

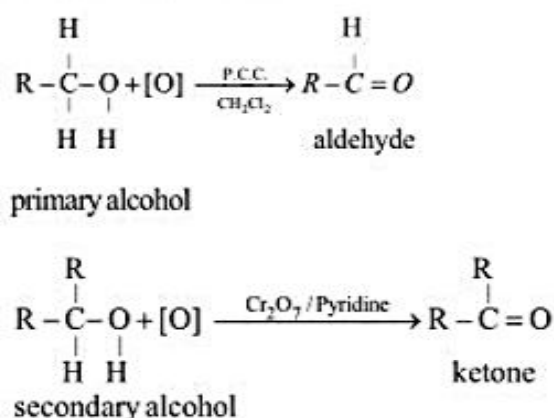
CARBONYL COMPOUND

INTRODUCTION

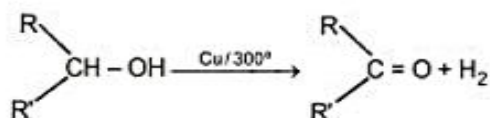
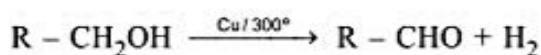
- (a) Organic compounds in which $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$ group is present are called 'Aldehyde & Ketone'.
- (b) The group $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$ is called as carbonyl group so, compound are also called carbonyl compounds. If H atom is attached with this carbonyl group then compound is called **aldehyde** and if alkyl group is present on both sides then compound is called **Ketone**.
- (c) In ketone if both alkyl group are same then they are called simple ketone, if different then called mixed ketone.
- (d) Their general formula is $\text{C}_n\text{H}_{2n}\text{O}$. Hybridisation state of carbon is sp^2 and $\text{C}=\text{O}$ bond length is 1.23 \AA .
- (e) The ratio of C, H & O in formaldehyde is $1 : 2 : 1$ (CH_2O). It is called simplest sugar.
- (f) Aldehyde shows chain, position and functional isomerism.
- (g) Ketone shows chain, position, functional and metamerism also. Aldehyde and ketone both are functional isomers with each other.

GENERAL METHODS OF PREPARATION

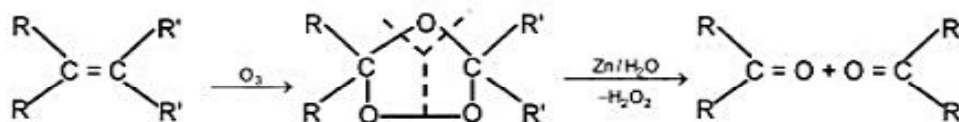
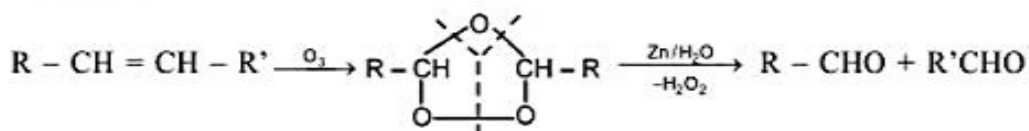
From Alcohol (By Oxidation) :- Primary alcohols can be oxidised to aldehydes by using pyridinium chlorochromate (P.C.C) ($\text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}^-$). A stronger oxidising agent (e.g. KMnO_4) oxidises primary alcohols to carboxylic acids.



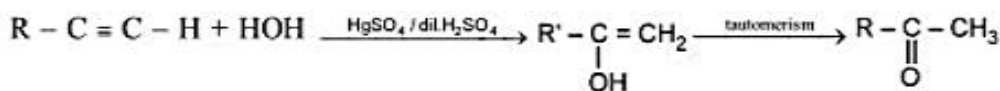
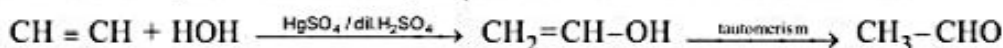
From Alcohol (By Catalytical Oxidation) :- When vapours of a primary alcohol (or secondary alkanol) are passed over heated copper (or zinc oxide) at 300° then aldehyde (or ketones) are formed.



From Alkene (Ozonolysis) : Desired aldehyde and ketones can be obtained by ozonolysis of appropriate alkenes.

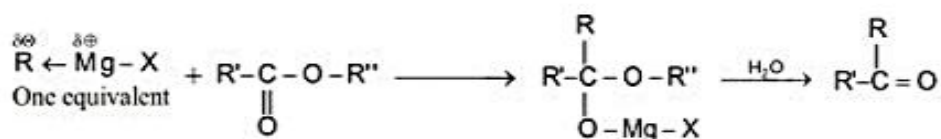


From Alkyne : Acetaldehyde is formed on passing acetylene in 40% aqueous solution of H_2SO_4 at 60° in the presence of 1% $HgSO_4$. It is called **Kucherov's reaction**.

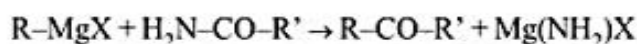
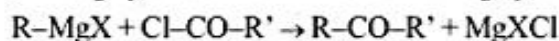
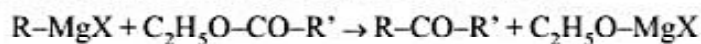


Note : Methanal cannot be formed from the above reaction.

From Grignard's Reagent : Alkanal is formed by reaction of formic ester and an alkylmagnesium halide.

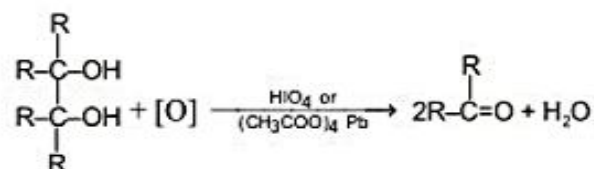
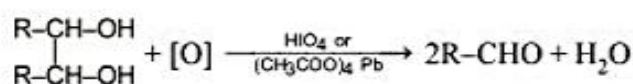


Ketones are obtained from acetic and higher esters. Acid chlorides and amides can be taken in place of esters. However $HCOCl$ cannot be taken because it is unstable.

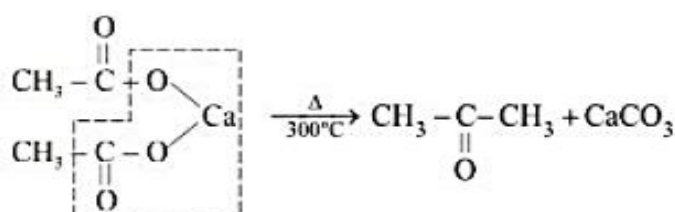
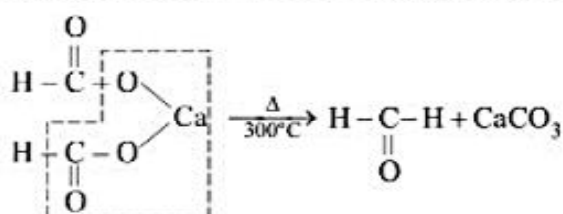


Note : Formaldehyde cannot be formed from the above reaction.

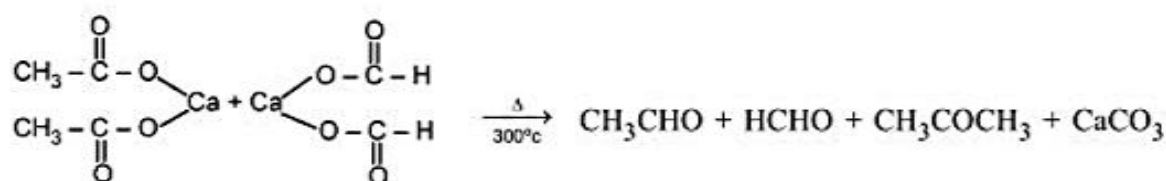
From Vicinal Glycol (Oxidation) : Carbonyl compounds are obtained on oxidation of vicinal alkanediols by periodic acid or lead tetraacetate



From Calcium or Barium salt of Carboxylic acid : 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 ($\text{R} = \text{H}$) and acetone is formed on taking calcium acetate ($\text{R} = \text{CH}_3$).

