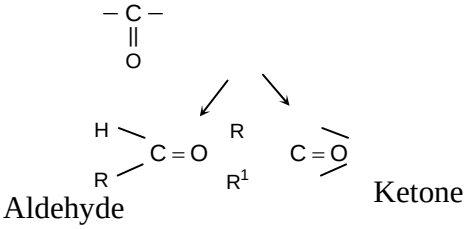
ORGANIC CHEMISTRY –II

3. CARBONYL COMPOUNDS

CARBONYL COMPOUNDS :

- The compounds with C = O are called as carbonyl compounds.
- Aldehydes and ketones are carbonyl compounds.
- –CHO group is a terminal group.

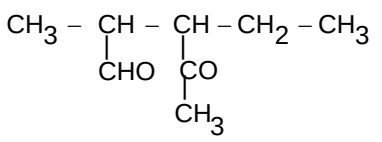


Aldehyde Ketone

Nomenclature :

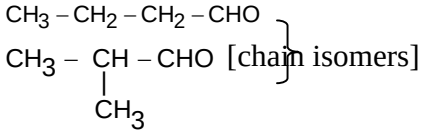
Formula of Aldehyde	**I U P A C**	**Common**
HCHO	Methanal	Formaldehyde
$CH_3 – CHO$	Ethanal	Acetaldehyde
$CH_3 – CH_2 – CHO$	Propanal	Propionaldehyde
$CH_3 – CH_2 – CH_2 – CHO$	Butanal	Butonaldehyde
$CH_3 – \underset{\displaystyle CH_3}{\underset{\vert}{CH}} – CHO$	2 –methyl propanal	α - methyl propionaldehyde
$CH_3 – \underset{\displaystyle OH}{\underset{\vert}{CH}} – \underset{\displaystyle Cl}{\underset{\vert}{CH}} – CHO$	2 – Chloro, 3 –Hydroxy butanal	α – Chloro, β - hydroxy butanaldehye

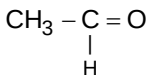
Formula of ketones	**I U P A C**	**Common**
$CH_3 – \underset{\displaystyle O}{\underset{\Vert}{C}} – CH_3$	Propanone	Acetone
$CH_3 – \underset{\displaystyle O}{\underset{\Vert}{C}} – C_2H_5$	Butanone	Ethyl methyl ketone
$C_2H_5 – \underset{\displaystyle O}{\underset{\Vert}{C}} – C_2H_5$	3-Pentanone	Diethyl ketone
$CH_3 – \underset{\displaystyle Cl}{\underset{\vert}{CH}} – \underset{\displaystyle O}{\underset{\Vert}{C}} – \underset{\displaystyle OH}{\underset{\vert}{CH}} – CH_3$	2-hydroxy– 4– chloro– 3- pentanone	α - chloro ethyl –α^1–oxy ethyl ketone
$CH_3 – \underset{\displaystyle CH_3}{\underset{\vert}{CH}} – \underset{\displaystyle O}{\underset{\Vert}{C}} – \underset{\displaystyle C_2H_5}{\underset{\vert}{C}} – CH_3$	2,4-diemthyl –3-hexanone	Isopropyl secondary butyl ketone

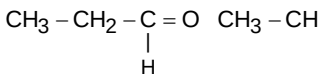
	2-methyl-3-ethyl- 4-ketopentanal	

- **Isomerism in Aldhydes :**

  Aldehydes will exhibit chain, functional and tautromerism.

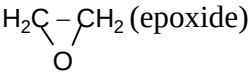
  

-  $CH_2 = CH - OH$ [Tautromers]

-  [Tautomers]

- Aldehydes, ketones, unsaturated alcohols and cyclic ethers are functional isomers of each other.

