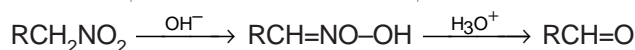
Above method is appropriate for preparation of ketones because ketones are more stable towards caustic alkali whereas aldehydes are very reactive in alkaline medium and form several by-products.

[f] By Oxidation of Alkyl Halide :

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



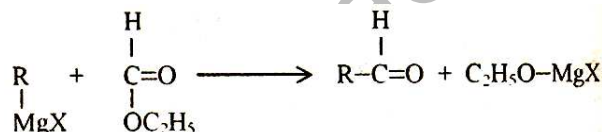
[g] By Oxidation of Nitroalkanes :



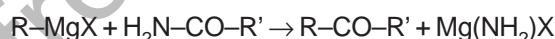
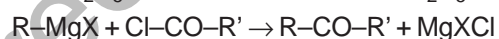
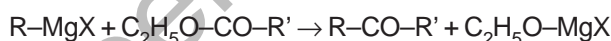
By Nef reaction, formaldehyde can be obtained from nitromethane, acetaldehyde from nitroethane and acetone from 2-nitropropane.

[h] By Grignard's Reagents :

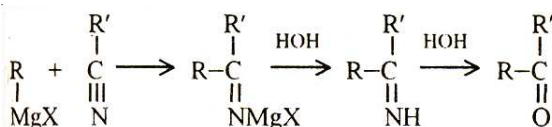
[i] With ethyl formate : Alkanal is formed by reaction of formic ester and an alkylmagnesium halide.



Ketones are obtained from acetic and higher esters. Acid chlorides and amides can be taken in place of esters. However HCOCl cannot be taken because it is unstable.

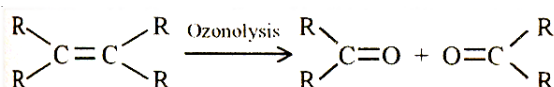


[ii] With higher alkyl cyanides : Alkanones are formed on hydrolysis after reaction of an alkylmagnesium halide with ethyl cyanide or its higher homologue.



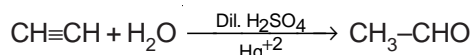
Reactivity of α hydrogen atom decreases due to +I effect of methyl group in ethyl cyanide. Therefore, better yield of the ketone is obtained by its reaction with an alkylmagnesium halide.

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



[j] By Hydration of Alkynes :

[i] Catalytic Acidic Hydration : Acetaldehyde is formed on passing acetylene in 40% aqueous solution of H_2SO_4 at 60° in the presence of 1% HgSO_4 . It is called Kucherov reaction.

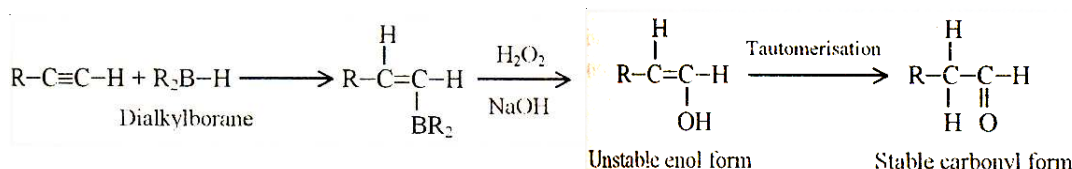


Alkanones are formed on using higher alkynes.



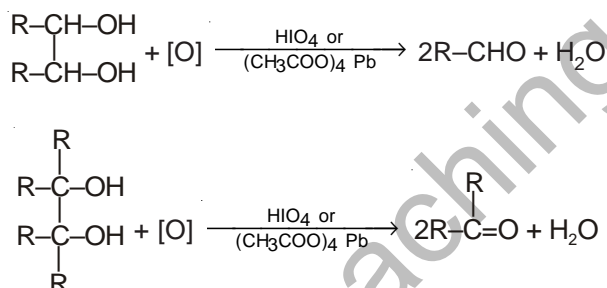
[ii] Hydration Through Hydroboration :

When a dialkylborane is reacted with an alkyne, then dialkylvinylborane adduct is formed, which on reacting alkaline hydrogen peroxide solution forms a carbonyl compound. Alkanals are formed from terminal alkynes, and alkanones from nonterminal alkynes.



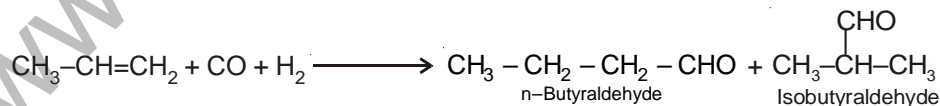
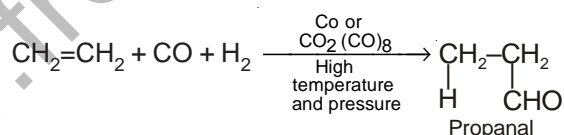
In the above reaction the ethanal is formed from acetylene propanal from propyne butanal from 1-butyne and butanone from 2-butyne.

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



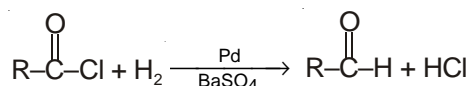
5. METHODS OF PERPARATION OF ONLY ALKANALS

[a] **By Oxo Reaction :** When a mixture of an alkene, carbon monoxide and hydrogen is passed over cobalt catalyst at high temperature and pressure, then alkanals are formed. Dicobalt octacarbonyl $[\text{Co}_2(\text{CO})_8]$ can be used as a catalyst in place of cobalt. Due to addition of hydrogen and formyl group on unsaturated carbon atoms of alkene, this reaction is called hydroformylation.



[b] **By Rosenmund Reaction :**

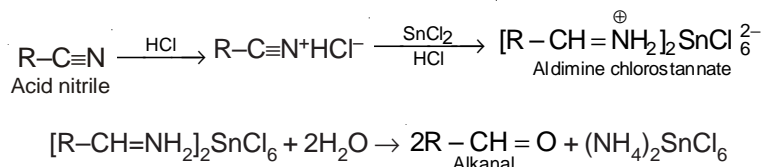
Aldehydes are formed on reduction of a carboxylic acid chloride in boiling xylene medium by hydrogen and palladised barium sulphate.



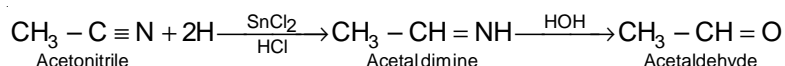
Acetaldehyde is formed on taking acetyl chloride ($\text{R} = \text{CH}_3$). Formaldehyde cannot be prepared by Rosenmund reaction, because HCOCl is not a stable compound, BaSO_4 acts as a catalyst poison and decreases the catalytic efficiency of Pd catalyst, due to which further reduction of acetaldehyde formed to primary alcohol cannot take place.

[c] By Reduction of Acid Nitriles :

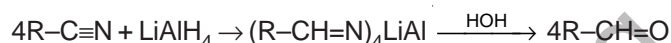
[i] By Stephen Reaction : By dissolving an alkyl cyanide in ether and reacting it with stannous chloride and conc. hydrochloride, aldimine chlorostannate salt is obtained. Alkanal is formed on hydrolysis of this salt.



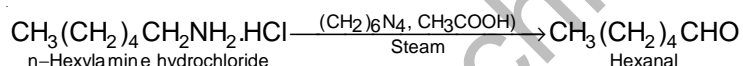
Taking the example of acetonitrile (methyl cyanide) Stephen reaction can be shown expressed as follows.

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

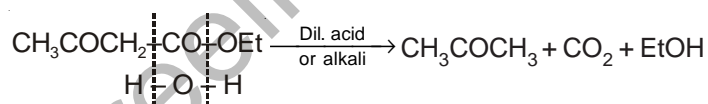
When calculated amount of LiAlH_4 is dissolved in ethereal solution of an alkyl cyanide, followed by hydrolysis of the product then an alkanal is formed at low temperature.