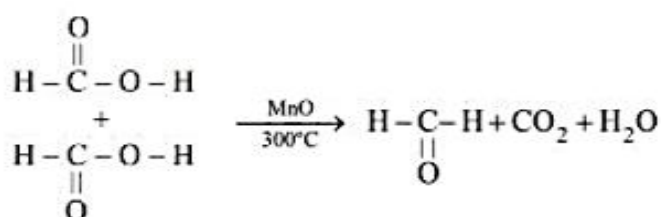


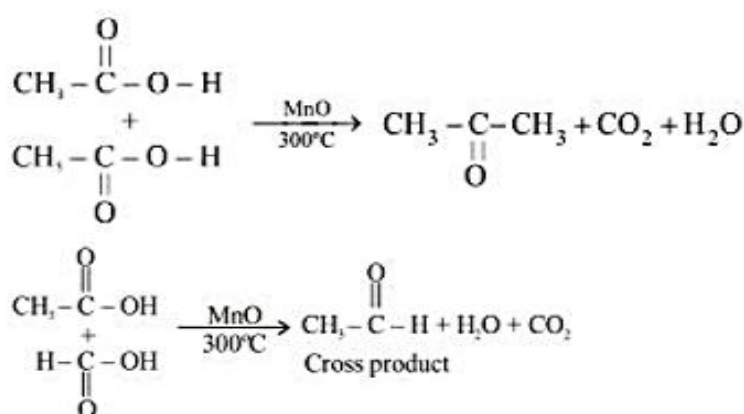
Acetaldehyde can be formed by taking a mixture of calcium formate and calcium acetate.



From Carboxylic Acid : – When vapours of carboxylic acid are passed on manganese oxide MnO at 300°C , then carbonyl compounds are formed.

Formaldehyde is prepared from formic acid ($\text{R} = \text{R}' = \text{H}$), acetone from ($\text{R} = \text{R}' = \text{CH}_3$), and acetaldehyde from a mixture of acetic acid ($\text{R}' = \text{CH}_3$) and formic acid ($\text{R} = \text{H}$).

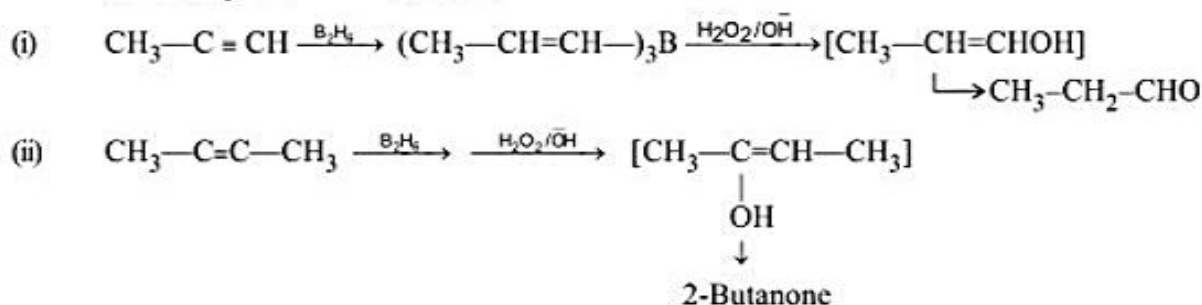




From Alkyne (Hydroboration) : When a dialkylborane is reacted with an alkyne, then dialkylvinylborane adduct is formed, which on reacting alkaline hydrogen peroxide solution forms a carbonyl compound. Alkanals are formed from terminal alkynes, and alkanones from nonterminal alkynes.

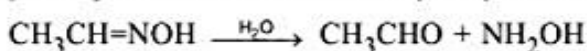
1-Alkyne \longrightarrow Aldehyde

Other alkynes \longrightarrow Ketone

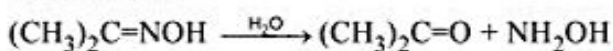


By the Hydrolysis of oximes and acetals :

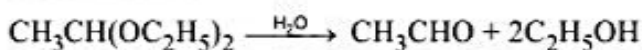
Carbonyl compounds are formed from hydrolysis of oximes and acetals.



Acetaldoxime



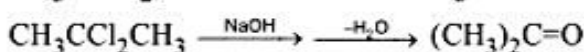
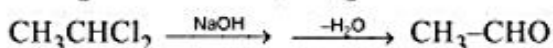
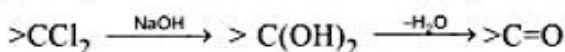
Acetone-oxime



Acetal

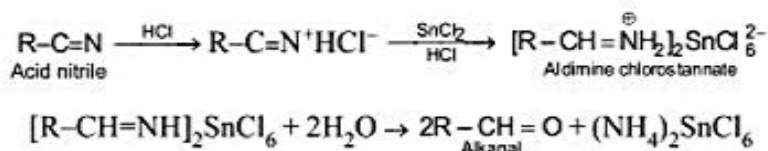
By the Hydrolysis of gemdihalide :

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

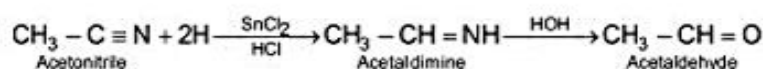


METHODS OF PREPARATION ONLY FOR ALDEHYDES

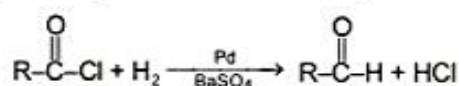
Stephen's Method : By dissolving an alkyl cyanide in ether and reacting it with stannous chloride and conc. hydrochloride, aldimine chlorostannate salt is obtained. Alkanal is formed on hydrolysis of this salt.



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

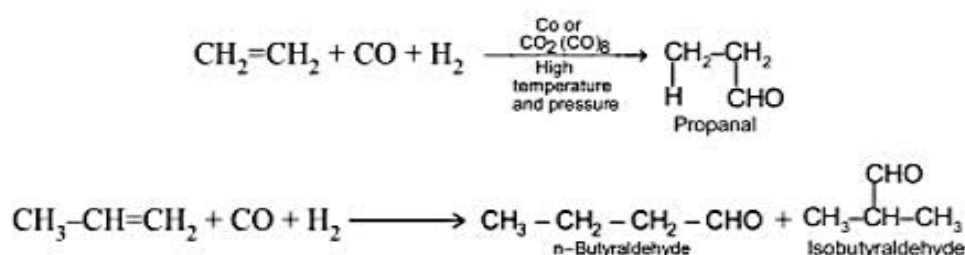


Rosenmund Reaction : Aldehydes are formed on reduction of a carboxylic acid chloride in boiling xylene medium by hydrogen and palladised barium sulphate.



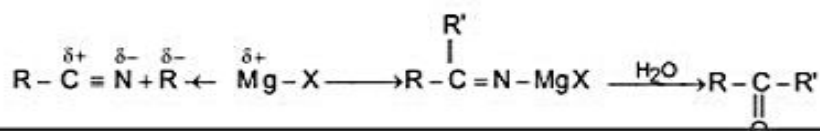
Acetaldehyde is formed on taking acetyl chloride ($\text{R} = \text{CH}_3$). Formaldehyde cannot be prepared by Rosenmund reaction, because HCOCl is not a stable compound, BaSO_4 acts as a catalyst poison and decreases the catalytic efficiency of Pd catalyst, due to which further reduction of acetaldehyde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

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.