  Ex: C_2H_4O : $CH_3 - CHO$

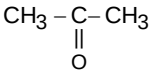
   (epoxide)

  $CH_3 - CHO$

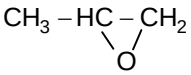
  $CH_2 = CH - OH$ (Tautomers)

  Ex. C_3H_6O :

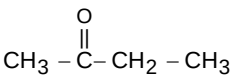
  $CH_3 - CH_2 - CHO \rightarrow CH_3 - CH = CH - OH$

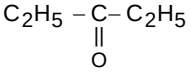
  

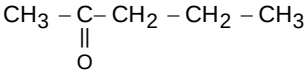
  $CH_2 = CH - CH_2 - OH$

  Ex. C_4H_8O : $CH_3 - CH_2 - CH_2 - CHO \rightarrow CH_3 - CH_2 - CH = CH - OH$

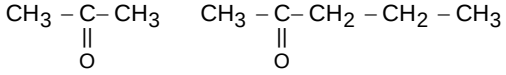
   metamers (position)

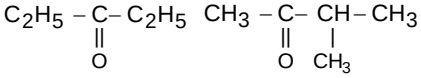
  

- Ketones are of two types based on the nature of alkyl groups attached to the functional groups.

  Simple ketones mixed ketones

  $R = R^1$ $R \neq R^1$



[chain isomers]

- Acetaldehyde and acetone are not isomers.

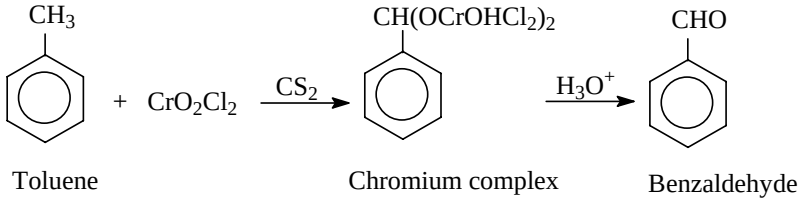
METHOD OF PREPARATION OF ACETALDEHYDE AND ACETONE

Acetaldehyde : $CH_3-\underset{\underset{H}{|}}{C}=O$	**Acetone :** $CH_3-\underset{\underset{CH_3}{|}}{C}=O$
1) By the oxidation of ethyl alcohol $CH_3-CH_2-OH+\frac{1}{2}O_2 \xrightarrow[CH_2Cl_2]{PDC\ (or)\ PCC} CH_3-CHO + H_2O$	1) By the oxidation of isopropyl alcohol $CH_3-\underset{\underset{CH_3}{|}}{CH}-OH+\frac{1}{2}O_2 \xrightarrow[dil\ H_2SO_4]{K_2Cr_2O_7} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{||}}{C}}+H_2O$
2) By the dehydrogenation of ethyl alcohol $CH_3-CH_2-OH \xrightarrow{Cu\ 300^0C} CH_3-CHO+H_2$	2) BY the dehydrogenation of isopropyl alcohol $CH_3-\underset{\underset{CH_3}{|}}{CH}-OH \xrightarrow{Cu\ 300^0C} CH_3-\underset{\underset{CH_3}{|}}{C}=O+H_2$
3) By the hydration of Acetylene $CH\equiv CH+H-OH \xrightarrow[1\%\ HgSO_4,60^0C]{40\%,\ H_2SO_4} CH_2=CH-OH$ $\xrightarrow{rearrangement}$ CH_3-CHO	3) By the hydration of propyne $CH_3-C\equiv CH+H-OH \xrightarrow[1\%\ HgSO_4,60^0C]{40\%,\ H_2SO_4} CH_3-\underset{\underset{OH}{|}}{C}=CH_2$ $\xrightarrow{rearrangement}$ $CH_3-\overset{\overset{O}{||}}{C}-CH_3$
4)By the hydrolysis of gem dichloride that is CH_3–$CHCl_2$ $CH_3-CHCl_2+2KOH_{(aq)} \xrightarrow[-2KCl]{} CH_3-CH(OH)_2 \xrightarrow{-H_2O}$ CH_3-CHO	4) By the hydrolysis of gem dichloride that is isopropy- ldene chloride $CH_3-\underset{\underset{CH_3}{|}}{CCl_2}+2KOH_{(aq)} \xrightarrow{2KCl} CH_3-\underset{\underset{CH_3}{|}}{C(OH)_2} \xrightarrow{-H_2O}$ $CH_3-\underset{\underset{CH_3}{|}}{C}=O$
5) Wacker's process : ethylene reacts with aqueous palladium chloride in presence of catalyst to give Acetaldehyde. $CH_2=CH_2+PdCl_2+H_2O \xrightarrow[H^+]{CuCl_2} CH_3-CHO+2HCl+Pd$	5) Propene reacts with aqueous palladium chloride to give acetone. $CH_3-CH=CH_2+PdCl_2+H_2O \rightarrow CH_3-\overset{\overset{O}{||}}{C}-CH_3+2HCl+Pd$
6) The distillation of calcium acetate and calcium formate $Ca\begin{matrix}OOCCH_3\\OOCCH_3\end{matrix} + \begin{matrix}HCOO\\HCOO\end{matrix}Ca \xrightarrow{\Delta} 2CH_3-CHO+2CaCO_3$ Calcium ethanoate calcium methanoate	6) By the dry distillation of calcium acetate alone $Ca\begin{matrix}COOCH_3\\COOCH_3\end{matrix} + \begin{matrix}CH_3COO\\CH_3COO\end{matrix}Ca \xrightarrow{\Delta} 2CH_3-CO-CH_3+2CaCO_3$
7) Rosenmund's reduction : Acetyl chloride (acid chloride) on reduction with H_2 in presence Lindlar's catalyst gives acetaldehyde $CH_3-\overset{\overset{O}{||}}{C}-Cl+H_2 \xrightarrow{Pd.BaSO_4\ /\ Quinoline} CH_3-\overset{\overset{O}{||}}{C}-H+HCl$ only aldehydes can be prepared by this method	7). Ketones can not be prepared by this method
Physical properties : 1) Colourless liquid with pungent smell 2) Soluble in water, alcohol, ether etc, . 3) It is more volatile with very low boiling point [21^0C] 4) Its aqueous solution has pleasant smell as it exist as ethyledene glycol. CH_3- CHO + H – OH → CH_3- $CH(OH)_2$	**Physical properties :** 1) Colourless liquid with pleasent smell 2) Soluble in water, alcohol, ether etc. 3) It is less volatile with higher boiling point 56°C]. 4) Highly inflammable .

