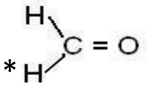
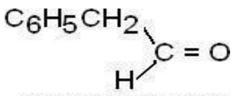
ALDEHYDES AND KETONES

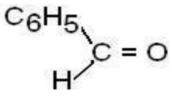
- In aldehydes, the carbonyl group is linked to either two hydrogen atom or one hydrogenatom and one carbon containing group such as alkyl, aryl or aralkyl group Examples



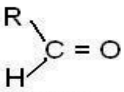
formaldehyde



phenyl acetaldehyde

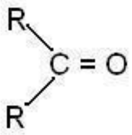


benzaldehyde

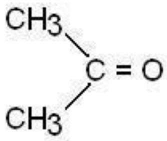


aldehyde

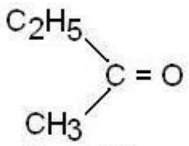
- In ketones, the carbonyl group is linked to two carbon containing groups which may be same or different alkyl, aryl group. If two R and R' groups are same, the ketone is called simple or symmetrical ketone and if R and R' are different, then ketone is known as mixedor an unsymmetrical ketone.



ketone



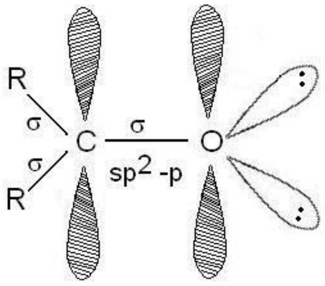
dimethyl ketone
(simple ketone)

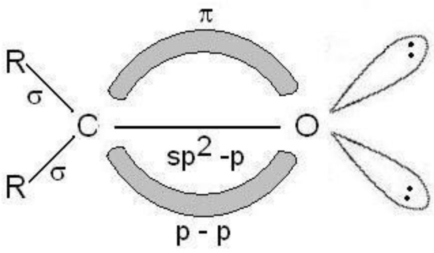


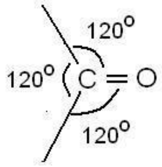
ethyl methyl ketone
(mixed ketone)

STRUCTURE

- Carbonyl carbon of both aldehyde and ketones is sp^2 – hybridised, One of the three sp^2 hybridised orbital get involved in σ- bond formation with half –filled p-orbital of oxygen atom whereas rest of the two are consumed in σ-bond formation with hydrogen and carbondepending on the structure of aldehyde or ketone.
- Unhybridised p-orbital of carbonyl carbon form π-bond with another half-filled p-orbital ofoxygen atom by sideways overlapping.





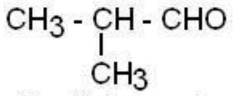


ISOMERISM IN ALDEHYDES AND KETONES

(a) Chain isomerism: Aldehydes (with 4 or more carbon atoms) and ketone (with 5 or morecarbon atoms) show chain isomerism. Example

i) C4H8O

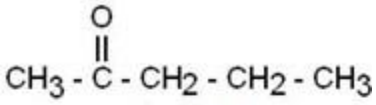
CH3-CH2-CH2-CHO (butanal)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO$

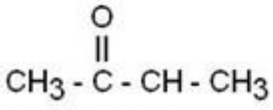
2-methylpropanal

ii) $C_5H_{10}O$



$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$

pentan-2-one



$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH-CH_3$

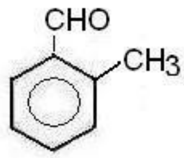
3-methylbutan-2-one

(b) Position isomerism: aliphatic aldehydes do not show position isomerism, because –CHOgroup is always present at the end of carbon chain.

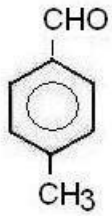
Aromatic aldehyde show position isomerism. Example

(c) Metamerism: Higher ketones show metamerism due to presence of different alkylgroups attached to the same functional group

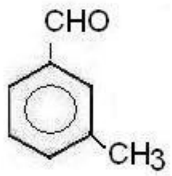
$C_5H_{10}O$



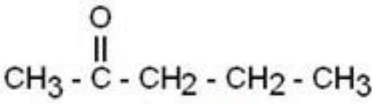
2-methylbenzaldehyde or
o - tolualdehyde



4-methylbenzaldehyde
or p-tolualdehyde

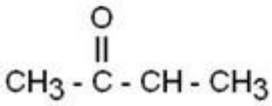


3-methylbenzaldehyde
or m-tolualdehyde



$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$

pentan-2-one

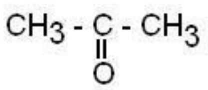


$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH-CH_3$

3-methylbutan-2-one

(d) Functional isomerism: Aldehydes and ketones show functional isomerism in them. In addition, they are also related to alcohols, ethers and other cyclic compounds. ExampleC_3H_6O

CH_3CH_2CHO propanal



$CH_3-\overset{\|}{\underset{O}{C}}-CH_3$ propanone

$CH_2=CH-CH_2-OH$ Prop-2-en-1-ol

$CH_2=CH-OCH_3$ methoxy ethene

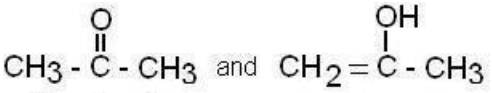
(e) Tautomerism : Aldehydes and ketones also show tautomerism

(I) C_2H_4O

$CH_3-\overset{\overset{O}{\|}}{C}-H$ and $CH_2=\overset{\overset{OH}{|}}{CH}$

acetaldehyde vinyl alcohol

(II) C_3H_6O



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ and $CH_2=\overset{\overset{OH}{|}}{C}-CH_3$

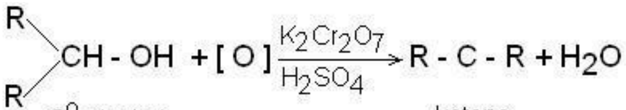
(keto form) (Enol form)

GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

1. From alcohol

(i) Oxidation of alcohol

$$R-CH_2-OH+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}R\text{-}CHO+H_2O$$



$$\begin{matrix}R\\R\end{matrix}\!\!>\!CH-OH+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}R-\overset{}{C}-R+H_2O$$

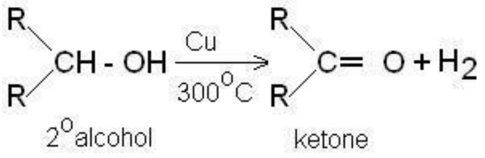
2^o alcohol ketone

- Since the oxidizing agent used in the above reactions is a strong oxidizing agent, it oxidizes aldehydes and ketone further to carboxylic acids
- To prevent further oxidation, a mild oxidizing agent such as pyridinium chlorochromate (pcc), $CrO3.C5H5N\cdot HCl$ or $CrO3NH^+CrO3Cl^-$ are used Collin's reagent [$(C5H5N)2\cdot CrO3$] can also used.

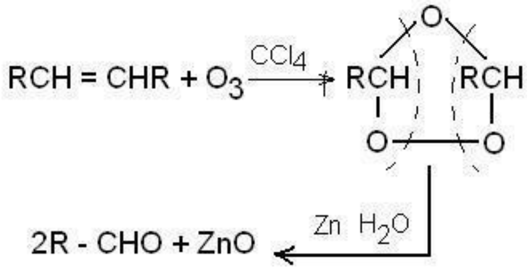
$$\underset{1^o\ \text{alcohol}}{R-CH_2OH}\xrightarrow[\text{collin's reagent}]{\text{pcc,}}\underset{\text{aldehyde}}{RCHO}$$

(ii) Catalytic dehydrogenation of alcohols

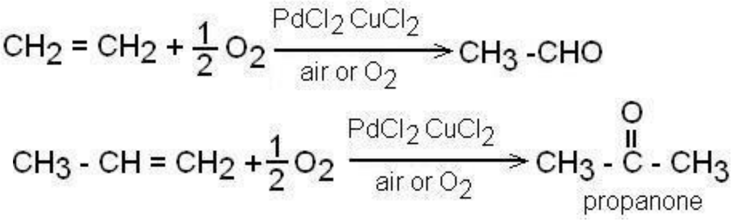
$$\underset{1^o\ \text{alcohol}}{RCH_2OH}\xrightarrow[300^oC]{Cu}\underset{\text{Aldehyde}}{RCHO}+H_2$$



2. From alkenes
   (i) Reductive ozonolysis of alkenes.



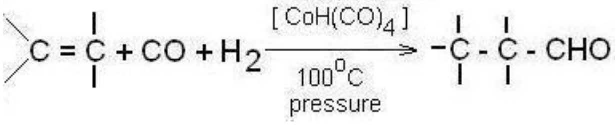
   (ii) Wacker process.