METHODS OF PREPARATION ONLY FOR KETONES

From Alkyl Cyanide : Alkanones are formed on hydrolysis after reaction of an alkylmagnesium halide with ethyl cyanide or its higher homologue.



In this reaction if we take HCN with GR., product will be aldehyde but major product will be alkane because HCN is an example of active H compound and with active hydrogen compound GR forms alkane.

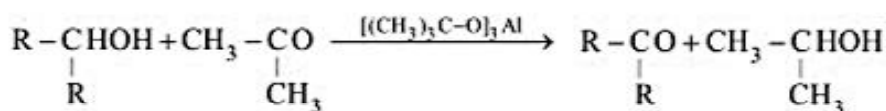
Dialkyl cadmium with acid chlorides : A ketone and an alkylcadmium chloride are formed on reacting a dialkylcadmium with an acid chloride.



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



Oppenaur 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.

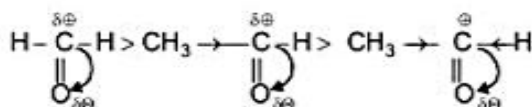


PHYSICAL PROPERTIES

- (a) Aldehydes are colourless with pungent smell liquid while ketones are pleasant smell liquids but formaldehyde is gaseous in nature.
- (b) Lower carbonyl compounds are soluble in water. It is due to polarity in carbonyl group.
- (c) Higher carbonyl compounds are insoluble in water due to more covalent character.
- (d) Melting point & Boiling point \propto Molecular mass

$$\propto \frac{1}{\text{No. of branches}}$$

- (e) Melting point and boiling point of carbonyl compounds are more than to corresponding alkanes due to dipole-dipole attraction present between molecules in carbonyl compounds.
- (f) Reactivity of carbonyl compound is dependent on alkyl group which is linked with carbonyl group.



- (g) 40% solution of formaldehyde is known as '**FORMALIN**' (40% HCHO, 54-56% H₂O, 4-6% methanol)
- (h) Mixture of formaldehyde and lactose sugar is called '**FORMAMINT**' which is used in medicine of throat infection.
- (i) Boiling point of carbonyl compounds are as under -

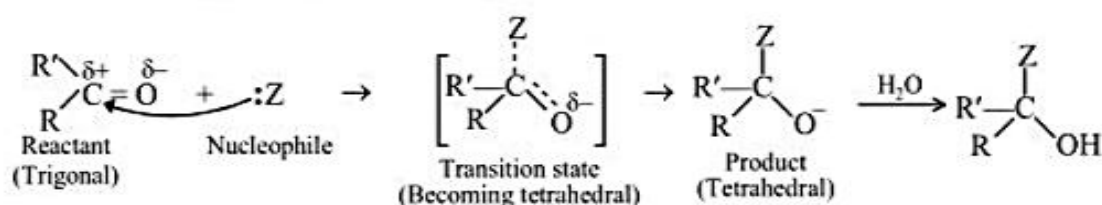
S.No.	Compound	Boiling Point
1.	Formaldehyde	- 21°C
2.	Acetaldehyde	+ 21°C
3.	Acetone	56°C

CHEMICAL PROPERTIES

Nucleophilic Addition Reactions

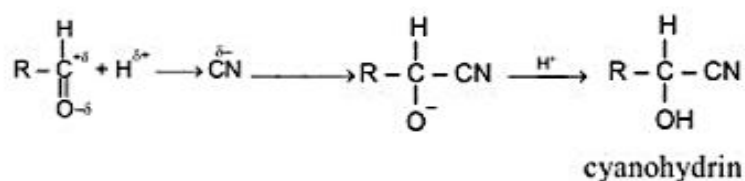
The typical reactions of aldehydes and ketones are nucleophilic addition reactions because

- the carbonyl carbon is electron deficient, since π -electrons are pulled towards the electronegative oxygen, and
- this part of molecule being flat is open to relatively unhindered attack



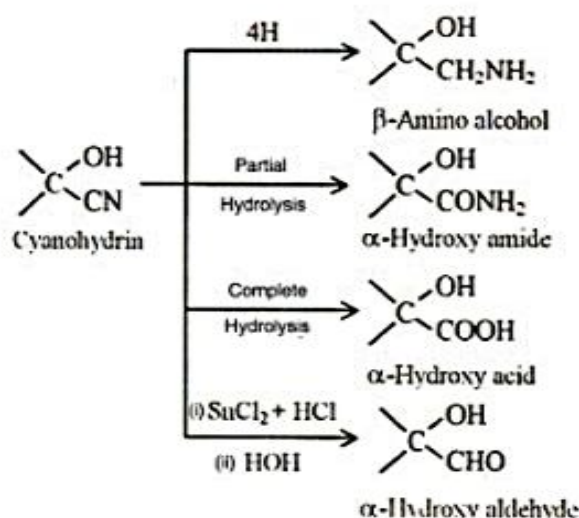
Note : There is a moderate steric hindrance in the transition state, that is, larger groups (R & R') will tend to resist crowding than smaller groups. Aldehydes thus undergo nucleophilic addition reactions faster than ketones. Thus, among the compounds HCHO , CH_3COCH_3 , and CH_3CHO , the order of reactivity to nucleophilic addition will be $\text{HCHO} > \text{CH}_3\text{CHO} > \text{CH}_3\text{COCH}_3$.

Reaction with Hydrogen Cyanide : -



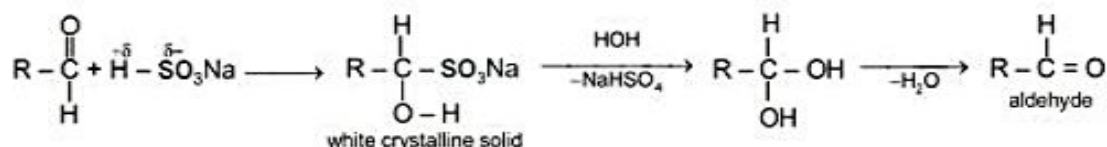
Note : -

- Reaction takes place in presence of mild base which abstract H^+ from HCN and produce CN^- ion which acts as nucleophile.
- If $\text{R} = \text{H}$ then product will be formaldehyde cyanohydrin.
- Cyanohydrin is an important compound which gives the following product on hydrolysis and reduction.



Reaction with Sodium bisulphite :

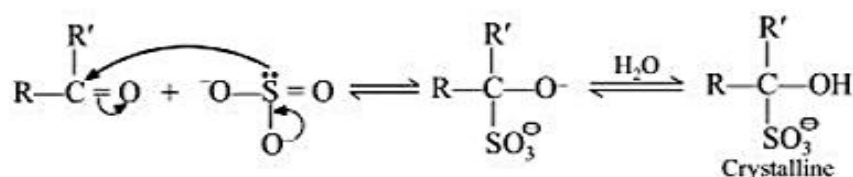
Carbonyl compound form a white crystalline addition product with sodium bisulphite called **Aldehyde / Ketone sodium bisulphite adduct**.



Mechanism : The attacking nucleophile is SO_3^{2-} rather than HSO_3^- .