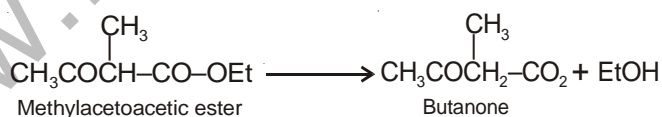
[d] By Sommelet Reaction : In 1953, Angyal first obtained hexanal in 50% yield on passing steam through the aqueous solution of n-hexylamine hydrochloride in the presence of urotropine and acetic acid.

**6. METHODS OF PREPARATION OF ONLY ALKANONES**

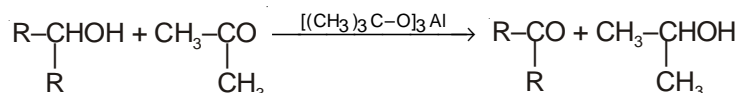
[a] By Alkaline Hydrolysis of Acetoacetic Ester of Its Alkyl Derivatives : Acetone is formed on hydrolysis of acetoacetic ester by dilute acid or alkali.



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



[b] By Oppenauer Oxidation : In order to prepare alkanone easily, Oppenauer oxidation of secondary alkanols is done. In this process, a secondary alkanols is refluxed with aluminum tert-butoxide in excess amount in acetone. Acetone is reduced to isopropyl alcohol.



[3] From Dialkylcadmium : A ketone and an alkylcadmium chloride are formed on reacting a dialkylcadmium with an acid chloride.



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



7. PHYSICAL PROPERTIES

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

8. REACTIONS

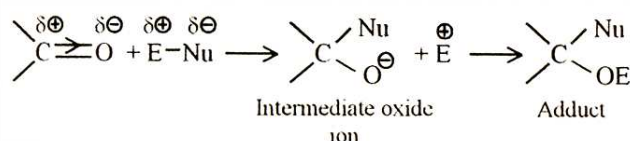
It would be appropriate to learn the reactions of carbonyl compounds under the following points.

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

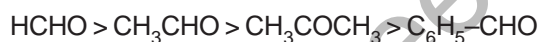
Reaction Similar in Aldehydes and Ketones :

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

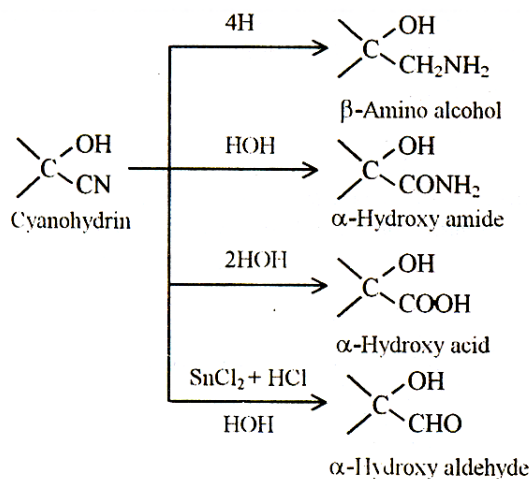
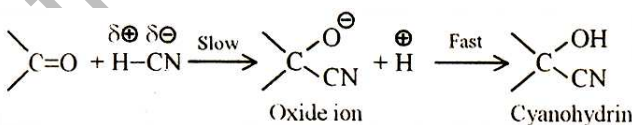
- [a] **Nucleophilic Addition :** Representative mechanism of carbonyl compounds is nucleophilic addition. Addition of a reagent E–Nu on carbonyl group of carbonyl compound can be exhibited as follows :

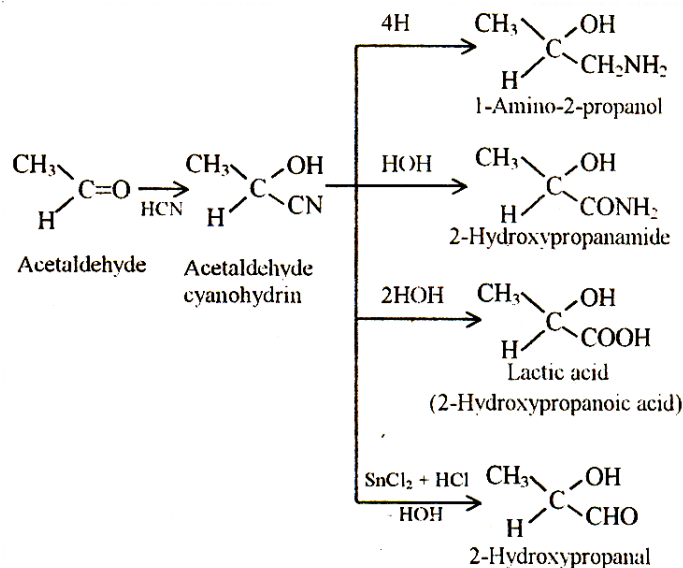


Rate of nucleophilic addition reaction of carbonyl compounds decreases in the following order :

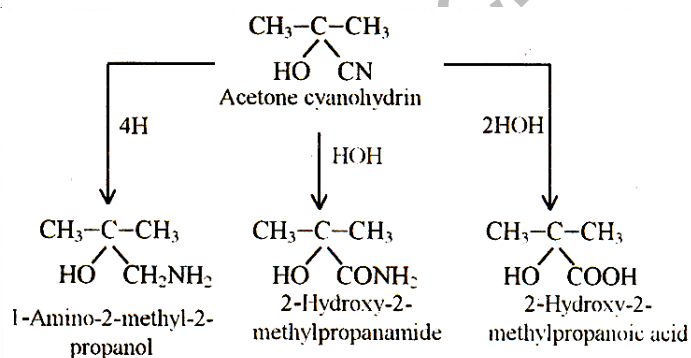
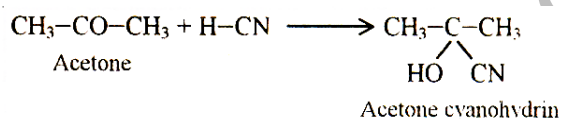


- [1] **With Hydrogen Cyanide :**

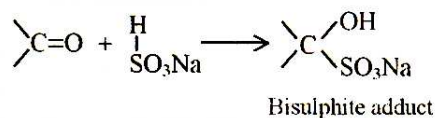




Acetone cyanohydrin is formed on reacting acetone with HCN.

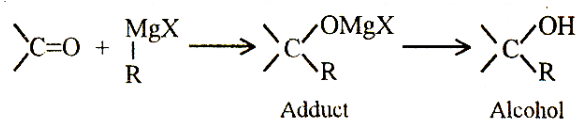


[2] With Sodium bisulphite :



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

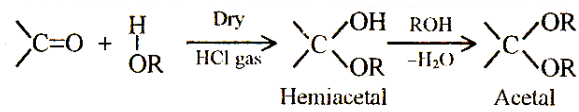
[3] With Grignard's Reagents :



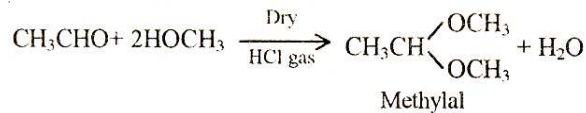
In the above reaction, HCHO forms primary alcohols, other aldehydes form secondary alcohols and ketones form tertiary alcohols.

[4] With Alcohols :

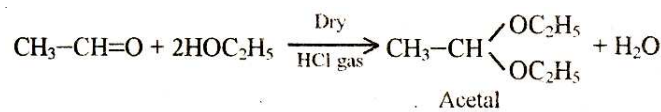
Acetals are obtained by the reaction of alkanals with alkanols in the presence of dry HCl gas. Hemiacetals are formed as intermediates, which are hydroxy ethers. Acetals are dialkoxyalkanes. Anhydrous $ZnCl_2$ can also be taken in place of dry HCl gas.



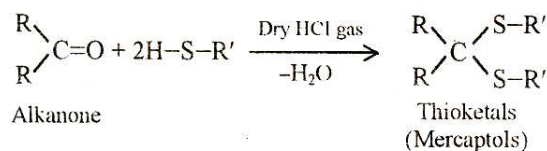
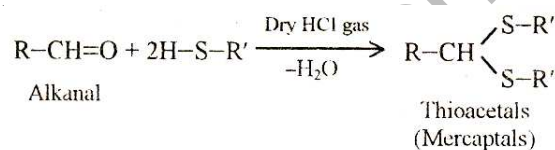
Methylal is the common name of the acetal formed by the reaction of acetaldehyde and methanol.