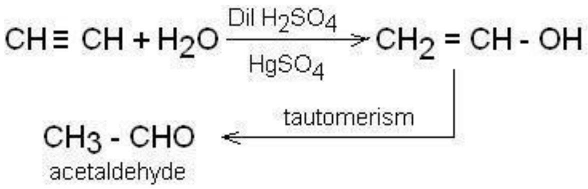
$$CH_2=CH_2+\frac{1}{2}O_2\xrightarrow[\text{air or }O_2]{PdCl_2\ CuCl_2}CH_3-CHO$$

$$CH_3-CH=CH_2+\frac{1}{2}O_2\xrightarrow[\text{air or }O_2]{PdCl_2\ CuCl_2}CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

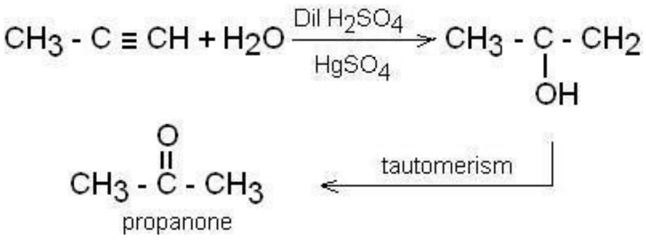
   (iii) OXO process [Carbonylation / Hydroformylation]



3. From alkynes

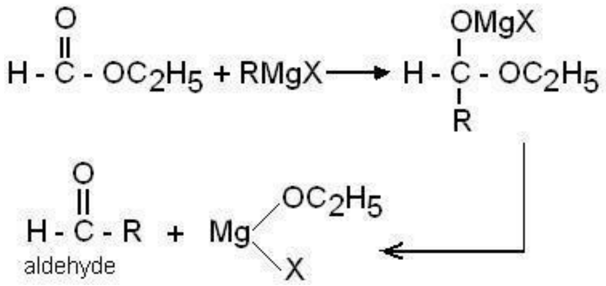


$$CH\equiv CH+H_2O\xrightarrow[HgSO_4]{Dil\ H_2SO_4}CH_2=CH-OH\xrightarrow{\text{tautomerism}}CH_3-CHO$$

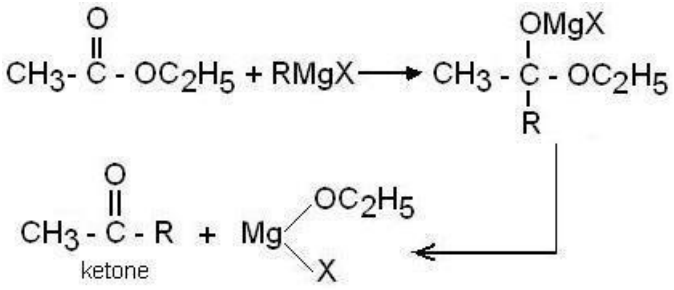


$$CH_3-C\equiv CH+H_2O\xrightarrow[HgSO_4]{Dil\ H_2SO_4}CH_3-\underset{\underset{OH}{|}}{C}=CH_2\xrightarrow{\text{tautomerism}}CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

4. From Grignard reagent
   (1) By addition to ester

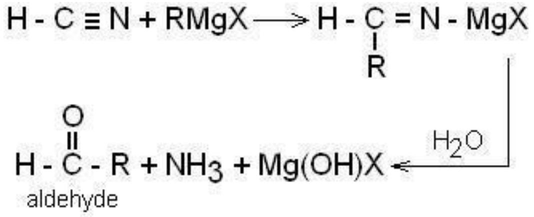


$$H-\overset{\overset{O}{\|}}{C}-OC_2H_5 + RMgX \longrightarrow H-\underset{R}{\overset{OMgX}{C}}-OC_2H_5 \longrightarrow \underset{\text{aldehyde}}{H-\overset{\overset{O}{\|}}{C}-R} + Mg\begin{matrix}OC_2H_5\\X\end{matrix}$$

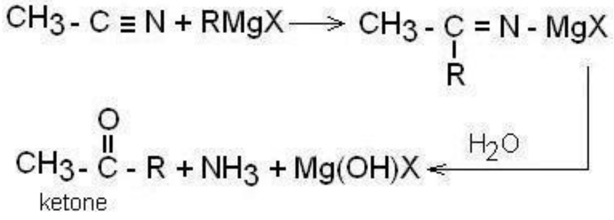


$$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + RMgX \longrightarrow CH_3-\underset{R}{\overset{OMgX}{C}}-OC_2H_5 \longrightarrow \underset{\text{ketone}}{CH_3-\overset{\overset{O}{\|}}{C}-R} + Mg\begin{matrix}OC_2H_5\\X\end{matrix}$$

(iii) By addition to nitriles



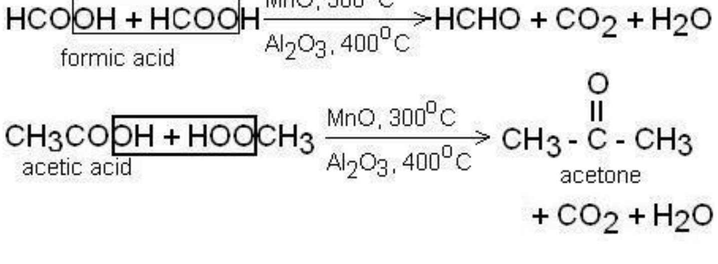
$$H-C\equiv N + RMgX \longrightarrow H-\underset{R}{C}=N-MgX \xrightarrow{H_2O} \underset{\text{aldehyde}}{H-\overset{\overset{O}{\|}}{C}-R} + NH_3 + Mg(OH)X$$



$$CH_3-C\equiv N + RMgX \longrightarrow CH_3-\underset{R}{C}=N-MgX \xrightarrow{H_2O} \underset{\text{ketone}}{CH_3-\overset{\overset{O}{\|}}{C}-R} + NH_3 + Mg(OH)X$$

5. From carboxylic acids

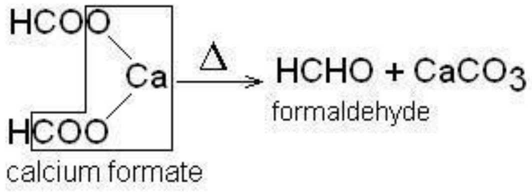
(i) Catalytic decomposition of carboxylic acid.



$$\underset{\text{formic acid}}{HCO\boxed{OH + HCOO}H} \xrightarrow[Al_2O_3,\ 400^0C]{MnO,\ 300^0C} HCHO + CO_2 + H_2O$$

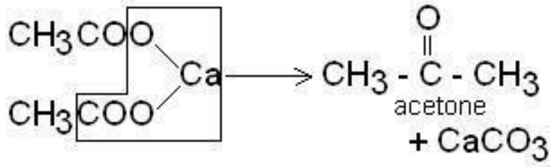
$$\underset{\text{acetic acid}}{CH_3CO\boxed{OH + HOO}CH_3} \xrightarrow[Al_2O_3,\ 400^0C]{MnO,\ 300^0C} \underset{\text{acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + CO_2 + H_2O$$

(ii) From calcium salt of carboxylic acids



$$(HCOO)_2Ca \xrightarrow{\Delta} \underset{\text{formaldehyde}}{HCHO} + CaCO_3$$

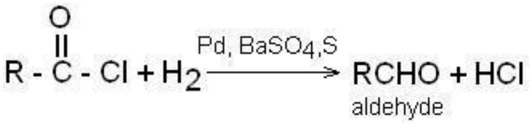
calcium formate



$$(CH_3COO)_2Ca \longrightarrow \underset{\text{acetone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + CaCO_3$$