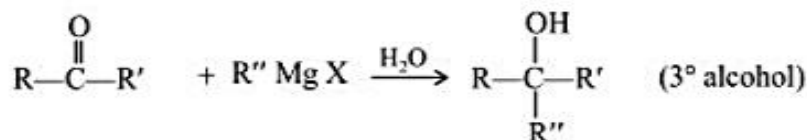
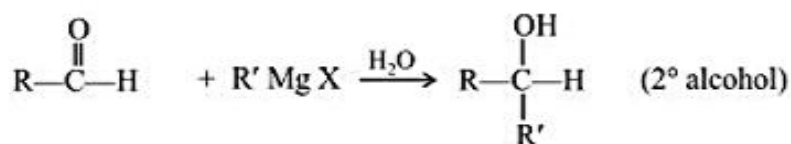
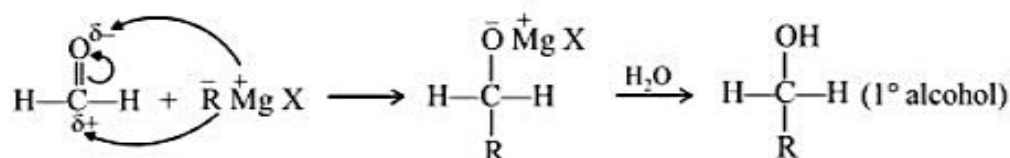


Though HSO_3^- is present in higher concentration, SO_3^{2-} is a better nucleophile.



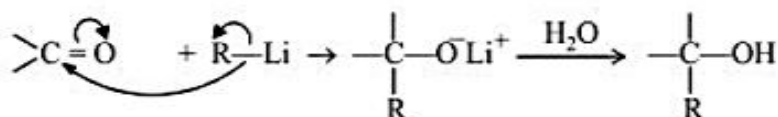
Note : -

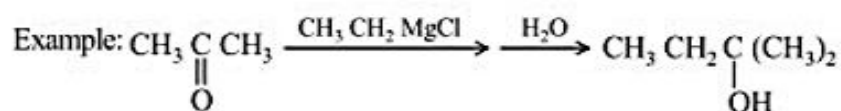
- Bisulphite adduct is an important compound because it gives carbonyl compound on further hydrolysis.
- The above reaction is used in purification of carbonyl compound.
- The reaction is given by only methyl ketone & aldehyde.

Reaction with Grignard Reagents

Formaldehyde yields primary alcohols, higher aldehydes produce secondary alcohols, and ketones produce tertiary alcohols with Grignard reagents.

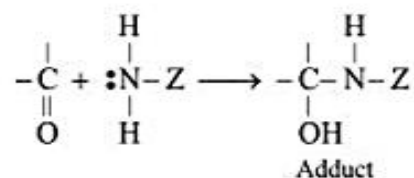
Organolithium compounds also react with aldehydes and ketones in the same manner.



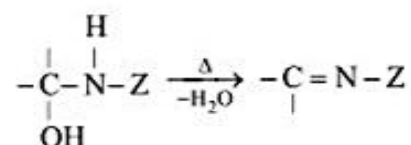


Reaction with Ammonia derivatives :

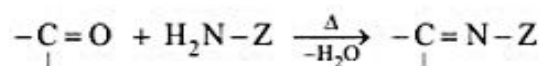
Addition of nitrogenous nucleophile on carbonyl group takes place according to the following mechanism.



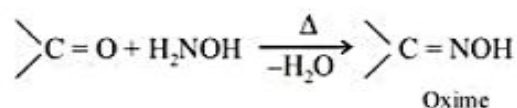
The end product is formed by elimination of water from the adduct under appropriate energy condition.



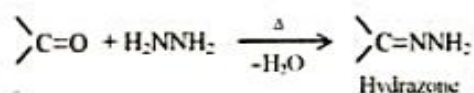
In the above two steps, it appears that an unsaturated condensation product is formed by liberation of the water molecule from carbonyl group and nitrogenous nucleophile.



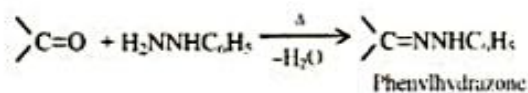
(i) With Hydroxylamine :



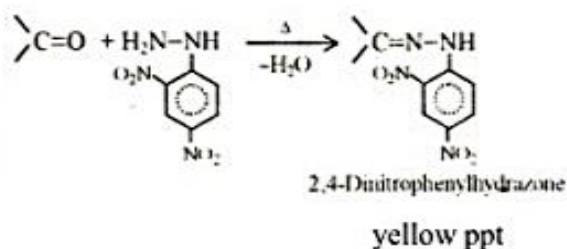
(ii) With Hydrazine :



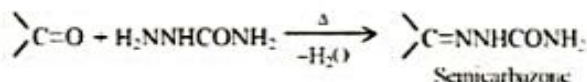
(iii) With Phenylhydrazine :



(iv) With 2,4-Dinitrophenylhydrazine :



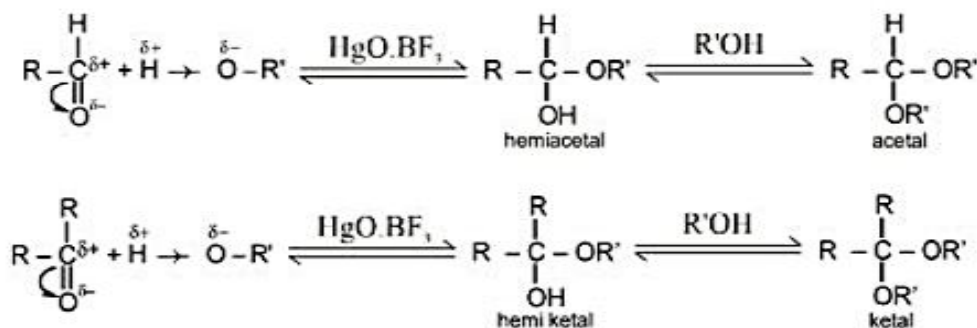
(v) With Semicarbazide :



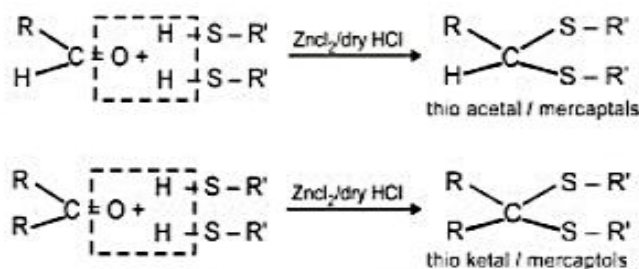
On reacting a carbonyl compound with 2,4-dinitrophenylhydrazine, a yellow precipitate of 2,4-dinitrophenylhydrazone derivative is obtained. White precipitate is obtained by the reaction with hydroxylamine, hydrazine phenylhydrazine and semicarbazide. The pure parent carbonyl compound can be obtained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



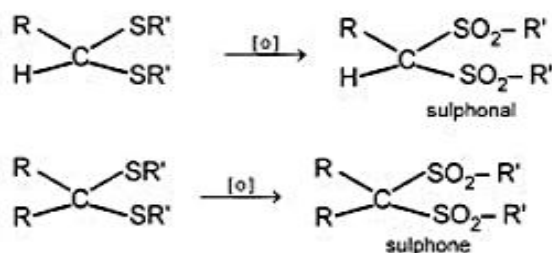
Reaction with Alcohol : In the presence of catalyst ($\text{HgO} \cdot \text{BF}_3$) aldehyde form acetal with alcohol while ketone form ketal with alcohol.



Reaction with Alkane Thiol : Aldehyde form thio acetal with alkane thiol while ketone form thio ketal with alkane thiol.

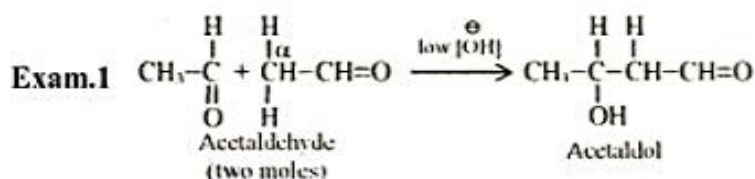


These are important compounds because they form sulphonyl compounds on oxidation which are used as hypnotic drugs.