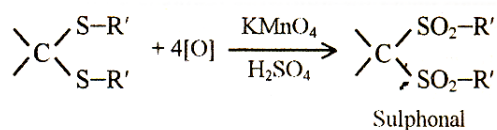
An acetal obtained by the reaction of acetaldehyde and ethanol is simply known as acetal, whose systematic IUPAC name is 1,1-diethoxyethane.

**[5] With Mercaptans :**

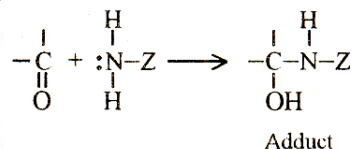
Thiols (Mercaptans) are stronger nucleophiles than alcohols. Therefore, they react with aldehydes as well as ketones to form thioacetals (or mercaptals) and thioketals (or mercaptols).



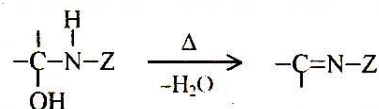
Sulphonals are formed on the oxidation of thioacetal and thioketal by acidified permanganate. Sulphonals are used as hypnotics.

**[6] With Ammonia :**

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



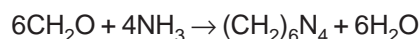
The end product is formed by elimination of water from the adduct under appropriate energy condition.



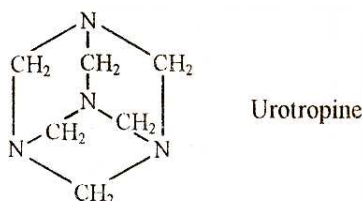
In the above two steps, it appears that an unsaturated condensation product is formed by liberation of the water molecule from carbonyl group and nitrogenous nucleophile.



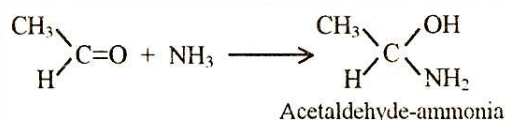
- [i] **With Formaldehyde** : When ammonia is added to formalin (40% aqueous solution of formaldehyde), then beautiful shining white crystals of urotropine are obtained at low temperature.



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

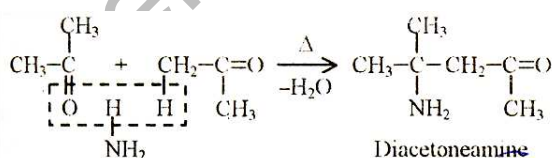


- [ii] **With Acetaldehyde** : The reaction between acetaldehyde and ammonia takes place at room temperature and an adduct acetaldehyde–ammonia is obtained.



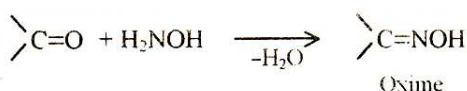
Acetaldimine is formed by the elimination of water molecule on heating acetaldehyde–ammonia, which undergoes polymerisation to form a nonaromatic heterocyclic addition trimer, named 2,4,6–trimethylhexahydro–1,3,5–triazine trihydrate as the main product.

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

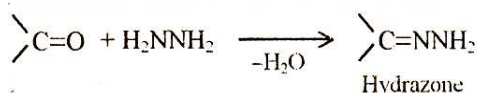


- [8] **With Ammonia Derivatives**

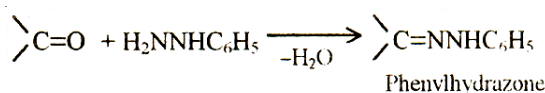
- [i] **With Hydroxylamine** :



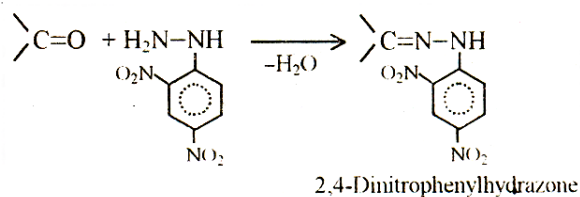
- [ii] **With Hydrazine** :



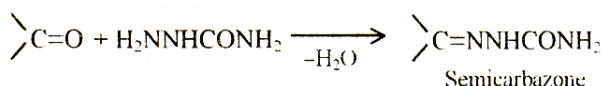
- [iii] **With Phenylhydrazine** :



[iv] With 2,4-Dinitrophenylhydrazine :



[v] With Semicarbazide :



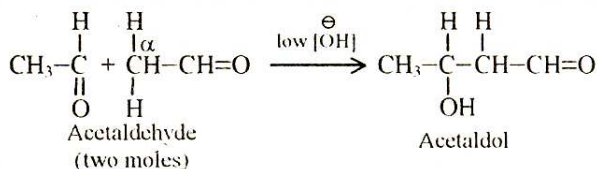
On reacting a carbonyl compound with 2,4-dinitrophenylhydrazine, a yellow precipitate of 2,4-dinitrophenylhydrazone derivative is obtained. White precipitate is obtained by the reaction with hydroxylamine, hydrazine phenylhydrazine and semicarbazide. The pure parent carbonyl compound can be obtained by hydrolysis of the above five derivatives.



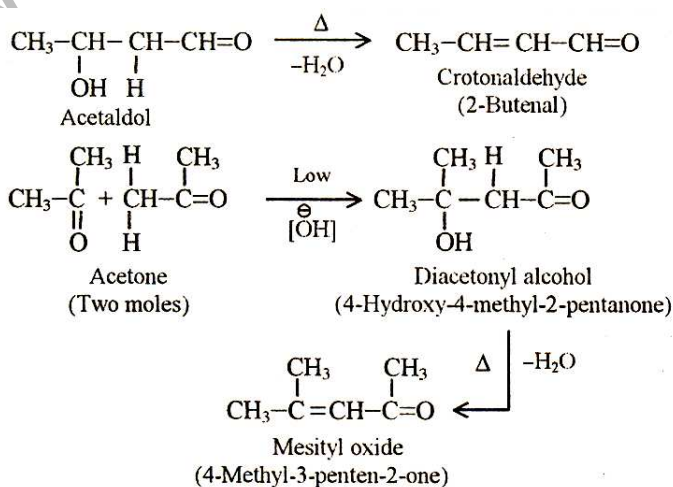
[9] With Dilute Alkali :

In the presence of small amounts of hydroxide ions two molecules of the carbonyl compound containing α -hydrogen atoms, give a β -hydroxy carbonyl compound. This reaction is normally called Aldol condensation. Aldol condensation of two identical carbonyl compounds is called simple aldol condensation.

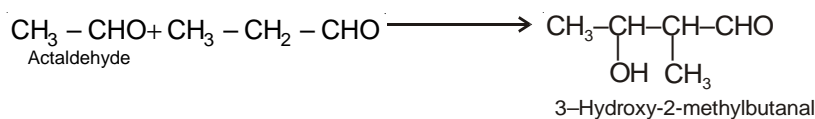
As a source of hydroxide ions, a few drops of very dilute aqueous solution of K_2CO_3 , Na_2CO_3 , NaOH , KOH , $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$ etc. are added.



A α,β -unsaturated aldehyde crotonaldehyde is formed by the elimination of a water molecule on heating acetaldol (3-hydroxybutanal)



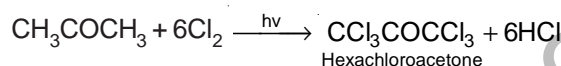
Aldol condensation of two nonidentical carbonyl compounds is called mixed or crossed aldol condensation. Theoretically four products can be formed from aldol condensation of the carbonyl compounds A and B.



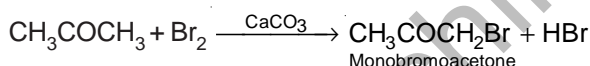
[b] **Halogenation**

[1] **With Halogen :**

The carbonyl compounds have reactive α hydrogen atoms, which are readily substituted on reacting with halogens. Halogenation of ketones takes place more satisfactorily as compared to aldehydes, because aldehydes readily undergo oxidation as well as polymerisation.



Monobromoacetone is formed by bromination of acetone in the presence of CaCO_3 .