6. From derivatives of carboxylic acids

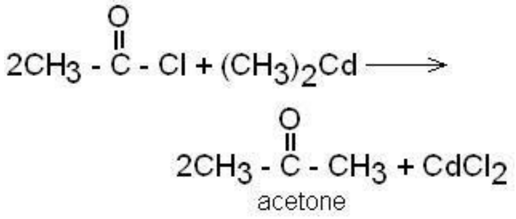
(i) Reduction of acid chlorides (Rosenmund's reaction)



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd,\ BaSO_4,S} \underset{\text{aldehyde}}{RCHO} + HCl$$

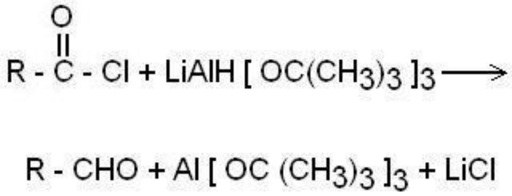
- Above reaction is known as Rosenmund's reduction and is applicable for preparation of aldehydes
- $BaSO_4$, sulphur act as poison for Pd catalyst and prevents reduction of RCHO into RCH_2OH

(ii) Reduction of acid chloride with dialkyl cadmium.



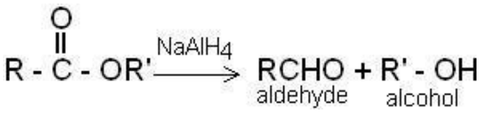
$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + (CH_3)_2Cd \longrightarrow \underset{\text{acetone}}{2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + CdCl_2$$

Reduction of acid chloride into ester can also be carried out by lithium tri--butoxy aluminium hydride, $LiAlH[OC(CH_3)3]$



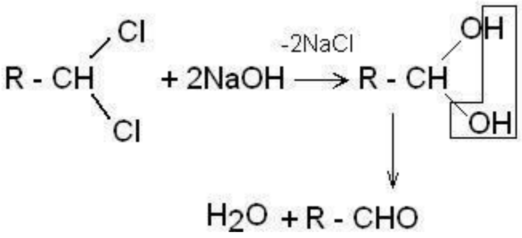
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + LiAlH[\,OC(CH_3)_3\,]_3 \longrightarrow R-CHO + Al[\,OC\,(CH_3)_3\,]_3 + LiCl$$

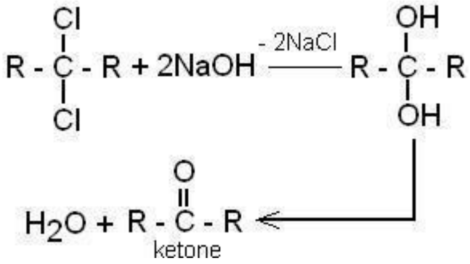
(iii) Reduction of esters



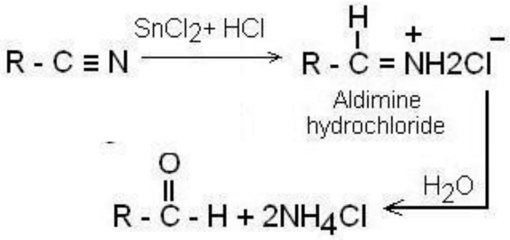
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' \xrightarrow{NaAlH_4} \underset{\text{aldehyde}}{RCHO} + \underset{\text{alcohol}}{R'-OH}$$

7. From gem-dihalides by hydrolysis

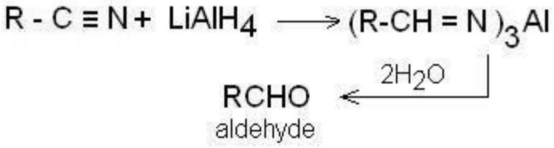


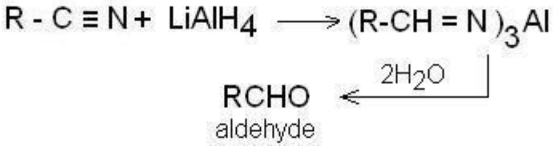


8. From nitriles by reduction
   (i) Stephen's reduction.

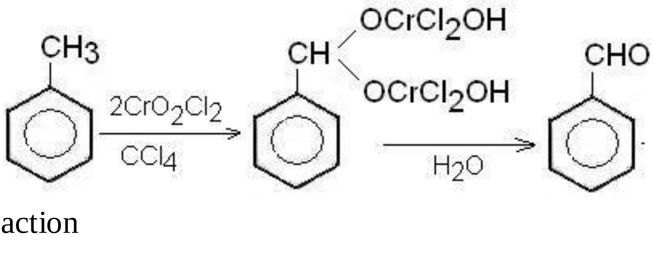


   (ii) Reduction with LiAlH4



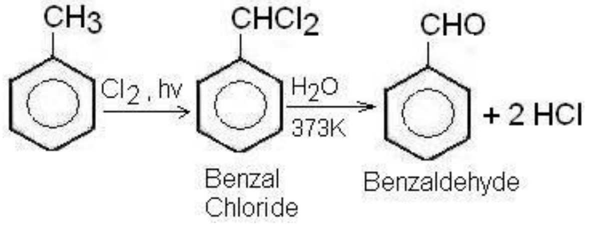


9. Preparation of aromatic carbonyl compounds.(i)

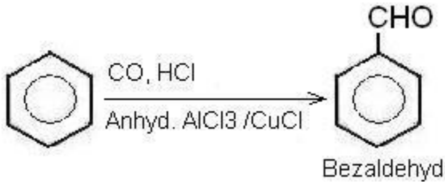


This is known as Etard reaction

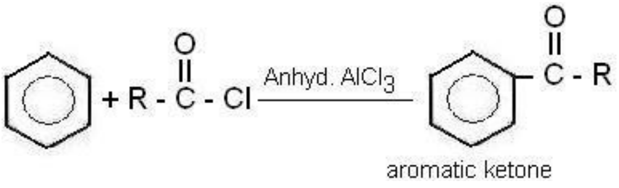
(ii) By side chain chlorination followed by hydrolysis

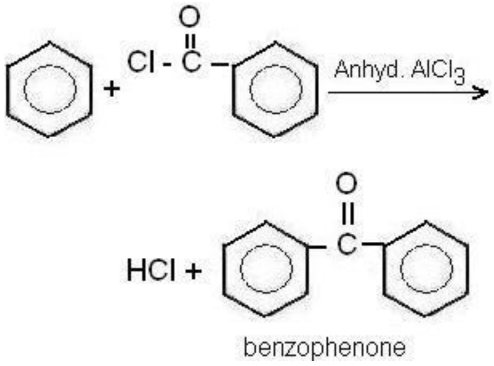


(iii) Gatterman – Koch reaction

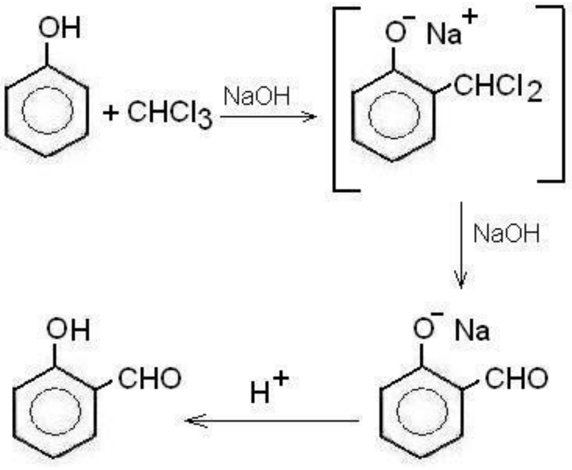


(iv) Friedel Craft Acylation





(v) Reimer – Tiemann reaction



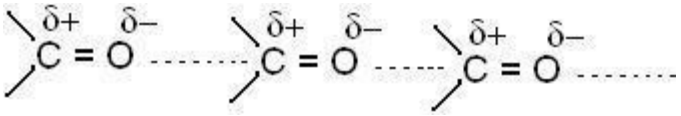
PHYSICAL PROPERTIES OF ALDEHYDES AND KETONE

1. Physical state

- Lower members of aldehydes and ketones (upto C10) are colourless volatile liquids except formaldehyde which is gas at ordinary temperature
- Higher members of aldehyde and ketones are solids with fruity odour
- Lower aldehydes have unplesent odour but ketones posses pleasant smell

2. Boiling point

- Boiling point of aldehyde and ketones is slightly lower than corresponding alcohol due to lack of hydrogen bonding. However their boiling point is slightly higher than that of corresponding non-polar hydrocarbon or weakly polar ether. This may attributed to reasonthat aldehydes and ketones are polar compounds and thus possess intermolecular dipole- dipole interaction



- Among isomeric aldehydes and ketones, boiling point of ketones is slightly higher than that of aldehydes due to the presence of two electron donating alkyl groups making them morepolar.