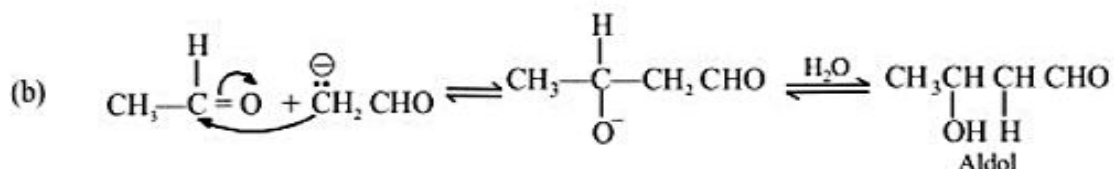
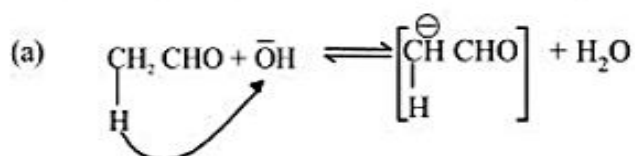
Aldol Condensation : In the presence of small amounts of hydroxide ions (base) two molecules of the carbonyl compound containing α -hydrogen atoms, give a β -hydroxy carbonyl compound. This reaction is normally called Aldol condensation. Aldol condensation of two identical carbonyl compounds is called 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 , $Ca(OH)_2$, $Ba(OH)_2$ etc. are added.



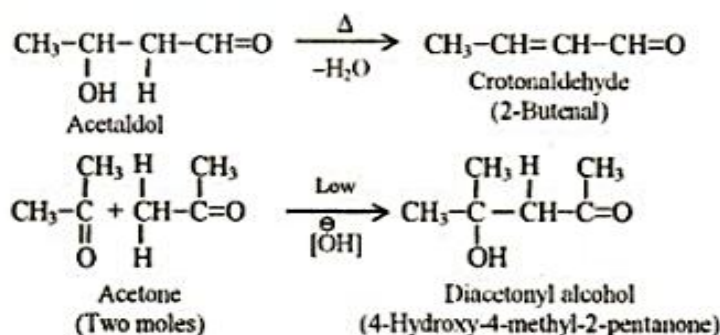
Mechanism :

The generally accepted mechanism for base-catalysed condensation involves the following steps:

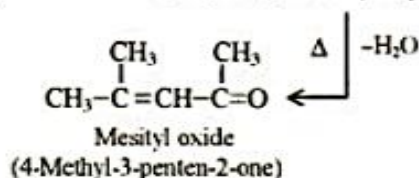


β -hydroxy aldehydes or ketones obtained are easily dehydrated, yielding a stable alkene in which a carbon-carbon double bond is conjugated with a carbon-oxygen double bond of the carbonyl group.

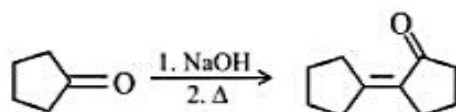
A α, β -unsaturated aldehyde crotonaldehyde is formed by the elimination of a water molecule on heating β -hydroxy butanol (3-hydroxybutanal)

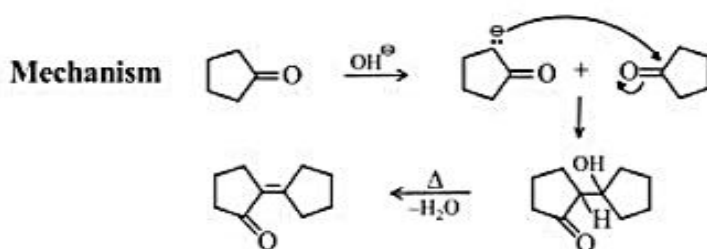


Exam. 2

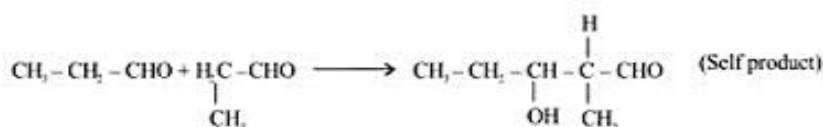
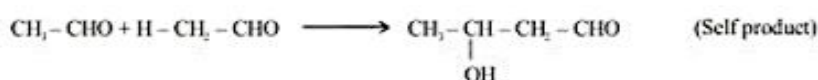
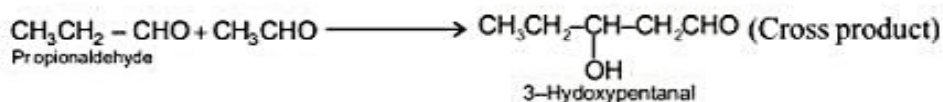
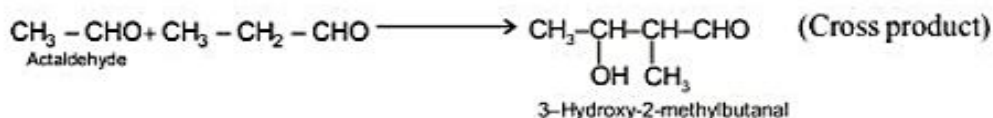


Exam.3



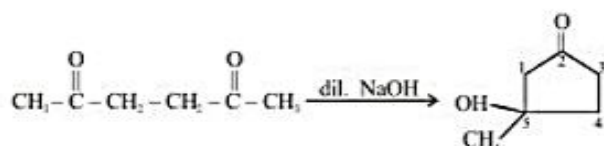


Aldol condensation of two non identical carbonyl compounds is called mixed or **cross aldol condensation**. Theoretically four products can be formed from aldol condensation of the carbonyl compounds A and B.

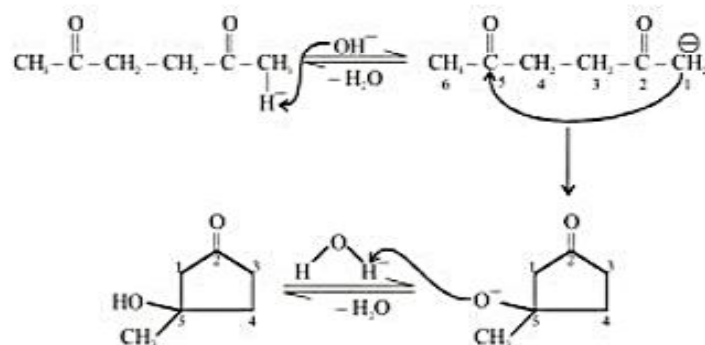


Intramolecular aldol condensation : It is given by dialdehydes or diketones. The diketones should be 2, 5; 2, 6; 2, 7; and 2, 8 diketones. Intramolecular aldol condensation offers a convenient method for the preparation of five & six membered rings. 2, 7 diketones gives five membered cyclic compound where as 2, 8-diketones gives six membered cyclic compound.

Ex.



Mechanism-

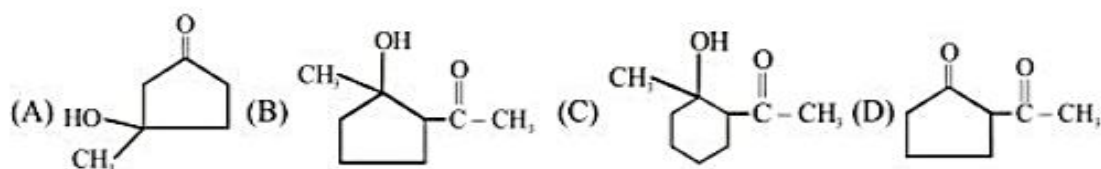


Note :- If diketones is 2, 7; 2, 8 or 2, 9 then inner α -carbon converts into carbanion in the presence of base.