PREPARATION OF BENZALDEHYDE

1.OXIDATION OF METHYLBENZENE:

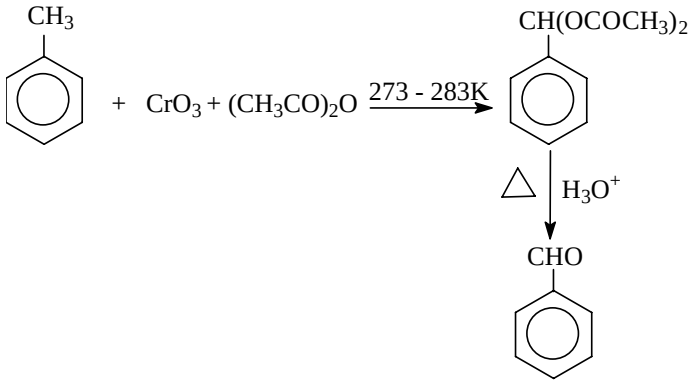
a) With chromyl chloride followed by hydrolysis



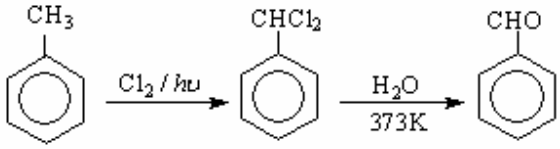
Toluene — Chromium complex — Benzaldehyde

This reaction is known as Etard reaction.

b) With chromtic oxide CrO_3 in acetic anhydride

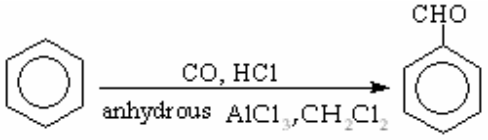


2. By side chain chlorination followed by hydrolysis



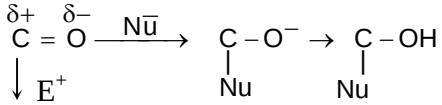
3. Gatterman - Koch benzal chloride reaction:

Here benzene is treated with carbon monoxide and HCl in the presence of anhydrous $AlCl_3$ and CH_2Cl_2

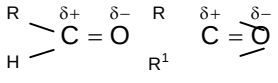


Chemical reactions :

1) They under go nucleophilic additions due to the presence of C = O
2) In case of nucleophilic attack a stable intermediate is formed that is anion.
3) In case electrophilic attack occurs first an unstable intermediate is formed. Therefore nucleophilic attack occurs first and it is called nucleophilic addition.