3. Solubility

- Lower members of aldehydes and ketones (upto C4) are soluble in water due to H-bondingbetween polar carbonyl group and water.
- However, solubility decreases with increase in molecular weight
- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to large benzene ring. However all carbonyl compounds arefairly soluble in organic solvents.

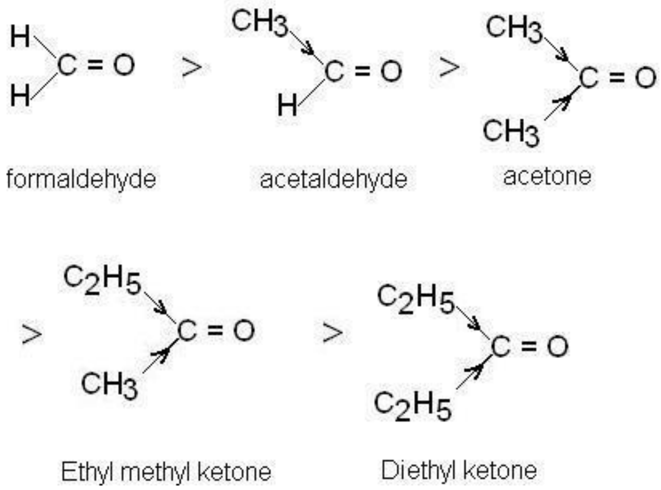
RELATIVE REACTIVITY OF ALDEHYDES AND KETONES

Aldehydes are more reactive than ketones on account of the following facts:

(a) Aliphatic aldehydes and ketones

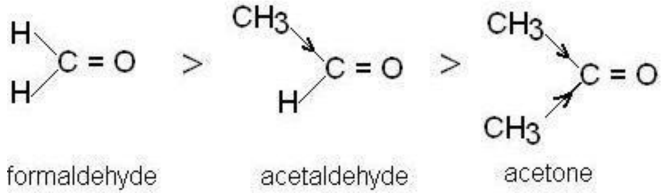
(i) Inductive effect:

The reactivity of the carbonyl group towards the addition reaction depends upon the magnitude of the positive charge on the carbonyl carbon atom. Hence, any substituent that increases the positive charge on the carbonyl carbon must increase its reactivity towards addition reactions. The introduction of negative group (-I effect) increases the reactivity, while introduction of alkyl group (+I effect) decreasesthe reactivity, therefore, greater the number of alkyl groups attached to the carbonyl group and hence, lower is its reactivity towards nucleophilic addition reactions. Thus,the following decreasing order of reactivity is observed



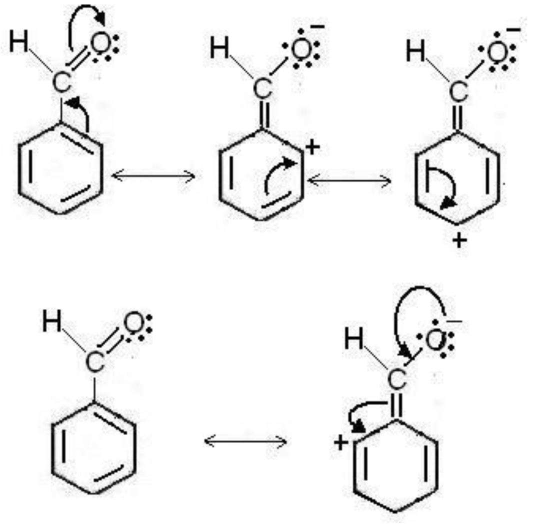
(ii) Steric effect

- In formaldehyde there is no alkyl group while in all other aldehyde there is one alkyl groupso here the nucleophile attack is relatively more easy but in ketones there are two alkyl groups attached to carbonyl group and these causes hinderance, to the attacking group. This factor is called steric hinderance (crowding). In other words the hindrance increases, the reactivity decreases accordingly. Thus order of reactivity is

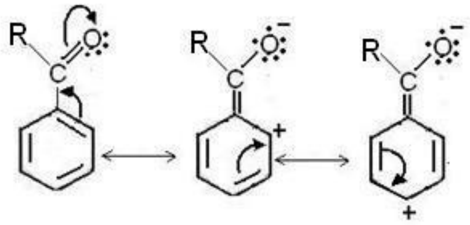


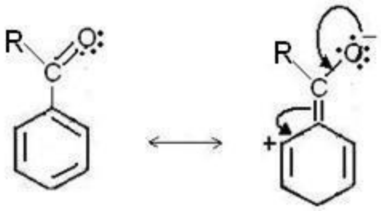
(b) Aromatic aldehydes and ketones

- In general, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones. It is due electron releasing resonance effect of bezene ring



- Due to electron withdrawing resonance effect (-R effect) of benzene ring, the magnitude ofpositive charge on carbonyl group decreases and consequently it becomes less susceptible to nucleophilic attack.





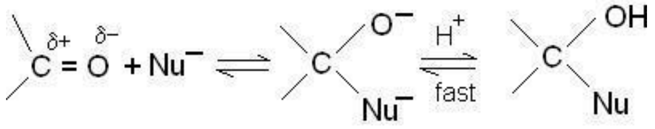
The order of reactivity of aromatic aldehydes and ketones is

$$\underset{\text{phenyl acetaldehyde}}{C_6H_5CH_2CHO} > \underset{\text{benzaldehyde}}{C_6H_5CHO} > \underset{\text{acetophenone}}{C_6H_5COCH_3}$$

$$> \underset{\text{benzophenone}}{C_6H_5COC_6H_5}$$

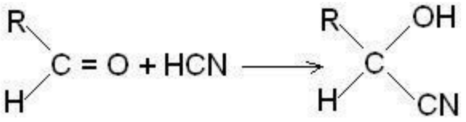
CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

Nucleophilic addition reaction

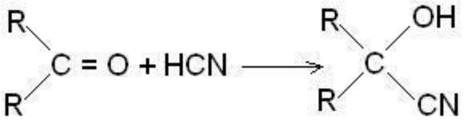


In this reaction carbon atom of carbonyl group changes from sp^2 to sp^3 hybridised

(i) Addition of hydrogen cyanide (HCN)



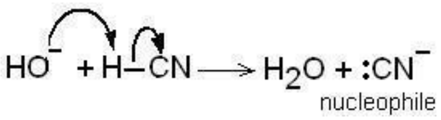
cyanohydrien



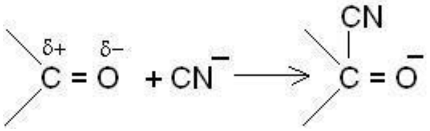
cyanohyrin

Mechanism

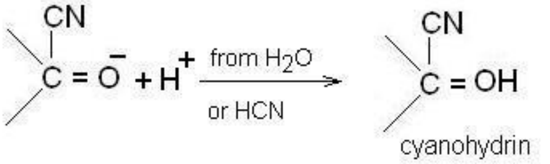
Step I : The hydrogen cyanide interacts with the base to form nucleophile



Step II : The nucleophile attacks the carbonyl carbon to form an anion

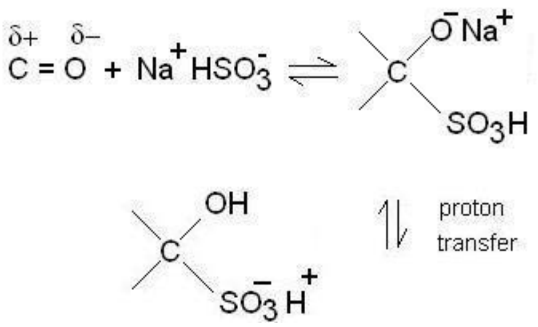


StepIII: The proton from the solvent (usually water) combines with the anion to form cyanohydrin.