Ex.

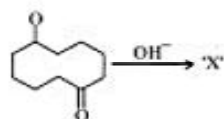


Product 'X' is

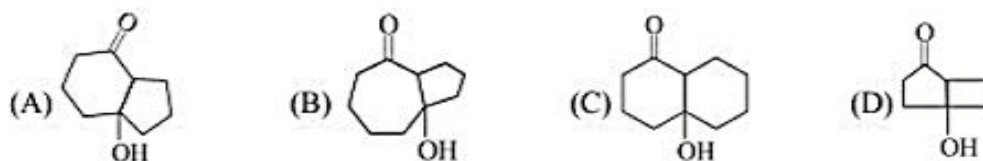


Ans. B

Ex.



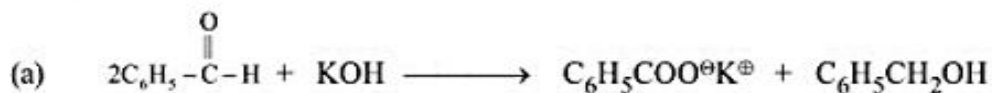
X is-



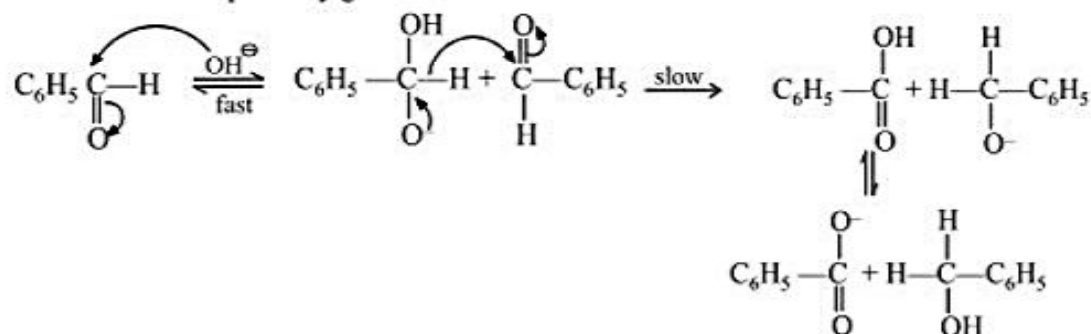
Ans. (B)

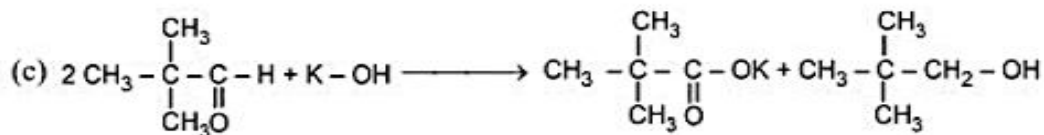
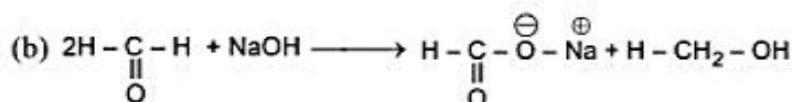
Cannizzaro Reaction : Carbonyl compound in which α -H atom is absent, when react with strong base like NaOH or KOH then forms sodium and potassium salt of carboxylic acid and alcohol. It is an example of the reaction in which one mole of the compounds is reduced. Such type of reaction is called disproportionation reaction, also known as cannizzaro reaction. In this reaction elimination of hydride ion takes place. In this reaction oxidation number changes from 0 to +2 and 0 to -2.

Compounds showing cannizzaro reaction are -



The reaction follows the pathway given below :





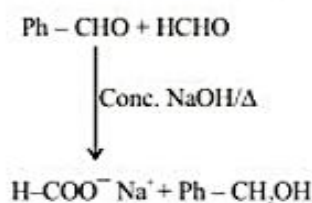
Note : -

(i) $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} - \text{CHO} \\ \diagup \\ \text{CH}_3 \end{array}$ gives cannizaro reaction although it has one α 'H'.

(ii) $\text{CCl}_3 - \text{CHO}$ does not give cannizaro reaction while it has no ' α ' H. It gives haloform reaction

(iii) Cannizaro reaction is an example of disproportionation reaction and it is also an example of redox reaction

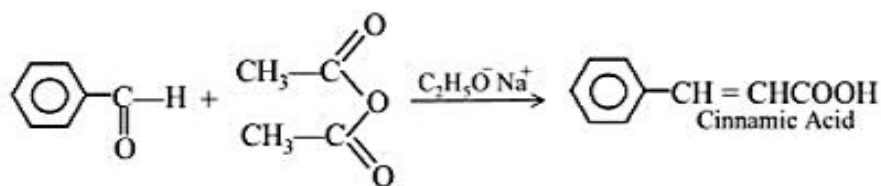
Cross Cannizaro Reaction : If two different aldehydes (α -hydrogen less) are used then one of the aldehyde under goes oxidation while other aldehyde under goes reduction



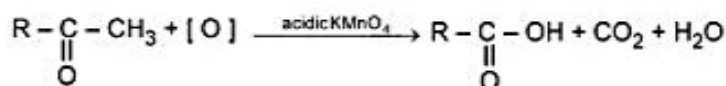
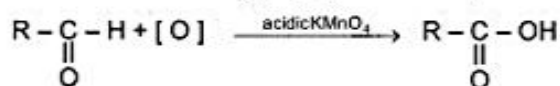
Note : α -hydrogen less aldehyde having more electron deficient carbonyl carbon under goes oxidation.

Perkin Condensation

Aromatic aldehydes lacking α -hydrogen condense with acid anhydrides having an α -hydrogen in the presence of a strong base (ethoxide ion), forming unsaturated acids.

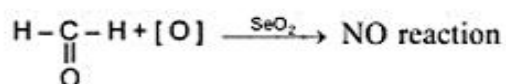


Oxidation : Aldehyde on oxidation forms respective acid while ketone forms less carbon carboxylic acid on oxidation according to popoff's rule (As discussed in Alcohol theory)

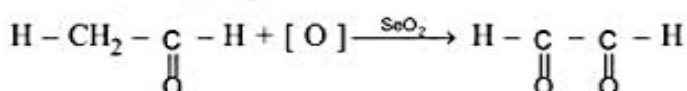


Note :-

(a) If oxidising agent is selenium oxide SeO_2 then, α -methylene group of carbonyl compound oxidises into $-\overset{\text{O}}{\parallel}\text{C}-$ group and resultant dicarbonyl compound will be formed.

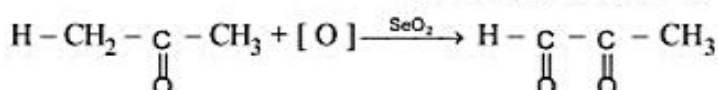


α - methylene group is absent.



glyoxal

(dicarbonyl compound)

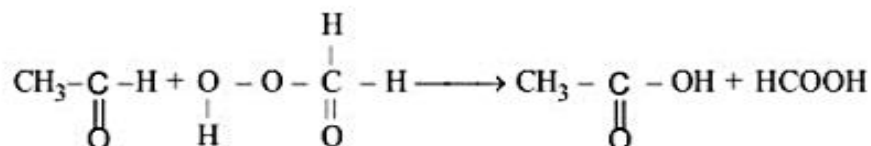
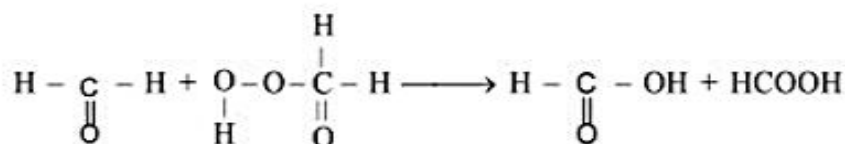


pyruvic aldehyde

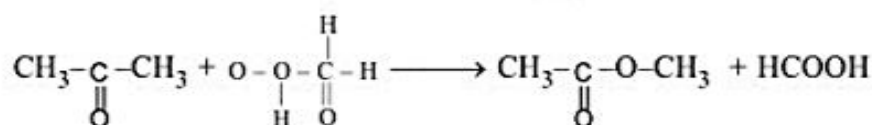
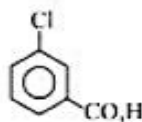
(methyl glyoxal)

- (b) If the oxidising agent is performic acid then aldehyde oxidises into respective acid while ketone oxidises into ester. The reaction is called '**Baeyer-villiger Oxidation**'. Other peroxy acid also give same product.