$C^+ - OE$



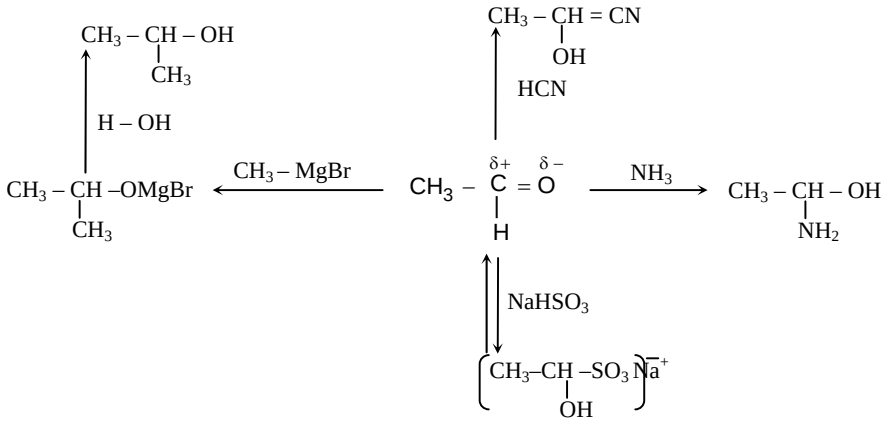
(Aldehydes) *(Ketones)*

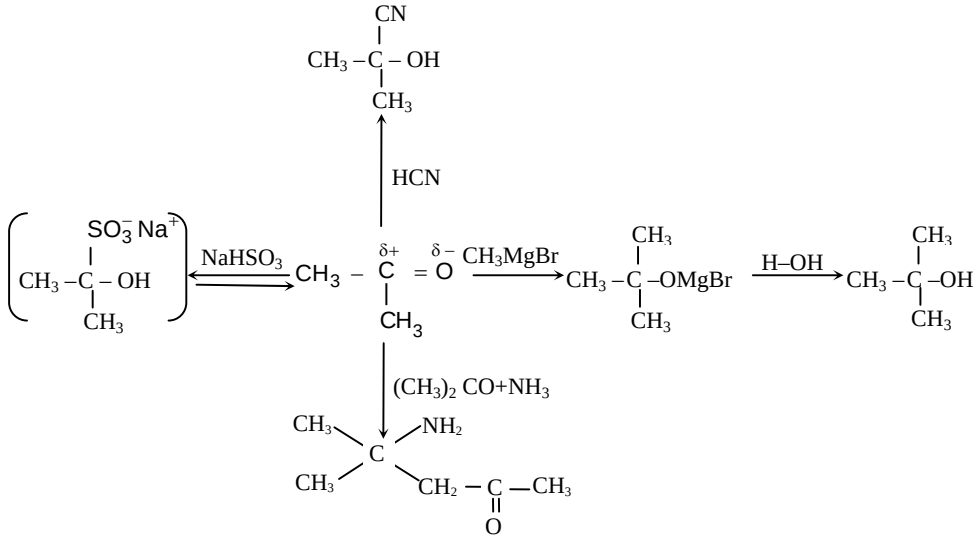
CHEMICAL REACTIONS : Carbonyl group is highly polar. Carbon of carbonyl group gets partial +ve charge and oxygen gets partial – ve charge. Carbon is added with nucleophile and forms a stable intermediate i.e. anion. Then electrophile is added to oxygen to complete the addition reaction.

- Thus aldehydes and ketones undergo nucleophilic additions.
- Aldehydes are more reactive than ketones due to greater magnitude of +ve charge on carbon of carbonyl group.