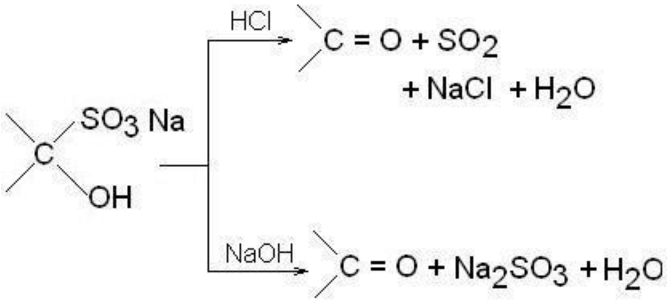


Cyanohydrins are formed by all aldehydes but in ketones, only acetone, butanone, 3-pethenone and pinacolone form cyanohydrins.

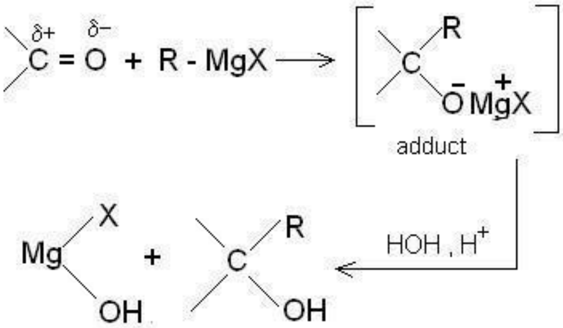
(ii) Addition of sodium bisulphate (NaHSO4)



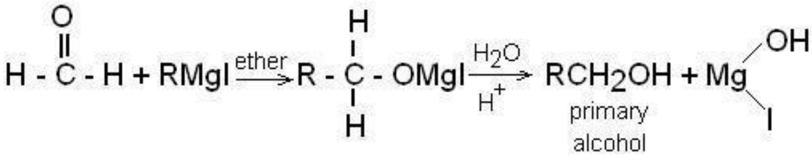
- All ketones do not undergo this reaction only methyl ketone form addition product withsodium bisulphate
- On reacting the crystalline solid bisulphate derivative with dilute HCl or alkali, these adducts decompose to regenerate the original aldehyde or ketones. Hence, this reaction is used in the separation and purification of aldehydes and ketones from non-carbonyl compounds.



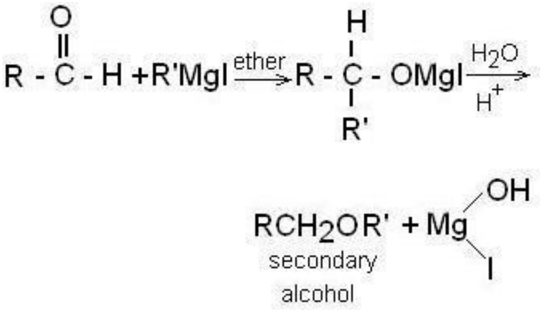
(iii) Addition of Grignard reagent



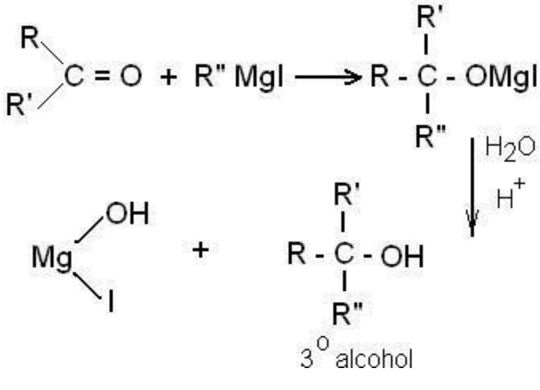
Formaldehyde form a primary alcohol



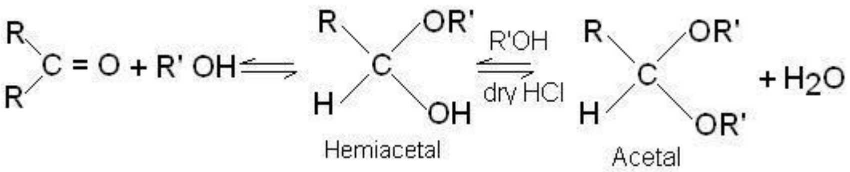
- Higher aldehydes give secondary alcohol



- Ketone give tertiary alcohols

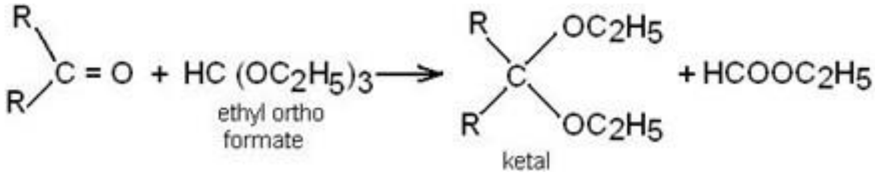


(iv) Addition of alcohols

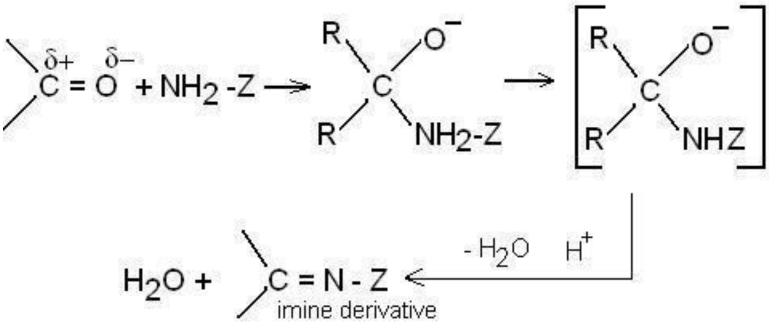


Dry HCl protonates the oxygen atom of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon and hence facilitating the nucleophilic attack by the alcohol molecule. Dry HCl gas also absorbs the water produced in these reactions and thereby shifting equilibrium in forward direction.

Ketals can be prepared by treating the ketone with ethyl ortho formate



(v) Addition of ammonia derivative

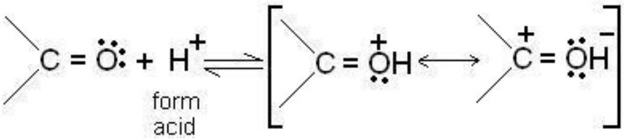


Z = OH, NH_2 , NHC_6H_5 , $NHCOCH_2$ etc.

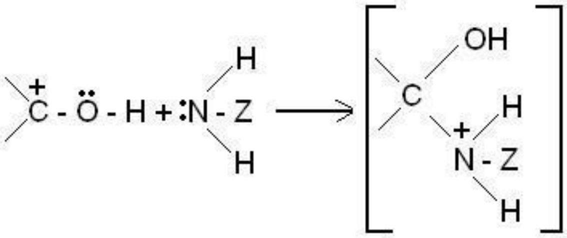
The reaction of ammonia derivatives to aldehydes and ketones is called by acids

Mechanism

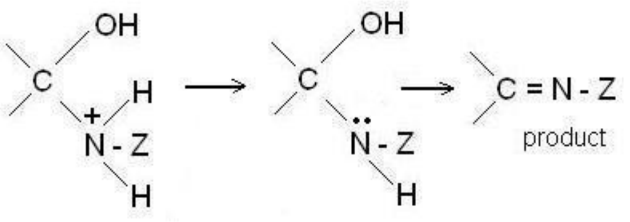
Step I: In acidic medium, the carbonyl oxygen gets protonated.