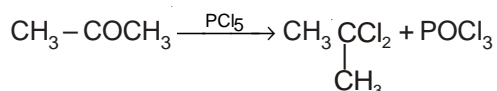
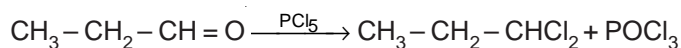
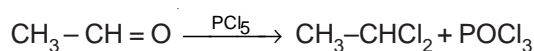
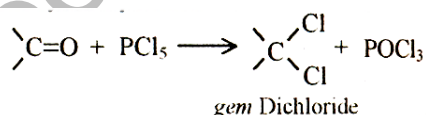


On trichlorination of acetaldehyde in the presence of antimony trichloride, chloral is formed, which is an important intermediate in the manufacture of D.D.T. and chloroform.



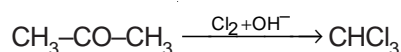
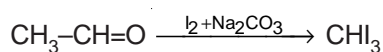
[2] **With Phosphorus Pentachloride :**

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



[3] **Haloform Reaction :**

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

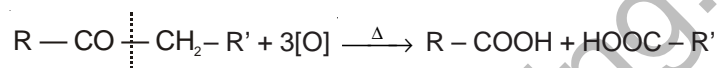
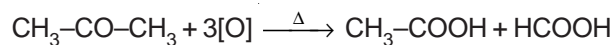
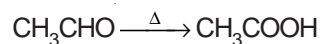


[c] Oxidation :

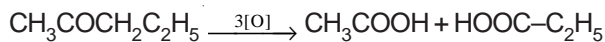
Oxidation of aldehydes takes place readily, whereas ketones resist oxidation and are oxidised under high energy conditions.

[1] With Inorganic Oxidants :

Alkanal gives alkanolic acid of same number of carbon atoms at room temperature on oxidation with even very weak oxidising agents, like Tollen's reagent, Fehling's solution, Benedict's solution, mercuric chloride, etc., as also with strong oxidants, like acidified permanganate, acidified dichromate, chromic acid, conc. HNO_3 , etc., Oxidation of alkanones takes place only on heating with strong oxidants, and alkanolic acids having less number of carbon atoms are formed.



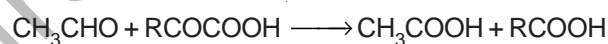
When two nonidentical alkanolic acids are formed on oxidation of alkanone then CO group of alkanone remains attached to the smaller alkyl group. This is called Popoff's rule.



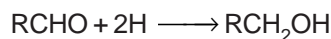
The α CH_2 group gets converted to CO group at room temperature by selenium dioxide.

**[2] Baeyer–Villiger Reaction :**

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

**[d] Reduction :****[1] Hydrogenation :**

The carbonyl group ($-\text{CO}-$) gets converted to alcoholic group ($-\text{CHOH}-$) on hydrogenation. Thus, aldehydes form primary alcohols, while ketones form secondary alcohols on hydrogenation.



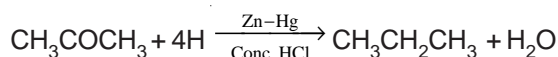
The following reagents can be used for hydrogenation of aldehydes and ketones.

[2] With Red Phosphorous and HI :

Alkanals and alkanones are converted to alkanes having same number of carbon atoms on reducing them with red phosphorous and HI. $\text{RCHO} + 4\text{H} \xrightarrow{\text{RedP/HI}} \text{RCH}_3 + \text{H}_2\text{O}$

[3] Clemmensen's Reaction :

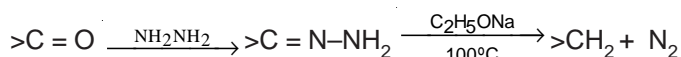
The CO group of alkanones is converted to CH_2 group on reduction of alkanones by zinc amalgam and concentrated hydrochloric acid.



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

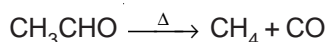
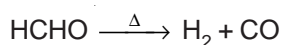
[4] Wolff-Kishner Reaction :

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



[e] Pyrolysis :

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



[f] Polymerisation :

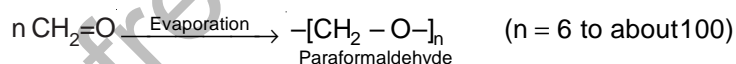
Carbonyl compounds form several polymerisation products. Alkanals generally undergo addition polymerisation reactions, whereas alkanones undergo condensation polymerisation reactions.

Addition polymerisation

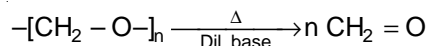
Formaldehyde

[1] In Neutral Medium

[i] White crystalline solid, paraformaldehyde is obtained on evaporation (not boiling) of formalin (40% aqueous solution of formaldehyde) carefully. It is a linear addition polymer, which is also called polyoxymethylene, because there is a repetition of oxymethylene ($-\text{CH}_2-\text{O}-$) units in its structure.



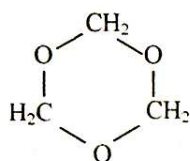
Paraformaldehyde undergoes depolymerisation on heating with dilute alkali or alone, and its monomer formaldehyde gas is liberated out.



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



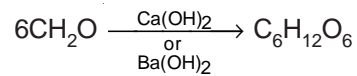
Metaformaldehyde is also called trioxymethylene, because it contains three CH_2O units bonded together. It has a nonaromatic six-membered heterocyclic structure, in which it may be regarded as a trioxa analogue of cyclohexane. Therefore, it is also called 1,3,5-trioxan or sym-trioxan.



Metaformaldehyde
or
Trioxymethylene
or
1,3,5-Trioxan
or
sym-Trioxan

[2] In Weak Alkaline Medium :

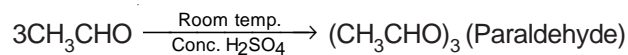
Leaving formalin in a weak alkali (lime water or baryta water) for a few days, a mixture of mainly hexoses (sugars containing six carbon atoms) is formed by repeated aldol condensation. This mixture is called formose or α -acrose. Pentoses (five carbon sugars) are also present in small amount in 'formose'.



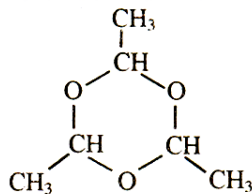
Formation of hexose sugars from formaldehyde is an example of hexamerisation.

Acetaldehyde :

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



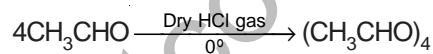
Paraldehyde has nonaromatic heterocyclic structure and it is called 2,4,6-trimethyl-1,3,5-trioxan.



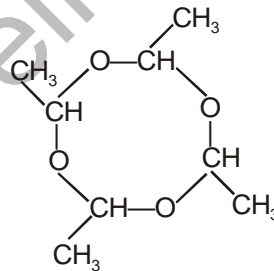
Paraldehyde or 2,4,6-trimethyl-1,3,5-trioxan

Paraldehyde is used as mild hypnotic.

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



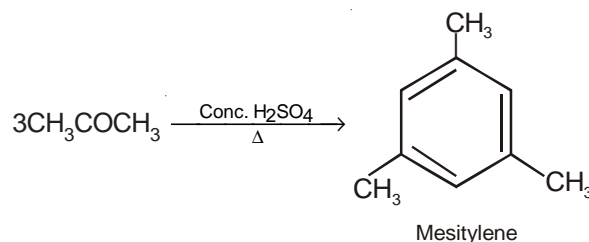
Metaldehyde has the following nonaromatic eight-membered heterocyclic structure.



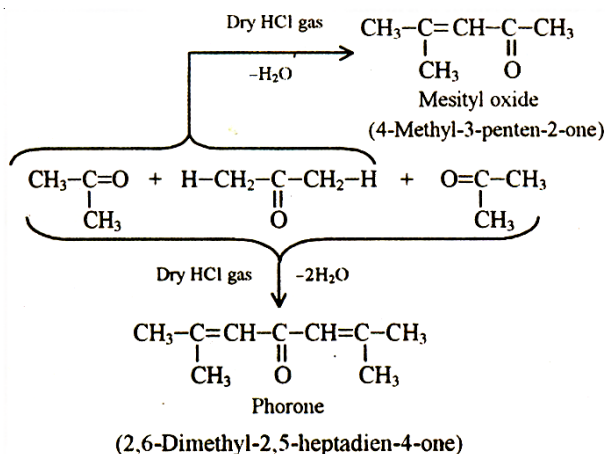
Metaldehyde is used as smokeless powder.