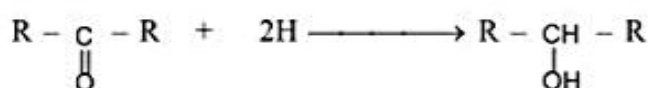
eg. CH_3COOOH , $\text{C}_6\text{H}_5\text{COOOH}$, MCPBA, CF_3COOOH



*** MCPBA \rightarrow meta chloro perbenzoic acid



Reduction : Aldehyde on reduction form primary alcohol while ketone on reduction form secondary alcohol.



secondary alcohol

Note :

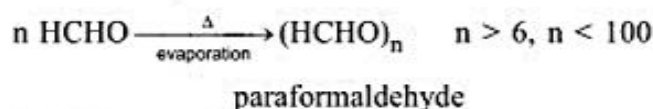
- In the above reaction if reducing agent is $\text{Na} + \text{C}_2\text{H}_5\text{OH}$ then reaction is called '**Bouveault- Blanc Reaction**'.
- If reducing agent is NaH reaction is called '**Darzen's Reaction**'. We can also use LiAlH_4 in this reaction.
- If reducing agent is (red P / HI) then product will be alkane.
- If reducing agent is $\text{Zn-Hg}/\text{conc. HCl}$ then product will be alkane. Reaction is called '**Clemmenson-Reduction**'.
- If reducing agent is alkaline solution of hydrazine, product will be alkane. Reaction is called '**Wolf - kishner Reduction**'.
- The percentage yield of alkane can be increased by using diethylene glycol in wolf kishner reduction then reaction is called '**Huang-Millan Conversion**'.
- If reducing agent is aluminium iso propoxide $(\text{CH}_3 - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{O})_3\text{Al}$, then product will be alcohol.

Reaction is called '**Meerwein-Pondorff Verley Reduction**'.

Polymerisation Reactions : Aldehyde shows addition as well as condensation polymerisation reactions while ketone shows only condensation polymerisation reactions.

ADDITION POLYMERISATION REACTION OF FORMALDEHYDE

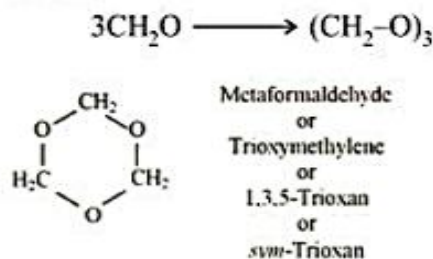
- When aqueous solution of formaldehyde is heated then it converts into a white crystalline solid called '**Paraformaldehyde**'.



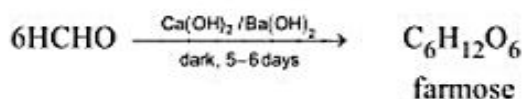
If $n \leq 50$ Linear structure polymer

If $n > 50$ Cyclic structure polymer

- If formaldehyde is kept with conc. H_2SO_4 at room temperature then it forms a cyclic trimer called meta formaldehyde or trioxane.

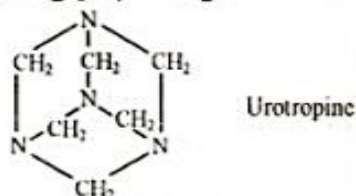
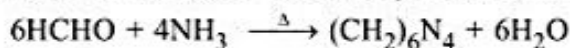


- If aqueous solution of formaldehyde is kept with lime water in dark room for 5-6 days then it converts into a sweet solution called '**FARMOSE**'. It is an example of linear polymer.



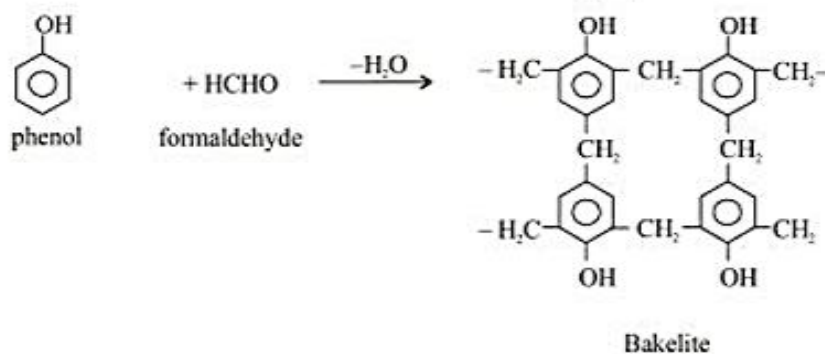
CONDENSATION POLYMERISATION REACTION OF FORMALDEHYDE

- (a) **With Ammonia** :– When formaldehyde is heated with NH_3 then a white crystalline heterocyclic compound is formed called 'Hexamethylene tetramine' or urotropene' or 'Aminoform'.



It is used in medicine or diabetes or urinary infection.

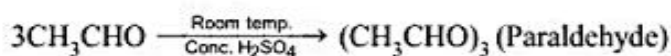
- (b) **With Phenol** :– In presence of dilute alkali formaldehyde first form o- & p- hydroxy benzyl alcohol with phenol which on self condensation form a cross link polymer called 'Bakelite'.



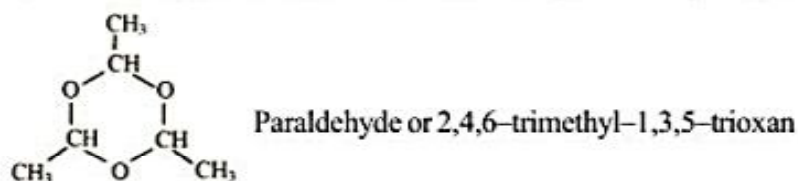
Bakelite is electric and thermal resistant. So, used in formation of electric appliances. Reaction is called 'Lederer-Manasse Reaction'.

Addition Polymerisation of Acetaldehyde :

- (a) When acetaldehyde is kept with conc. H_2SO_4 at room temperature then it form a cyclic trimer called paraldehyde.

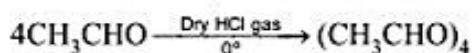


Paraldehyde has nonaromatic heterocyclic structure and it is called 2,4,6-trimethyl-1,3,5-trioxan.

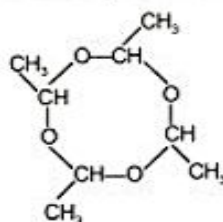


Paraldehyde is used as mild hypnotic.

- (b) If acetaldehyde is kept with highly conc. HCl at low temperature then it forms a cyclic tetramer called metaaldehyde.



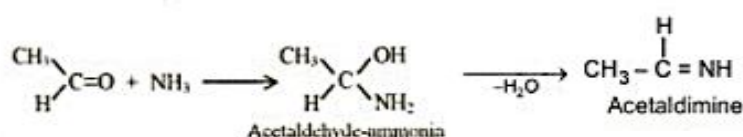
Metaldehyde has the following nonaromatic eight-membered heterocyclic structure.