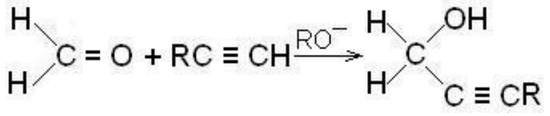
Step II : In ammonia derivatives, the nitrogen atom has a lone pair of electrons, which attack thepositively charged carbonyl carbon and results in positive charge on nitrogen atom



Step III : The unstable intermediate loses a proton, H^+ and water molecule to form stable product(imines)



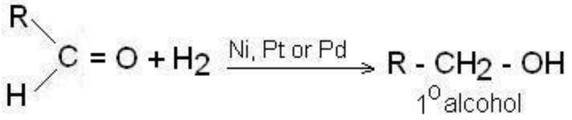
(vi) Addition of alkynes

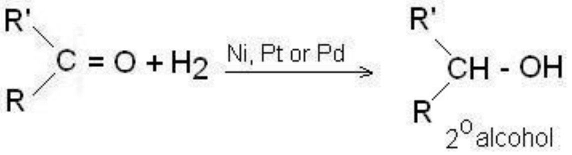


This reaction is also known as ethinylation

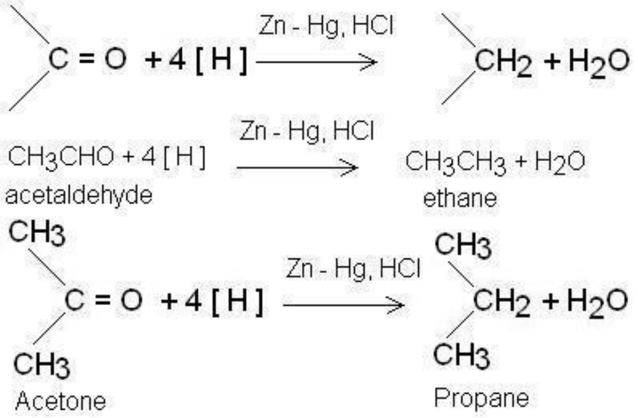
2. Reduction reactions

I. Catalytic reduction to alcohol

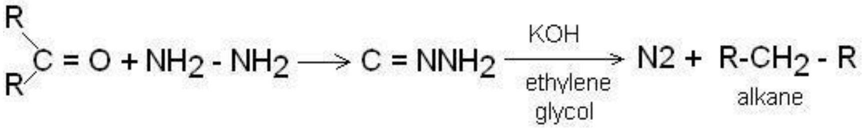


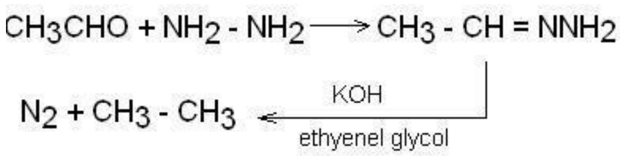


II. Clemmensen reduction



III. Wolf-Kishner reduction





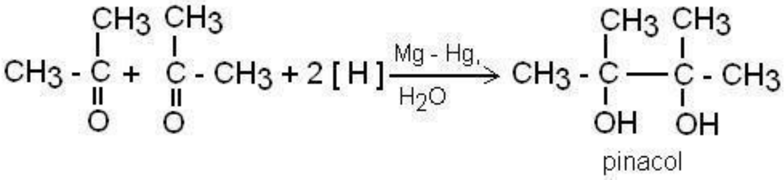
$$CH_3COCH_3 \xrightarrow[\text{ethylene glycol}]{NH_2\text{-}NH_2 + KOH} CH_3 - CH_2 - CH_3 + H_2O$$

IV. Reduction with HI + P (red)

$$CH_3 - CHO + 4HI \xrightarrow[150^0C]{\text{red P}} CH_3\text{-}CH_3 + H_2O + 2I_2$$

$$CH_3COCH_3 + 4HI \xrightarrow[150^0C]{\text{red P}} CH_3 - CH_2 - CH_3 + H_2O + 2I_2$$

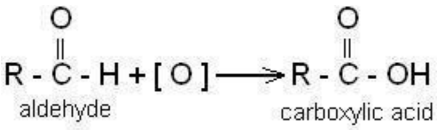
V. Reduction to pinacols



$$CH_3 - \underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} + \underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 + 2[H] \xrightarrow[H_2O]{Mg - Hg,} \underset{\text{pinacol}}{CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} — \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3}$$

3. Oxidation reactions

i. Oxidation with mild oxidizing agents



$$\underset{\text{aldehyde}}{R - \overset{\overset{O}{\|}}{C} - H} + [O] \longrightarrow \underset{\text{carboxylic acid}}{R - \overset{\overset{O}{\|}}{C} - OH}$$

Ketones are not oxidized by mild oxidizing agents

(a) Aldehydes reduces Tollen's reagent to metallic silver which appears as a silver mirror onwall of test tube. Thus the reaction is also known as silver mirror test.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow$$

$$RCOO^- + \underset{\text{silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

(b) Reduction of Fehling's solution

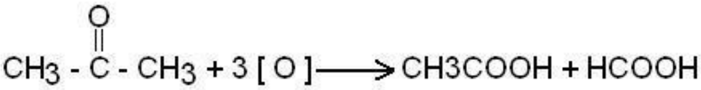
Fehling's solution is an alkaline solution of CuSO4 mixed with Rochelle slat i.e. sodium potassium tartarate. Aldehydes reduces cupric ion (Cu^{2+}) of Fehling's solution to cuprousions (Cu^+) to form red precipitate of cuprous oxide

$$RCHO + 2Cu_2^+ + 5\,OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$$

Fehling's solution is reduced by aliphatic aldehydes only. Aromatic aldehydes and ketonesso not give this reaction.

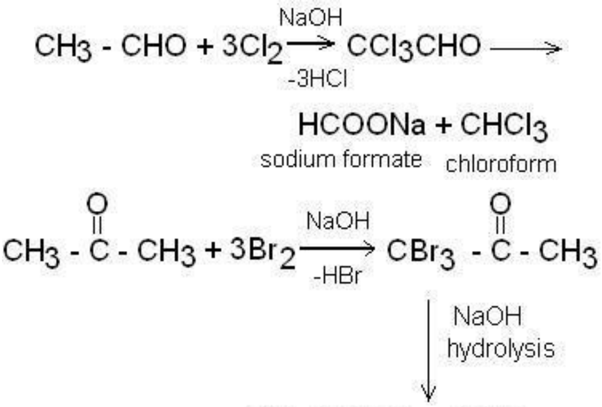
ii. Oxidation with strong oxidizing agent

$$\underset{\text{aldehyde}}{RCHO} + [O] \xrightarrow{NHO_3\ (\text{conc.})} \underset{\text{carboxylic acid}}{RCOOH}$$



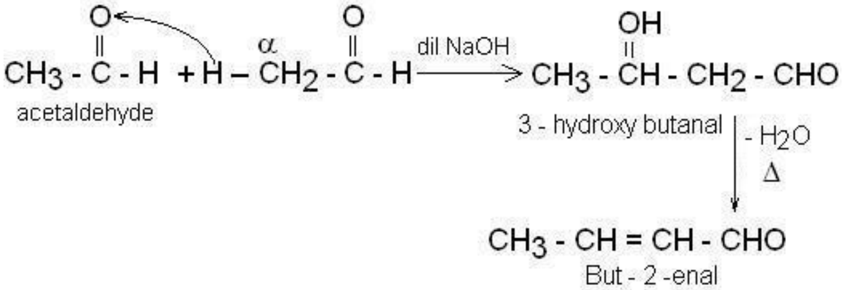
$$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3 + 3[O] \longrightarrow CH3COOH + HCOOH$$