Condensation Polymerisation :**Acetone :**

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



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



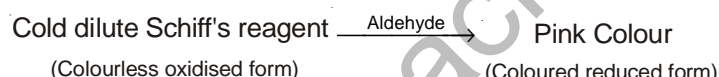
Reactions Different in Aldehydes and Ketones

[A] Reactions of only Aldehydes :

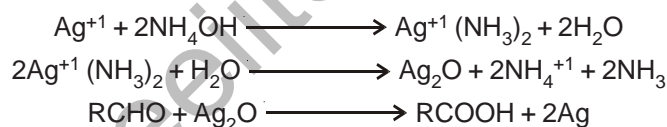
[1] Reducing Properties :

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

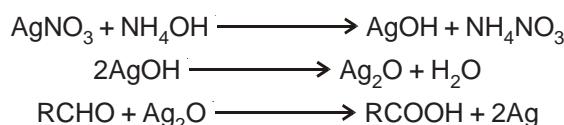
- [i] **With Schiff's Reagent** : Colourless solution obtained on passing SO_2 gas in deep red-coloured aqueous solution of magenta dye (also called fuchsine and rosaniline hydrochloride) is known as Schiff's reagent. All aldehydes restore the pink colour of dilute Schiff's reagent *in cold*. Therefore, it is a specific test of aldehydes, which is called **Schiff's test**.



- [ii] **With Tollen Reagent** : Ammoniacal silver nitrate ($\text{AgNO}_3 + \text{NH}_4\text{OH}$) is called *Tollen's reagent*. Silver mirror is formed on carefully heating an aldehyde with Tollen's reagent in a test tube on a water-bath. Greyish-black precipitate of silver is formed on heating directly and rapidly.



For convenience silver mirror test can be written as follows.

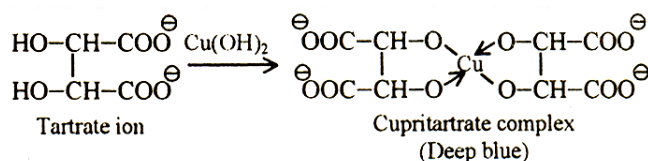


- [iii] **With Fehling's Reagent** : In laboratory, Fehling's solution is kept in two bottles, labeled as Fehling's Solution 'A' and Fehling's solution 'B'.

Fehling solution 'A' - Aqueous solution of CuSO_4 (Blue)

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

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

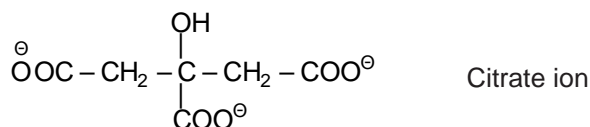


On heating the dark blue solution after adding aldehyde to it, cupric ions get separated from the complex, and oxidise the aldehyde to the corresponding carboxylic acid in the presence of hydroxide ions. The cupric ions get reduced to cuprous ions which get precipitated as insoluble cuprous oxide (red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

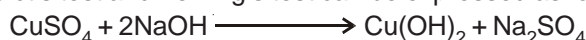


[iv] **With Benedict's Solution :**

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



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



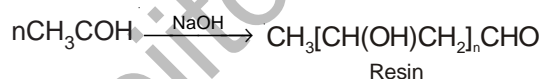
[v] **With Mercuric Chloride Solution :**

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



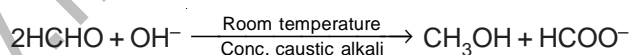
[2] **Resinification :**

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



[3] **Cannizzaro's Reaction :**

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

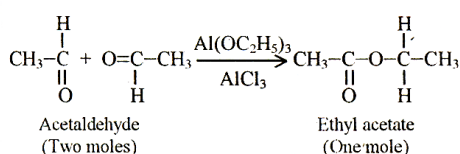
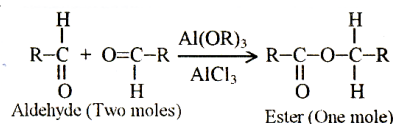


In Cannizzaro's reaction, two molecules of aldehyde reacts in such a way that one molecules gets oxidised and the other gets reduced. This process is called *disproportionation*. The following aldehydes, besides methanal, also give Cannizzaro's reaction.

Chloral, Benzaldehyde, Trimethylacetaldehyde.

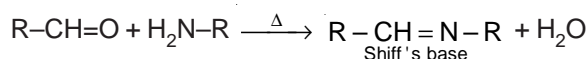
[4] **Tischenko Reaction :**

When an aldehyde is heated with an anhydrous aluminium alkoxide in the presence of anhydrous AlCl_3 , then a carboxylic acid ester having twice the number of carbon atoms is formed. All aldehydes give this reaction.

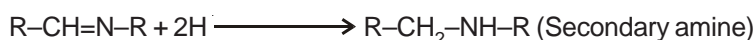


[5] With Primary Amines :

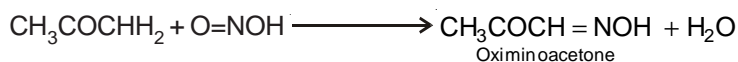
On heating an aldehyde with a primary amine, a Schiff's base is formed by liberation of a water molecule.



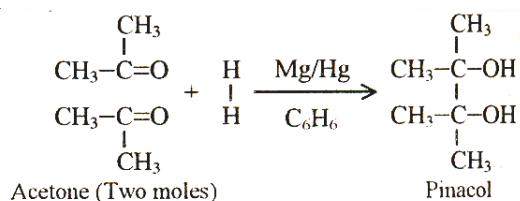
Secondary amines are formed on reduction of Schiff's bases.

**[B] Reactions of Ketones Only :****[1] With Nitrous Acid :**

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

**[2] Bimolecular Reductive Condensation :**

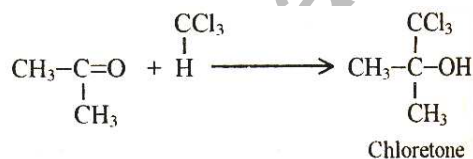
Pinacol is formed on reduction of acetone in an inert medium (like benzene) by using magnesium amalgam and hydrogen.



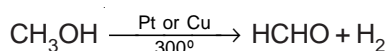
The derivative name of pinacol is tetramethylethylene glycol, and its IUPAC name is 2,3-dimethyl-2,3-butanediol.

[3] With Chloroform :

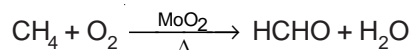
Chloretone is formed by nucleophilic addition of chloroform on acetone.

**Formaldehyde, Methanal, CH₂O, HCHO :**

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



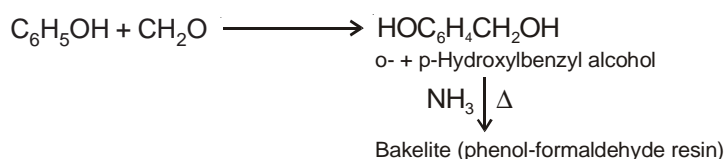
For the manufacture of formaldehyde on industrial scale, dehydrogenation of methanol is carried out by Cu at 300° or by controlled, air oxidation of methane in the presence of molybdenum oxide.



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

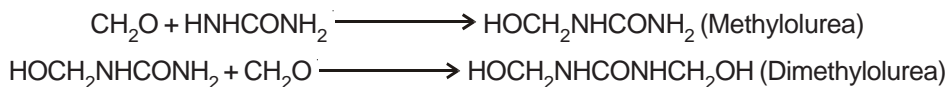
1. With Phenol :

A mixture of p-hydroxybenzyl alcohol (80%) and o-hydroxybenzyl alcohol (20%) is formed by the reaction of formaldehyde and phenol. This reaction is called *LedererManasse Reaction*. Synthetic resin or plastic called *phenol formaldehyde resin* or *bakelite* is formed by condensation polymerisation when a small amount of ammonia is added to the above mixture.