Note : Metaldehyde is used as smokeless powder and Para aldehyde is used as a sedative while meta aldehyde is used as a solid fuel.

Condensation Polymerisation of Acetaldehyde : –

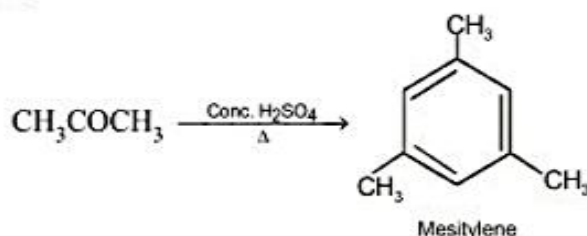
- (a) **Aldol condensation** – Discussed earlier.
- (b) **Reaction with NH_3 :**



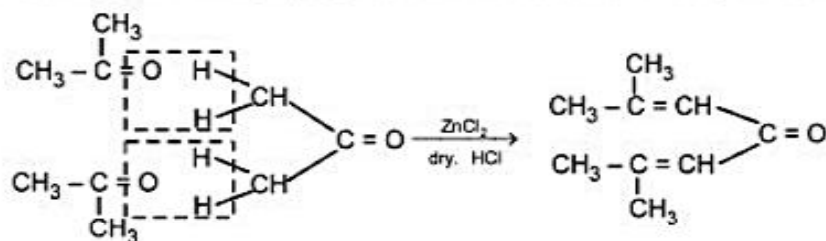
Acetaldimine is formed by the elimination of water molecule on heating acetaldehyde-ammonia, which undergoes polymerisation to form a nonaromatic heterocyclic addition trimer, name 2,4,6-trimethylhexahydro-1,3,5-triazine trihydrate as the main product.

Condensation Polymerisation of Acetone :

- (a) If acetone is heated with conc. H_2SO_4 then an aromatic compound is formed called 1,3,5-trimethyl benzene or mesitylene.

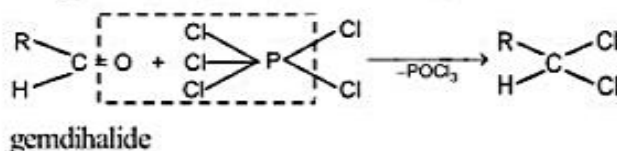


- (b) If acetone would be in excess in ketal condensation or catalyst (ZnCl_2 / dry HCl) is used then three moles of acetone undergoes condensation polymerisation and form a compound called '**Phorone**'.

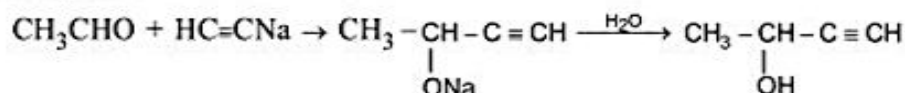


[molecular wt. of phorone = 3 mole of acetone – 2 mole of H_2O]

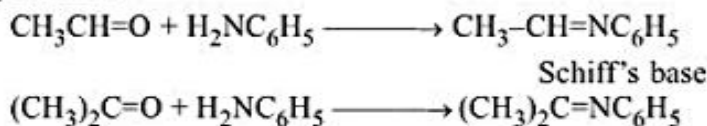
Reaction with PCl_5 : Carbonyl compound form gemdihalide with PCl_5 .



With sodium acetylide :



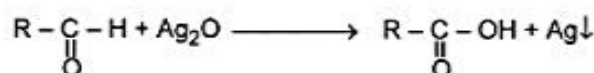
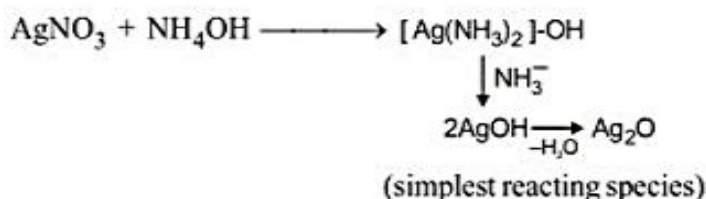
With primary amine :-



REACTIONS SHOWN BY ALDEHYDES ONLY

Reducing nature of Aldehyde : Aldehyde are reducing in nature, they can reduce Tollen's reagent, Fehling solution and mercuric chloride solution.

- (a) **Reaction with Tollen's Reagent :** - Ammonical silver nitrate solution is called Tollen's reagent. Aldehyde reduce the tollen's reagent and form silver mirror. Aldehyde oxidises itself into carboxylic acid.

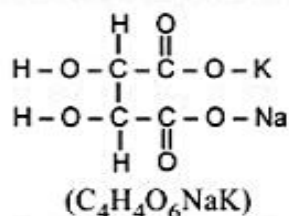


Note : In the above reaction oxidation number of Ag varies from +1 to 0.

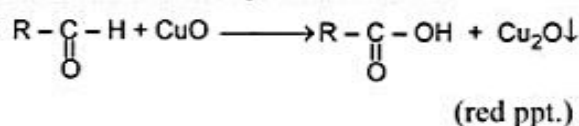
- (b) **Reaction with Fehling Solution :** It is the mixture of two solution called Fehling solution A and Fehling solution B.

Fehling Solution A : Aqueous solution of CuSO_4 (blue)

Fehling Solution B : Alkaline solution of Roschelle salt (sodium potassium tartarate)

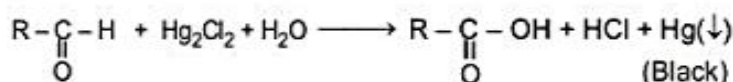


By the mixing of both solution we get a dark blue colour solution called final fehling solution. Reacting species of this solution is cupric oxide CuO .



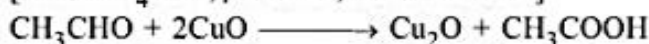
NOTE : Oxidation number of copper varies from +2 to +1

- (c) **Reaction with Mercuric Chloride solution :** Aldehyde reacts with mercuric chloride solution and initially form white ppt. of mercurous chloride solution, which further react with excess of aldehyde and form black ppt. of mercury.



- (d) **Benedict solution :**

[A-CuSO₄ soln, β-NaOH, Sodium citrate]

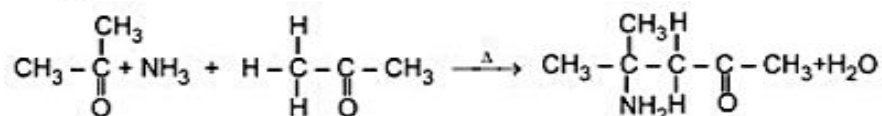


- (e) **Schiff's reagent :**

Magenta dye $\xrightarrow{SO_2}$ Colourless solution $\xrightarrow{CH_3CHO}$ Pink colour restored

REACTIONS SHOWN BY KETONES ONLY

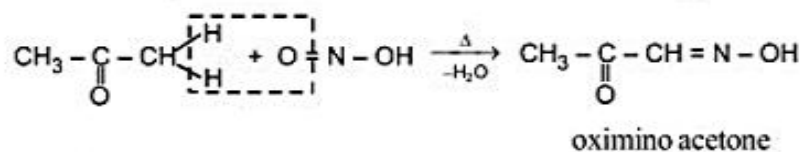
- (a) **Reaction with NH₃ :** If acetone is heated with ammonia then it forms diacetone amine.



If acetone and ammonia would be in excess then product would be tri acetone amine. If tri acetone amine is heated at high temperature then it converts into a heterocyclic compound by the elimination of water.

- (b) **Reaction with Nitrous Acid :**

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



- (c) **Bimolecular Reduction : -**

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