I. Nucleophilic additions:

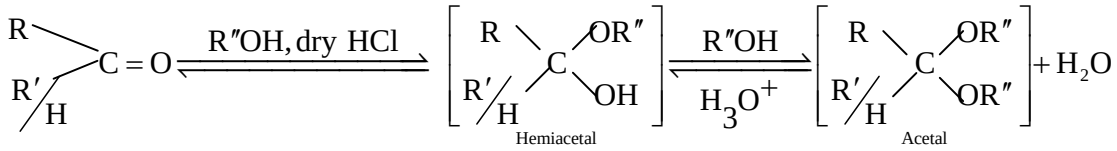
1) Addition of HCN : Acetaldehyde and acetone give corresponding cyanohydrins.
2) Addition of $NaHSO_3$: Acetaldehyde and acetone give corresponding sodium bisulphites. These are white crystalline and give back original acetaldehyde and acetone on treating with mineral acids. Thus $NaHSO_3$ is useful in the purification of carbonyl compounds.
3) Addition of NH_3 : Acetaldehyde gives acetaldehyde ammonia and acetone gives diacetone amine.
4) Addition of Grignard reagent : Aldehydes (except formaldehyde) give secondary alcohols and ketones give tertiary alcohols on addition with R – MgX.

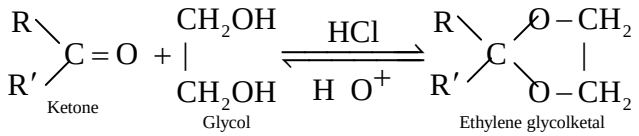




Addition of alcohols:

Aldehydes react with one molecule of alcohol in the presence of dry HCl to give alkoxyalcohol intermediates known as hemiacetals. Hemiacetals further react with one more molecule of alcohol to give a gem-dialkoxy compound called acetals.





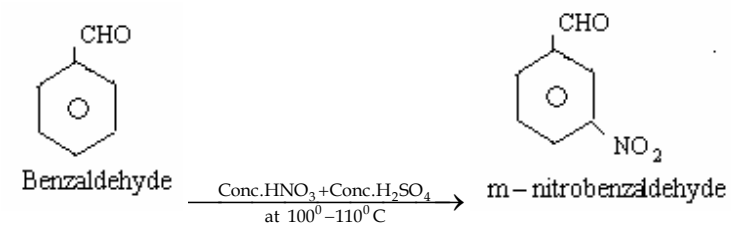
- **<u>CANNIZZARO'S REACTION :</u>**

  Aldehydes that have no hydrogen atom undergo this reaction involving disproportionation (self oxidation and reduction) on treating with strong conc. alkali.

  Eg. 1) $HCHO + HCHO \xrightarrow{conc.NaOH} CH_3OH + HCOONa$

  Eg. 2) $C_6H_5CHO + C_6H_5CHO \xrightarrow{conc.KOH} C_6H_5CH_2OH + C_6H_5COOK$

- During electrophilic substitution reactions, -CHO group deactivates benzene ring and it is a meta directing group.

Eg. 

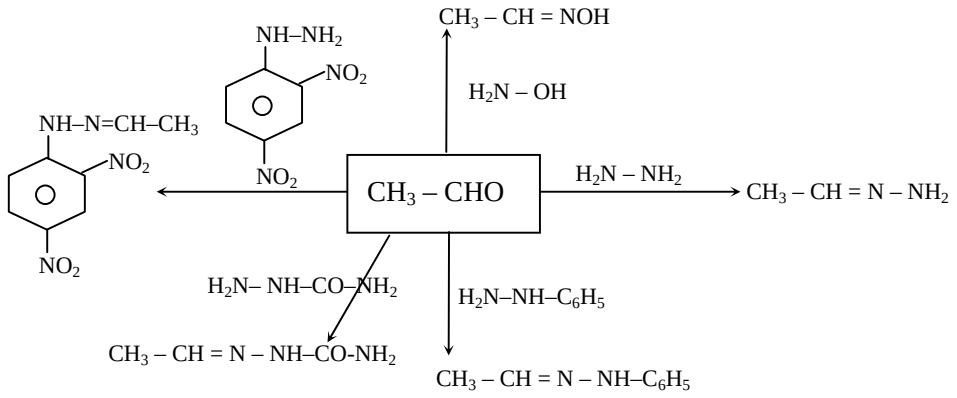
II. Condensation reactions:

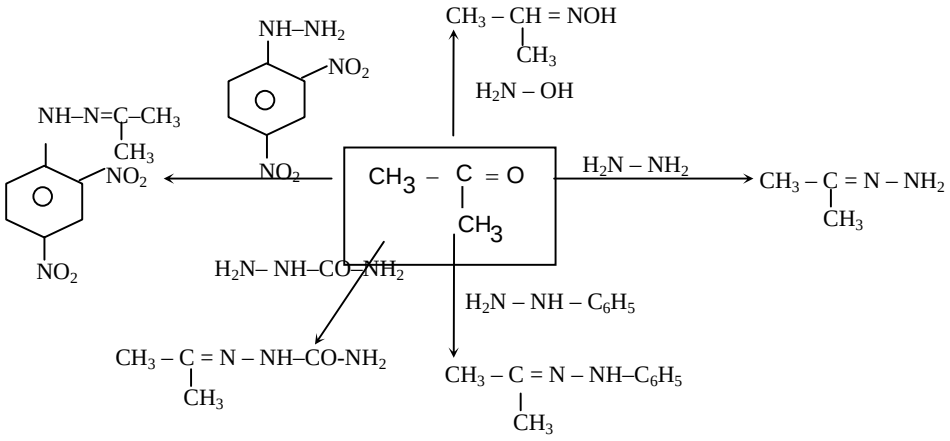
Acetaldehyde and acetone condense with ammonia derivatives such as

i) $H_2N - OH$ ii) $H_2N - NH_2$ iii) phenyl hydrazine iv) 2, 4-DNP v) semicarbazide

- In all these reactions, H_2O is eliminated.

  $\overset{\backslash}{C} = O + H_2N - X \rightarrow C \overset{\backslash}{=} N - X + H_2O$





III. Other Reactions:

1) **With PCl_5 :** Both acetaldehyde and acetone gives gem dichlorides

$CH_3 – CHO + PCl_5 \rightarrow CH_3 – CHCl_2 + POCl_3$

$CH_3 – \underset{\underset{CH_3}{|}}{C} = O + PCl_5 \rightarrow CH_3 – \underset{\underset{CH_3}{|}}{CCl_2} + POCl_3$

2) **α-chlorination:** The three α-hydrogens are substituted by chlorine or bromine on reaction with Cl_2 or Br_2

$CH_3 – CHO + 3Cl_2 \rightarrow CCl_3 – CHO + 3HCl$

$CH_3 – \underset{\underset{CH_3}{|}}{C} = O + 3Cl_2 \rightarrow CCl_3 – \underset{\underset{CH_3}{|}}{C} = O + 3HCl$

3) **Iodoform reaction :** (Haloform reaction)

Aldehydes and ketones containing α – methyl groups reacts with X_2 and a base to give CHX_3.

$CH_3 – CHO + 3I_2 + 4NaOH \rightarrow HCOONa + CHI_3\downarrow + 3H_2O + 3NaI$

$CH_3 – CO – CH_3 + 3I_2 + 4NaOH \rightarrow CH_3COONa + CHI_3 \downarrow + 3H_2O + 3NaI$

4) **Distillation with bleaching powder :**

Acetaldehyde and acetone on distillation with bleaching powder gives $CHCl_3$.

5) **Aldol condensation :**

- Aldehydes and ketones having atleast one α - hydrogen will give aldol condensation in presence of dilute base.
- It involves shifting of one α - hydrogen from one molecule to oxygen of another molecule.
- Two acetaldehyde molecules will condense to give aldol or β - hydroxy butyraldehyde.

$$2CH_3\text{–}CHO \xrightarrow{\overline{O}H \text{ or } H^+} CH_3 - \underset{\underset{OH}{|}}{CH}\text{–}\ CH_2 - CHO$$

(aldol)

- Aldol on heating forms unsaturated aldehyde, with the elimination of H_2O.

$$CH_3 - \underset{\underset{OH}{|}}{CH}\text{–}\ CH_2 - CHO \xrightarrow{\Delta} CH_3 - CH = CH - CHO$$

(Crotonaldehyde)

- Two acetone molecules undergo aldol condensation in presence of $Ba(OH)_2$ to give diacetone alcohol.