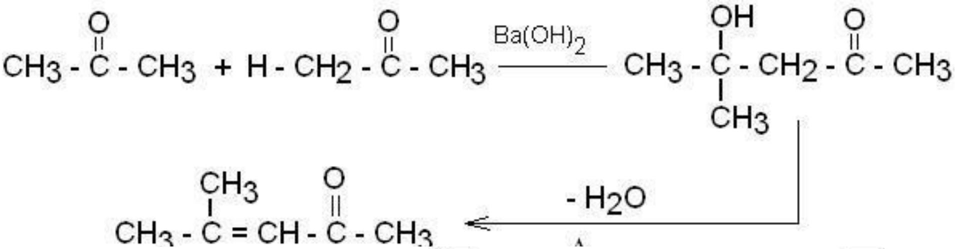
iii. Haloform reaction



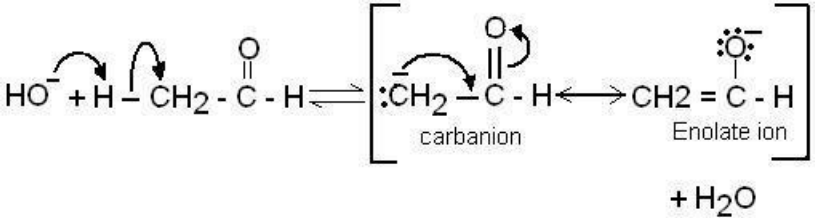
4. Condensation reactions

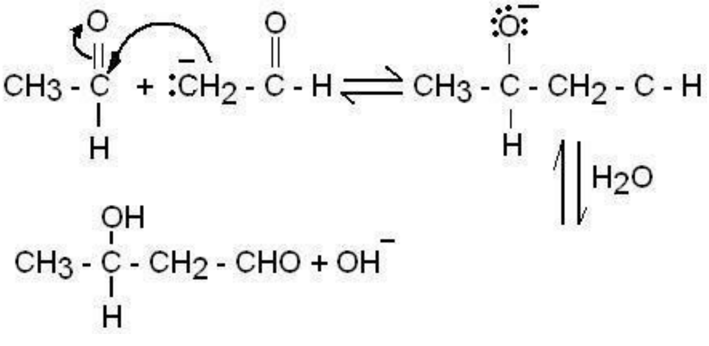
(1) Aldol condensation





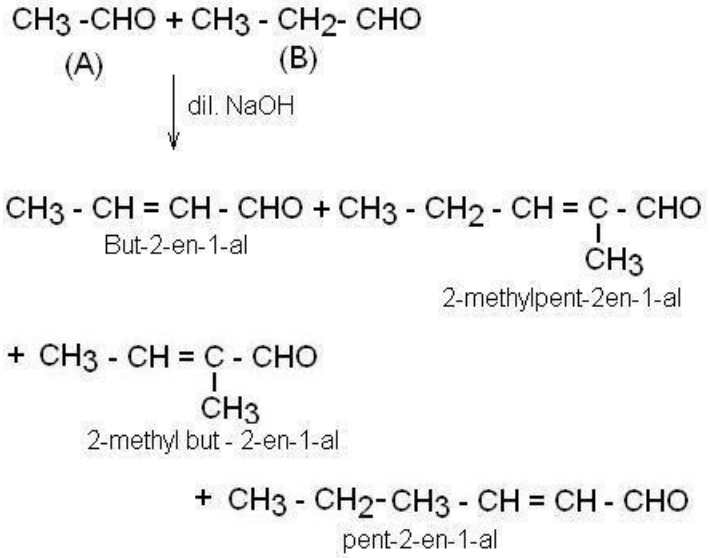
Mechanism





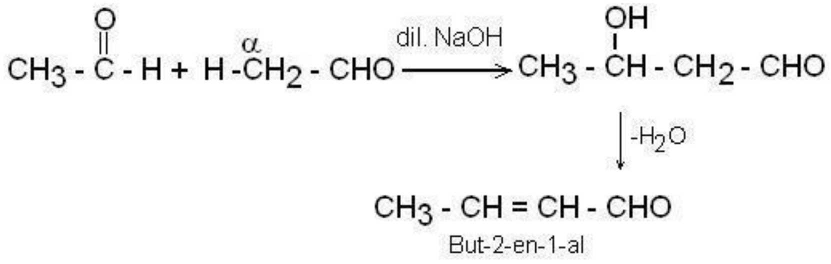
Aldehyde or ketones which do not contain α-hydrogen atom like formaldehyde (HCHO), benzaldehyde (C_6H_5CHO) and benzophenone ($C_6H_5COC_6H_5$) do not undergo aldol condensation.

(2) Cross aldol condensation



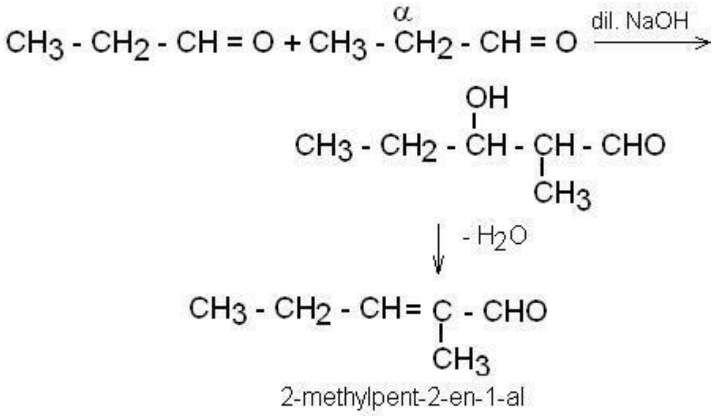
$$\underset{(A)}{CH_3-CHO} + \underset{(B)}{CH_3-CH_2-CHO} \xrightarrow{\text{dil. NaOH}} \underset{\text{But-2-en-1-al}}{CH_3-CH=CH-CHO} + \underset{\text{2-methylpent-2en-1-al}}{CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO} + \underset{\text{2-methyl but - 2-en-1-al}}{CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO} + \underset{\text{pent-2-en-1-al}}{CH_3-CH_2-CH_3-CH=CH-CHO}$$

A- A Condensation



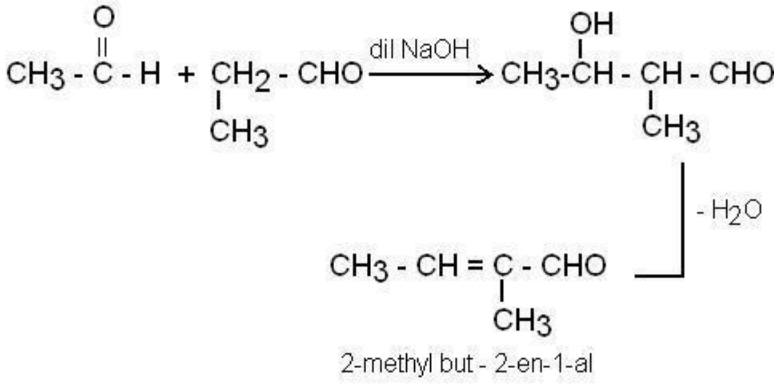
$$CH_3-\overset{O}{\overset{||}{C}}-H + H-\overset{\alpha}{C}H_2-CHO \xrightarrow{\text{dil. NaOH}} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO \xrightarrow{-H_2O} \underset{\text{But-2-en-1-al}}{CH_3-CH=CH-CHO}$$

B-B Condensation



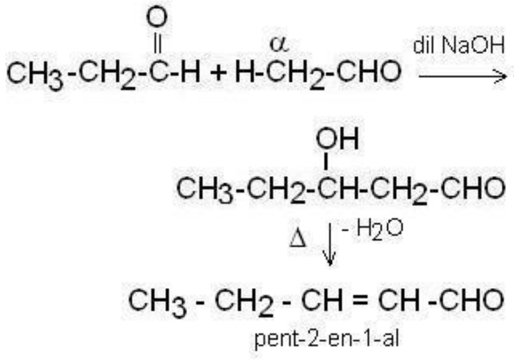
$$CH_3-CH_2-CH=O + CH_3-\overset{\alpha}{C}H_2-CH=O \xrightarrow{\text{dil. NaOH}} CH_3-CH_2-\overset{OH}{\overset{|}{C}H}-\underset{CH_3}{\underset{|}{C}H}-CHO \xrightarrow{-H_2O} \underset{\text{2-methylpent-2-en-1-al}}{CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