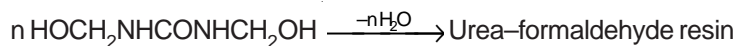


2. With urea :

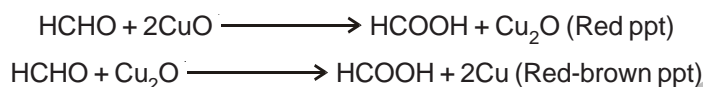
Reaction of formaldehyde and urea takes place very fast and methylolurea and after that dimethylolurea are formed.



A product, urea formaldehyde resin is obtained on the condensation polymerisation of dimethylolurea.

**3. With Fehling Solution :**

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

**4. Halogenation :**

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

5. With PCl_5 :

Dichloromethane is not obtained by the reaction of PCl_5 on formaldehyde.

6. With Proteins :

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

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

Uses :

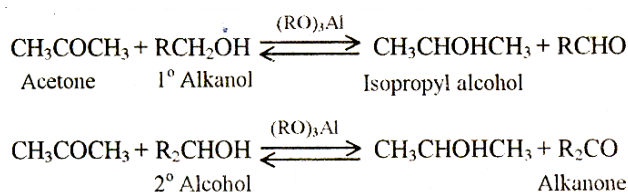
- [1] As an antiseptic and a disinfectant.
- [2] In preservation of zoological specimens.
- [3] In the manufacture of urinary antiseptic, urotropine.
- [4] In the manufacture of bakelite, urea-formaldehyde - resin, galolith, etc.
- [5] In the manufacture of chewable tablet, formamint, which is a mixture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

Acetaldehyde, Ethanal, CH_3CHO **Uses :**

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

Acetone, Propanone, CH_3COCH_3 :**[1] Meerwein-Ponndorf Oppenauer-Verley Reaction :**

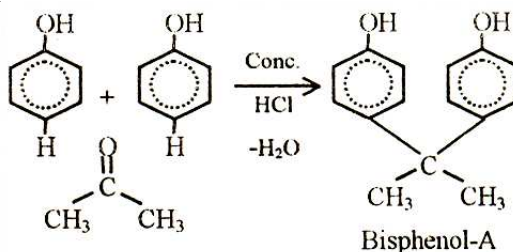
When acetone is heated with a primary or secondary alcohol in benzene or toluene solution in the presence of a weak base (aluminium alkoxide), then the ketone is reduced to secondary alcohol, Primary alcohols are oxidised to aldehydes and secondary alcohols are oxidised to ketones.



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

[2] Condensation With Phenol :

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



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

Uses :

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

Tests for Acetone :

1. No reaction takes place with Schiff's reagent. Tollen's reagent, Fehling's solution. Benedict solution and mercuric chloride solution (distinction from aldehydes), but reacts with HCN, NaHSO₃, NH₂OH, NH₂NH₂, NH₂NHC₆H₅ and NH₂NHCONH₂ (Similarity with aldehydes and ketones)
2. **Iodoform test** : Gives a yellow precipitate of iodoform on heating with iodine and alkali (Similarity with acetaldehyde and all methyl ketones, but distinction from other carbonyl compounds)
3. **Legal's Test** :
When sodium nitroprusside is added to acetone and basified with dilute NaOH, a red violet colour is obtained. This test is also given by other methyl ketones.

Distinction of formaldehyde and Acetaldehyde :

1. **Odour** : Formaldehyde has a characteristic pungent odour, but the pungent odour of acetaldehyde is not characteristic.
2. **Iodoform Test** : Acetaldehyde gives iodoform test, but formaldehyde does not.
3. **Fehling's Solution** : Acetaldehyde gives red precipitate of Cu₂O, whereas formaldehyde gives red–brown precipitate of Cu.
4. **Benedict's Solution** : Acetaldehyde gives red precipitate of Cu₂O, whereas formaldehyde gives red–brown precipitate of Cu.

Benzaldehyde

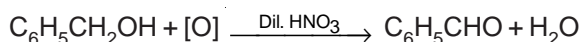
9. BENZALDEHYDE, C₆H₅CHO, OIL OF BITTER ALMONDS

Benzaldehyde is present in the form of glucoside called amygdalin in bitter almonds. One molecule of amygdalin is composed of one molecule of benzaldehyde, two molecules of glucose and one cyano groups bonded to one another. Benzaldehyde is obtained on hydrolysis of amygdalin by dilute acid or by an enzyme emulase.

10. METHOD OF PREPARATION

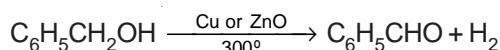
[1] By Oxidation of Benzyl Alcohol :

Benzaldehyde is obtained on oxidation of benzyl alcohol by dilute nitric acid



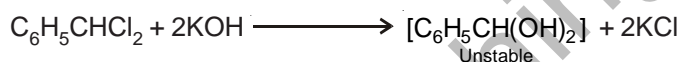
[2] By Catalytic Dehydrogenation of Benzyl Alcohol :

Benzaldehyde is obtained on passing benzyl alcohol vapour over copper catalyst or zinc oxide heated to 300°.

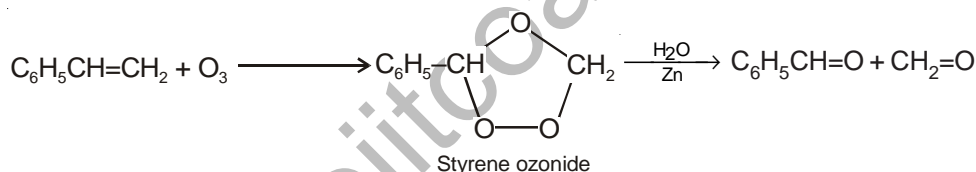


[3] By Alkaline Hydrolysis of Benzal Chloride :

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



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



[5] By Dry Distillation of Calcium Salts of Acids :

Benzaldehyde can be obtained by dry distillation of a mixture of calcium benzoate and calcium formate taken in equimolar ratio.



Barium salts can also be used in place of calcium salts of carboxylic acids.

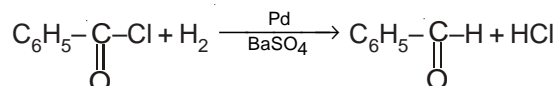
[6] By Grignard's Reagent :

Benzaldehyde is formed by the reaction of phenylmagnesium bromide with ethyl formate :



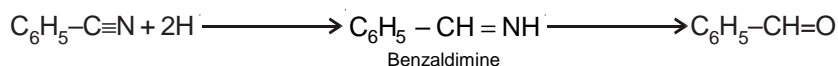
[7] By Rosenmund's Reaction :

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



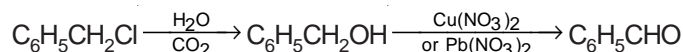
[8] By Stephen's Reaction :

Benzaldehyde is obtained on reduction of benzaldimine, which is formed on reduction of benzonitrile (cyanobenzene) by stannous chloride and conc. HCl in ethereal solution.

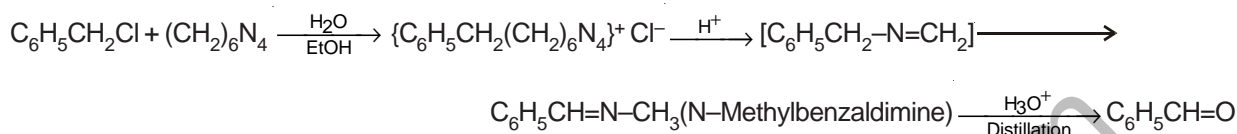


[9] By Oxidation of Benzyl Chloride :

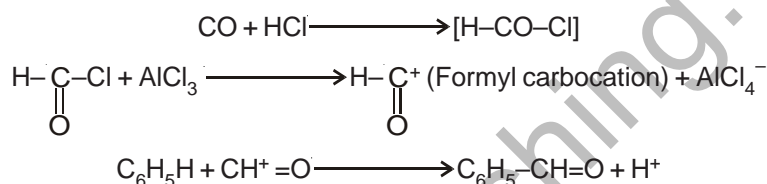
Slow oxidation of benzyl chloride takes place on passing a stream of carbon dioxide through the aqueous solution of copper nitrate or lead nitrate and benzaldehyde is formed.