$$2CH_3 - \underset{\underset{O}{||}}{C}\text{–}\ CH_3 \xrightarrow{Ba(OH)_2} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}} - CH_2 - \underset{\underset{O}{||}}{C}\text{–}\ CH_3$$

(Diacetone alcohol)

6) **Condensation of acetone in presence of HCl:**

In presence of con.HCl, two acetone molecules will condense to give mesityl oxide.

$$2CH_3COCH_3 \xrightarrow{HCl} CH_3 - \underset{\underset{CH_3}{|}}{C} = CH - CO - CH_3 + H_2O$$

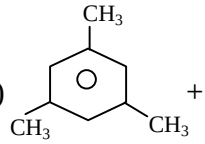
(Mesityl oxide)

In presence of HCl, three acetone molecules will condense to give phorone.

$$3CH_3 - CO - CH_3 \xrightarrow{HCl} CH_3 - \underset{\underset{CH_3}{|}}{C} = CH - \underset{\underset{O}{||}}{C}\text{–}\ CH = \underset{\underset{CH_3}{|}}{C} - CH_3 + 2H_2O$$

7) **Condensation of acetone in presence of conc. H_2SO_4 :**

Three acetone molecules condenses to give mesitylene or 1, 3, 5 – trimethyl benzene in presence of con.H_2SO_4.

$$3CH_3COCH_3 \xrightarrow{conc.H_2SO_4} \underset{\text{Mesitylene}}{C_6H_3(CH_3)_3}$$ (or)  $+ 3H_2O$

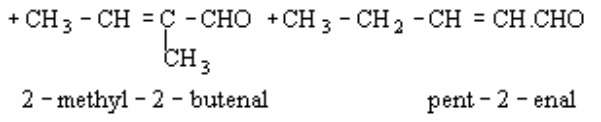
- **<u>Crossed aldol condensation :</u>** If the aldol condensation is between two different aldehydes or ketones, it is called crossed aldol condensation. When both of them have hydrogen, a mixture of four products are formed.

Eg : $CH_3 - CHO + CH_3 - CH_2CHO \xrightarrow{i)\ NaOH\ ,\ ii)\ \Delta}$

$$CH_3 - CH = CH - CHO + CH_3 - CH_2 - CH = \underset{\underset{CH_3}{|}}{C} - CHO$$

2 - butenal

2 - methyl - 2 - *Pentenal*



- Acetone may also be involved in cross condensation

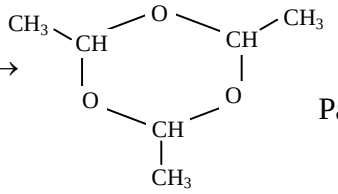
Eg: $C_6H_5CHO + CH_3 - CO - C_6H_5 \xrightarrow{OH^-, 293K} C_6H_5 - CH = CHCO.C_6H_5$

. $1,3-diphenyl \quad prop-2-en-1-one$

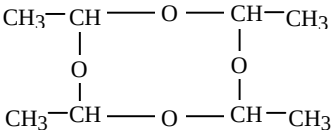
(benzal acetophenone)

8) **Polymerisation of acetaldehyde :**

Acetaldehyde polymerizes to paraldehyde at high temperature in presence of conc. H_2SO_4.

$3CH_3 - CHO \xrightarrow{conc.H_2SO_4}$  Paraldehyde (Pleasant smelling liquid)

Acetaldehyde polymerizes to tetramer (metaldehyde) in presence of conc. H_2SO_4 at 0°C.

$4CH_3 - CHO \xrightarrow{conc.H_2SO_4}$  (tetramer) Metaldehyde (white solid)

9) **Reduction :** Aldehydes and ketones on reduction will give alcohols or alkanes depending on the nature of reducing agent.

i) $\underset{}{\overset{}{C}} = O \xrightarrow[iii)\ NaBH_4 \quad iv)\ Na|\ alcohol]{i)\ H_2|Ni \quad ii)\ LiAlH_4} CH - OH$ Aldehydes give 1°-alcohol and ketones give secondary alcohol.