A-B Condensation



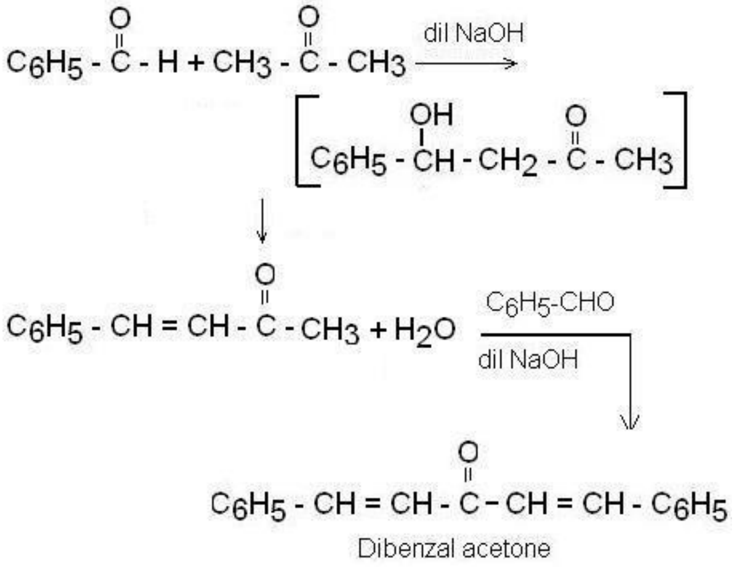
$$CH_3-\overset{O}{\overset{\|}{C}}-H + \underset{CH_3}{\underset{|}{CH_2}}-CHO \xrightarrow{\text{dil NaOH}} CH_3-\overset{OH}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CHO \xrightarrow{-H_2O} CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO$$

B-A Condensation



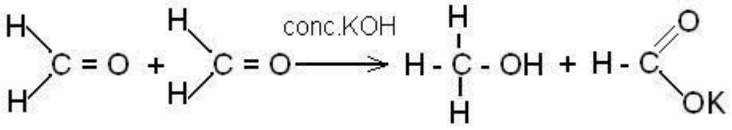
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + H-\overset{\alpha}{C}H_2-CHO \xrightarrow{\text{dil NaOH}} CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-CHO \xrightarrow[\Delta]{-H_2O} CH_3-CH_2-CH=CH-CHO$$

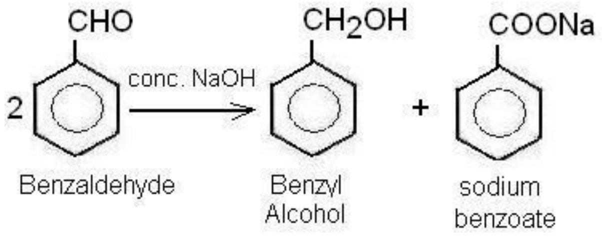
(3) Claisen – Schmidt condensation



$$C_6H_5-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{dil NaOH}} \left[C_6H_5-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3\right] \rightarrow C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O \xrightarrow[\text{dil NaOH}]{C_6H_5-CHO} C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-CH=CH-C_6H_5$$

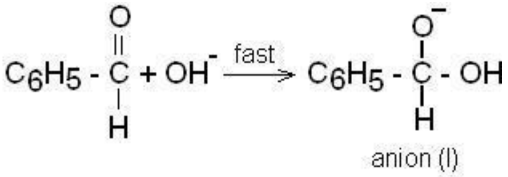
5. Cannizzaro reaction





Mechanism

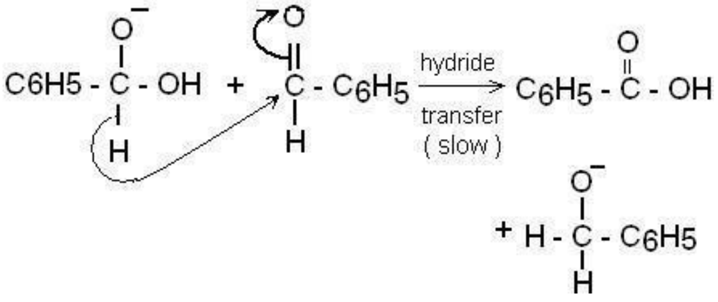
Step I : The OH^- ion attacks the carbonyl carbon to form hydroxyl alkoxide

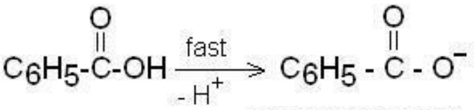


$$C_6H_5-\overset{\overset{O}{\|}}{\underset{H}{C}} + OH^- \xrightarrow{fast} C_6H_5-\overset{O^-}{\underset{H}{C}}-OH$$

anion (I)

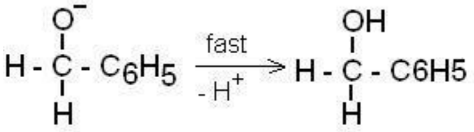
Step II : Anion (I) acts as hybride ion donor to the second molecule of aldehyde. In thefinal step of the reaction, the acid and the alkoxide ion transfer H^+ to acquire stability.





$$C_6H_5\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH \xrightarrow[-H^+]{fast} C_6H_5-\overset{\overset{O}{\|}}{C}-O^-$$

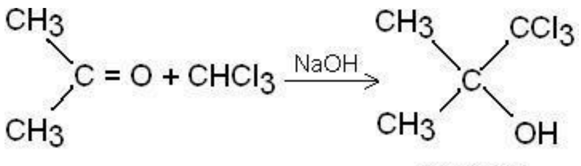
salt of benzoic acid



$$H-\overset{O^-}{\underset{H}{C}}-C_6H_5 \xrightarrow[-H^+]{fast} H-\overset{OH}{\underset{H}{C}}-C6H5$$

benzyl alcohol

6. Reaction with chloroform



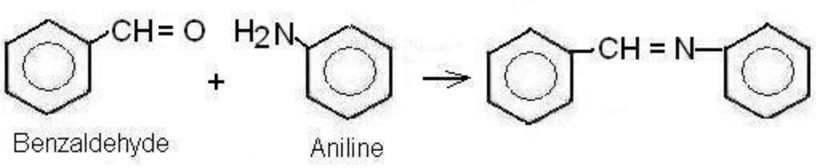
chloretone

Chloretone is used as hypnotic.

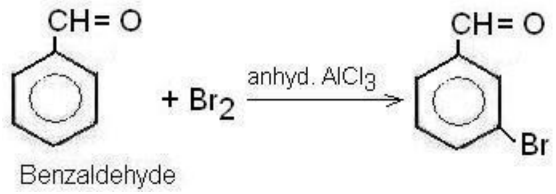
7. Reaction with primary amine

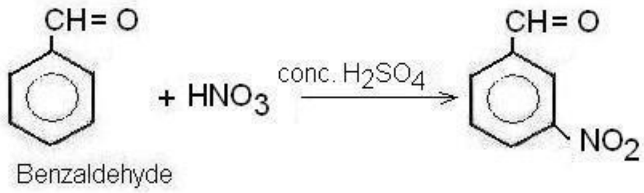
$$RCH\boxed{O + H_2}NR' \xrightarrow[\Delta]{H^+} R\ CH = NR' + H_2O$$

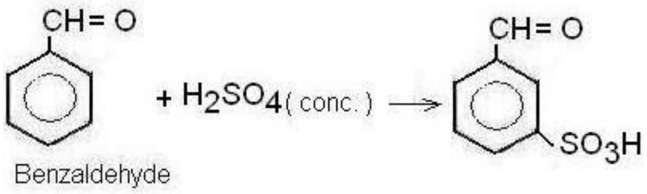
schiff's base



8. Electrophilic substitution reaction of aromatic carbonyl compounds







USES OF ALDEHYDES AND KETONES

(a) Uses of formaldehyde
   i. The 40% solution of formaldehyde in water (formaline) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens
   ii. It is used for silvering of mirrors
   iii. It is used for making synthetic plastics, like Bakelite, urea- formaldehyde resinetc

(b) Uses of acetaldehyde
   i. It is used in preparation of acetic acid, dyes, drugs, etc
   ii. As an antiseptic inhalant in nose troubles

(c) Uses of benzaldehyde
   i. As flavouring agent in perfume industry
   ii. In manufacture of dyes.

(d) Uses of acetone
   i. As a solvent for cellulose acetate, resin etc.
   ii. As a nailpolish remover
   iii. In the preparation of an artificial scent and synthetic rubber