**[10] By Sommelet Reaction of Benzyl Chloride :**

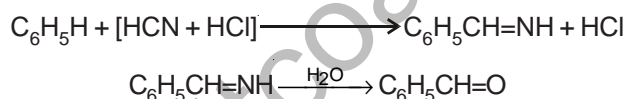
Benzyl chloride is refluxed with urotropine in aqueous alcoholic solution, when a product is formed. This product is subjected to hydrolysis by steam-distillation after adding small amount of an acid, when benzaldehyde is obtained.

**[11] By Gattermann–Koch Aldehyde Synthesis :**

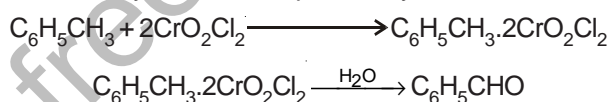
Benzaldehyde is formed on heating a mixture of benzene, carbon monoxide and HCl in nitrobenzene medium in the presence of anhydrous AlCl_3 . It is assumed that an unstable formyl chloride is formed as intermediate, which forms formyl cation (an electrophile).

**[12] By Gattermann Aldehyde Synthesis :**

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

**[13] By Etard's Reaction :**

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

**11. PHYSICAL PROPERTIES**

Benzaldehyde is a colourless, volatile oily liquid (boiling point 179°) having characteristic odour of bitter almonds. It is miscible with organic liquids, like alcohol, ether, etc., and immiscible with water. Its solubility in water is very low. It is poisonous and volatile in steam.

12. REACTION

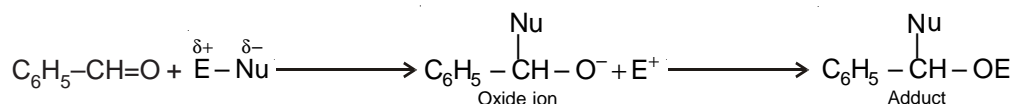
Benzaldehyde gives the following two types of reactions.

[A] Reactions due to aldehyde group

[B] Reactions due to benzene ring

[A] Nucleophilic Addition on Aldehyde group :

Nucleophilic addition on -CHO group in benzaldehyde takes place as follows.



[B] Electrophilic Substitution Reactions Due to Benzene Ring :

Aldehyde group bonded to the benzene ring is deactivating and meta-directing group due to strong negative mesomeric effect (-M effect). Therefore, the attack of an electrophile on aromatic ring of benzaldehyde takes place at slower rate as compared to unsubstituted benzene. and *m*-S_E substitution product is formed under strong conditions, *i.e.*, not easily.

[A] Reaction Due to Aldehyde Group :**[1] Reduction :**

Benzyl alcohol is formed on reaction of benzaldehyde by sodium amalgam + HCl or Zn + HCl.

**[2] Oxidation :**

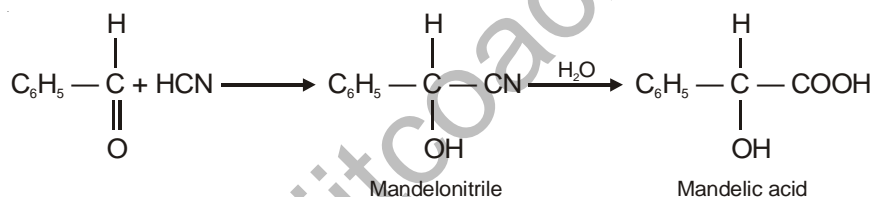
Benzoic acid is formed by slow auto-oxidation of benzaldehyde in the presence of air and light. Other oxidants bring about oxidation very fast.



Due to its easy oxidation, benzaldehyde behaves as a reducing agent. However, it is a weaker reducing agent as compared to aliphatic aldehydes. It restores pink colour of Schiff's reagent, gives white precipitate turning grey with mercuric chloride solution, and it reduces silver ions of Tollen reagent, *i.e.*, ammoniacal silver nitrate solution to metallic silver. But it does not give red precipitate of cuprous oxide with Fehling's solution and Benedict's solution due to strong steric hindrance of benzene ring.

[3] With Hydrogen Cyanide :

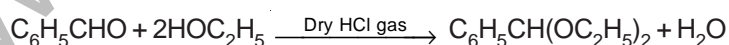
Mandelic acid is obtained on hydrolysis of mandelonitrile *i.e.*, benzaldehyde cyanohydrin, formed by addition of hydrogen cyanide on benzaldehyde.

**[4] With Sodium Bisulphite :**

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

**[5] With Alcohols :**

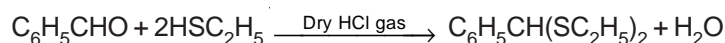
An aromatic acetal is obtained on heating a mixture of benzaldehyde and alcohol in the presence of dry HCl gas.



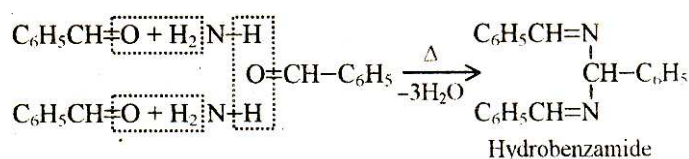
The above aromatic acetal obtained from benzaldehyde and ethanol is called phenylal.

[6] With Thiols :

Aromatic thioacetals are formed by reacting benzaldehyde and thioalcohols in the presence of dry HCl gas.

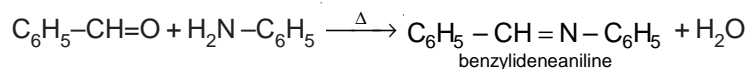
**[7] With Ammonia :**

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

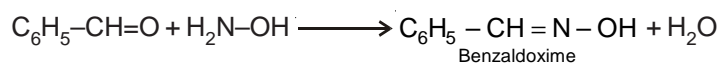


[8] With Primary Amines :

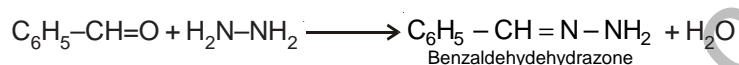
Schiff's bases are formed on heating benzaldehyde with primary amines. The reaction of benzaldehyde and aniline gives a Schiff's base, named benzlideneaniline or benzalaniline or N-phenylbenzaldimine.

**[9] With Hydroxylamine :**

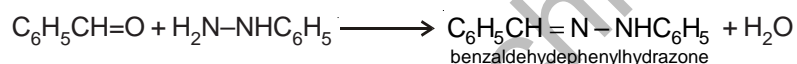
Benzaldoxime is formed by the reaction of benzaldehyde and NH_2OH .

**[10] With Hydrazine :**

Benzaldehydehydrazone is formed by the reaction of benzaldehyde and NH_2NH_2 .

**[11] With Phenylhydrazine :**

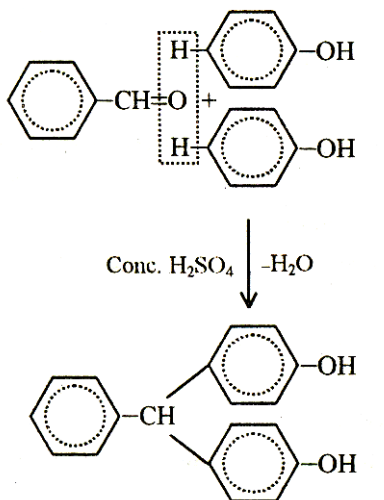
The reaction of benzaldehyde and $\text{C}_6\text{H}_5\text{NHNH}_2$ gives benzaldehydephenylhydrazone.

**[12] With Semicarbazide :**

The reaction of benzaldehyde and semicarbazide gives benzaldehyde semicarbazone.