ii) $C = O \xrightarrow[ii)\ N_2H_4 + KOH + alcohol]{i)\ Zn-Hg + HCl} CH_2$

i) Clemensen's reduction

$$CH_3 - CH_3 \xleftarrow[\text{ii) Wolff–kishner reduction } (N_2H_4+KOH+alcohol)]{(Zn-Hg+HCl)} CH_3 - CHO \xrightarrow[iii)\ NaBH_4 \quad iv)\ Na/alcohol]{i)\ H_2/Ni\ ii)\ LiAlH_4} CH_3 - CH_2 - OH$$

i) Clemensen's reduction

$$CH_3 - CH_2 - CH_3 \xleftarrow[\text{ii) Wolff–kishner reduction } (N_2H_4+KOH+alcohol)]{(Zn-Hg+HCl)} CH_3 - \underset{\underset{O}{\|}}{C} - CH_3 \xrightarrow[iii)\ NaBH_4 \quad iv)\ Na/alcohol]{i)\ H_2/Ni\ ii)\ LiAlH_4} CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3$$

10) **Oxidation :**

- Aldehydes are easily oxidised than ketones because ketones involve C – C bond cleavage aldehydes do not involve C – C bond cleavage
- Aldehydes on oxidation give carboxylic acids having same number of carbons and ketones give carboxylic acids having less number of carbons.
- Aldehydes can be oxidised by mild oxidising agents like Ag^+, Cu^{2+}

i) $CH_3 - CHO \xrightarrow{(O)} CH_3COOH$

ii) $CH_3 - CO - CH_3 + 4(O) \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - COOH + CO_2 + H_2O$

11) **Distinguishing tests for aldehydes :**

- Aldehydes are easily oxidised than ketones. Aldehydes easily respond to mild oxidising agents like Ag^+, Cu^{2+} etc but ketones do not respond to the mild oxidising agent.
- Based on the difference in their reducing nature, aldehydes can be distinguished from ketones.

a) **Tollen's test or silver mirror test :**

- Tollen's reagent is ammonical silver nitrate i.e. $NH_4OH + AgNO_3$ (or) $[Ag(NH_3)_2]$ OH (or) $[Ag(NH_3)_2]^+$
- Acetaldehyde reduces Ag^+ to Ag

$CH_3 - CHO + 2[Ag(NH_3)_2]\ OH \rightarrow 2Ag\downarrow + 4NH_3 + CH_3COOH + H_2O$

b) **Fehling's test :**

- Fehling's reagent is alkaline copper sulphate complexed with Rochelle's salt (Na –K tartarate)
- Acetaldehyde reduces Cu^{2+} of Fehling's solution to Cu^+ giving yellow or brick red color.
- $CH_3 - CHO + 2Cu^{2+} + 5OH^- \rightarrow CH_3COO^- + Cu_2O\downarrow + 3H_2O$

(Red)

c) **Benedict's test:**

- Benedict's solution is alkaline copper sulphate complexed with citrate ions.
- Acetaldehyde reduces Benedict's solution (Cu^{2+}) also as that of Fehling's solution.

d) **Schiff's Base test :**

- Schiff's reagent is decolorized pink colored p – rosaniline hydrochloride with SO_2.
- Acetadehyde restores the pink color of Schiff's reagent.

Tests for Acetone :

1) Legal test : Acetone $\xrightarrow[\text{prusside+NaOH}]{\text{sodium nitro}}$ wine red solution $\xrightarrow[\text{standing}]{\text{long}}$ yellow

- 2) Indigo test : Acetone $\xrightarrow[+KOH]{\text{orthonitro benzaldehyde}}$ blue color (indigotin)

USES OF ACETALDEHYDE :

- In the preparation of acetic acid, chloral , rubber, dyes and drugs
- In the preparation of paraldehyde, used as hypnotic drug
- In the preparation of metaldehdye, used as solid fuel.
- In the silver coating of mirrors
- As antiseptic inhalent in nose troubles.

Uses of Acetone :

- As solvent for cellulose acetate, cellulose nitrate, resins.
- As nail polish remover
- For storing of acetylene
- In the preparation of plexiglass (unbreakableg lass)
- In the preparation of synthetic rubber
- In the preparation of CORDITE (smokeless bomb)
- As reaction medium and as extractant.