**[13] With Phosphorus Pentachloride :**

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

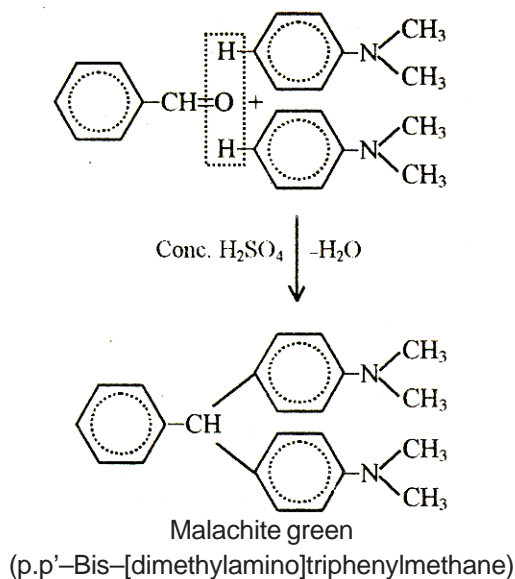
**[14] With Phenol :**

p,p'-Dihydroxytriphenylmethane

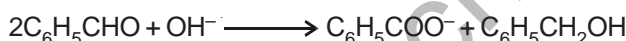
The above product is a triphenylmethane dye :

[15] With N,N-Dimethylaniline :

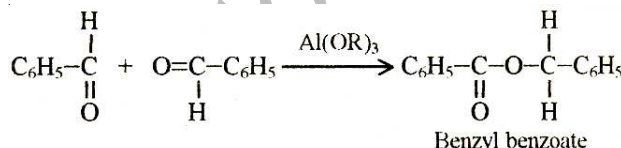
If the reaction of benzaldehyde and N,N-dimethylaniline is carried out in the presence of a few drops of conc. H_2SO_4 or anhydrous ZnCl_2 , then a green coloured triphenylmethyl dye, called Malachite green is obtained.

**[16] Cannizzaro's Reaction :**

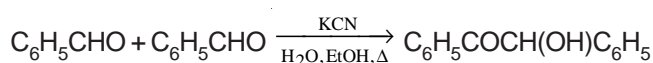
Due to absence of α hydrogen atom in benzaldehyde, oxidation of one molecule to benzoate ion and reduction of the second molecule to benzyl alcohol takes place on adding strong solution of caustic alkali at room temperature

**[17] Tischenko Reaction :**

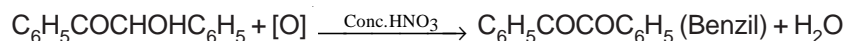
When benzaldehyde is heated in the presence of an aluminium alkoxide (ethoxide, isopropoxide, etc.) taken in an inert solvent (CCl_4 , xylene, etc.), benzyl benzoate is formed by bimolecular addition.

**[18] Benzoin Condensation :**

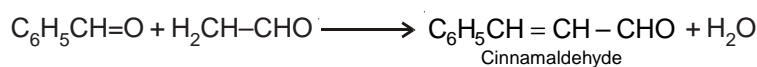
When benzaldehyde is heated with aqueous alcoholic KCN solution, a ketonic secondary alcohol, benzoin is formed by bimolecular condensation.



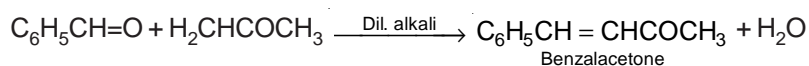
On Oxidation of benzoin with conc. nitric acid, the secondary alcohol group is converted to a ketone group and a diketone, called benzil is formed.

**[19] Claisen Reaction :**

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

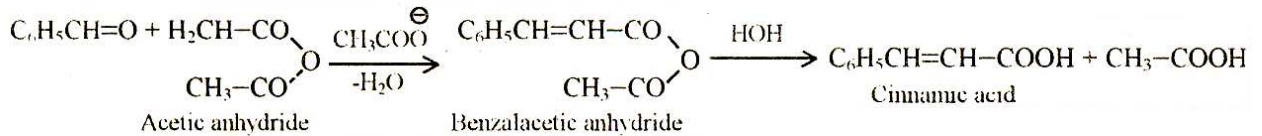


Benzalacetone, i.e. benzlideneacetone is obtained on condensation of benzaldehyde with acetone.

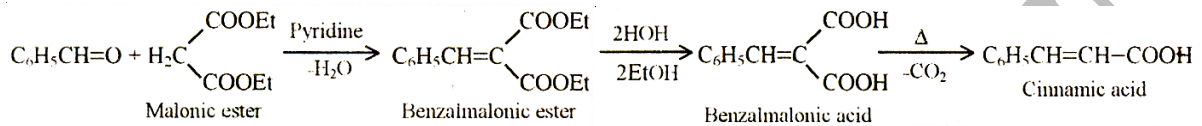


[20] Perkin's Reaction :

When benzaldehyde is heated at 180° with an anhydride and the sodium salt of a carboxylic acid, then an unsaturated carboxylic acid is formed. For example, Cinnamic acid is obtained on the reaction of acetic anhydride and sodium acetate on benzaldehyde.

**[21] Knoevenagel Reaction :**

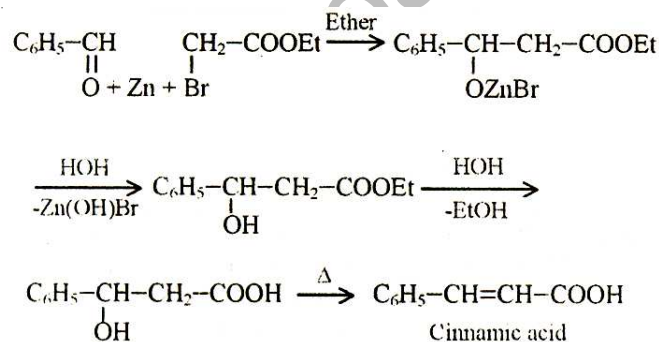
When benzaldehyde is heated with malonic ester in the presence of pyridine, then cinnamic acid is formed in the following steps.



Malonic ester contains one reactive methylene group, whose two reactive hydrogen atoms take away the oxygen atom from benzaldehyde to form a water molecule. A reactive methylene group is present between two strongly electron-attracting groups (like CO, CN, etc.), due to which the hydrogen atoms of methylene group acquire a tendency of getting released in the form of protons.

[22] Reformatsky Reaction :

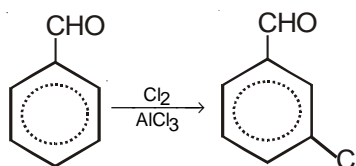
When benzaldehyde is reacted with bromoacetic ester in the presence of zinc in dry ether, then cinnamic acid is obtained in the following steps.

**[B] Reactions Due to Benzene Ring :**

Benzaldehyde gives the following S_E reactions.

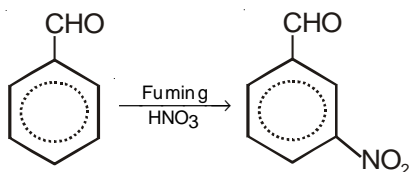
[23] Halogenation :

m-Chlorobenzaldehyde (or m-Bromobenzaldehyde) is formed on heating benzaldehyde with chlorine (or bromine) in the presence of AlCl₃.

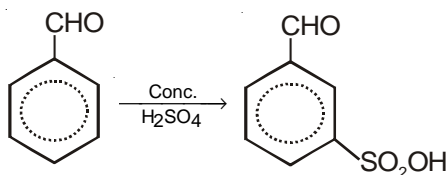


[24] Nitration :

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

**[25] Sulphonation :**

Benzaldehyde undergoes sulphonation on heating with conc. sulphuric acid to form m-formylbenzenesulphonic acid.

**[26] Friedel-Crafts Reaction :**

It should be noted that due to strong deactivation of benzene ring in benzaldehyde, Friedel-Crafts reaction does not take place.

13. USES

Benzaldehyde is used

- [1] As a deodorant.
- [2] In the manufacture of synthetic dyes, and
- [3] In the synthesis of many aromatic compounds.

Some Important Point :**Uses :**

S.No.	Formaldehyde	Acetaldehyde	Acetone
1	Disinfectant and preservative for biological specimens. (formalin)	In the preparation of dyes polish, varnishes	Solvent for cellulose,
2	Urotropine, a urinary antiseptic	In the manufacture of ethanol, acetic acid, synthetic rubber etc.	In the preparation of sulphonals (hypotic)
3	Formamint, for throat treatment (formalin + lactose)	For the preparation of metaldehyde (a solid fuel)	In the preparation of chloroform, iodoform

Distinction between Aldehydes and Ketones :

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