Aldehydes and ketones

Aldehydes and Ketones are simple organic compounds containing a carbonyl group. Carbonyl group contains carbon-oxygen double bond. These organic compounds are simple because the carbon atom presents in the carbonyl group lack reactive groups such as OH or Cl.

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Note:

This is to bring to kind notice that the matter of this e-content is for the B.Sc. IV semester students. It has been taken from the following sources. The students are advised to follow these books as well.

- A TEXTBOOK OF ORGANIC CHEMISTRY by **Arun Bahl & B.S. Bahl**, S. Chand & Company Ltd. Publication.
- *Graduate* Organic Chemistry by **M. K. Jain and S.C. Sharma,** Vishal Publishing Co.
- Pradeep's Organic Chemistry **Vol II** by **R. N. Dhawan,** Pradeep Publication, Jalandhar.

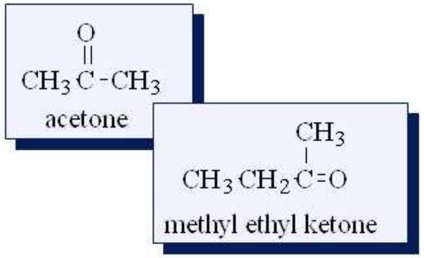
Aldehydes

- An aldehyde is one of the classes of carbonyl group-containing alkyl group on one end and hydrogen on the other end. The R and Ar denote alkyl or aryl member respectively. In the condensed form, the aldehyde is written as –CHO.

ketones

Ketones

- Ketones
  - Carbonyl C is connected to two alkyl groups
  - RCOR'

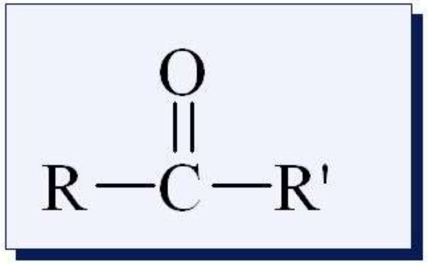


$CH_3\overset{O}{\overset{\|}{C}}-CH_3$

acetone

$CH_3CH_2\overset{CH_3}{\overset{|}{C}}=O$

methyl ethyl ketone



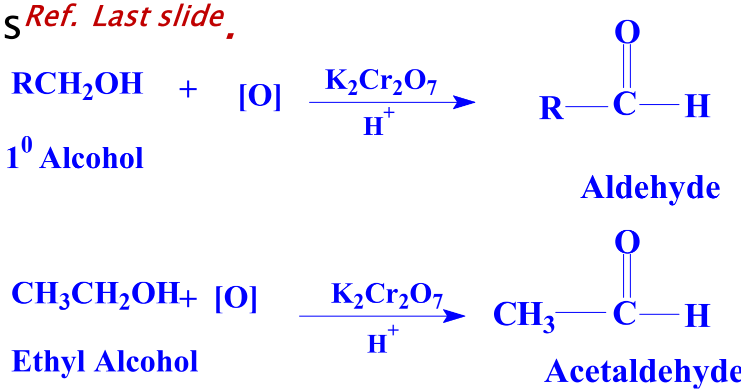
$R-\overset{O}{\overset{\|}{C}}-R'$

Ketones

Preparation of Aldehydes and ketones

1. From Alcohols:

a. By oxidation of Alcohols: Aldehydes and ketones can be prepared by the controlled oxidation of primary and secondary alcohols using an acidified solution of potassium dichromate or permanganate. Primary alcohol produces aldehydes*Ref. Last slide*.



$$RCH_2OH + [O] \xrightarrow[H^+]{K_2Cr_2O_7} R-\overset{\overset{O}{\|}}{C}-H$$

1^0 Alcohol

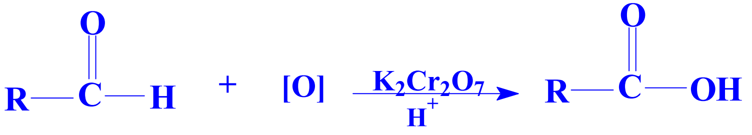
Aldehyde

$$CH_3CH_2OH + [O] \xrightarrow[H^+]{K_2Cr_2O_7} CH_3-\overset{\overset{O}{\|}}{C}-H$$

Ethyl Alcohol

Acetaldehyde

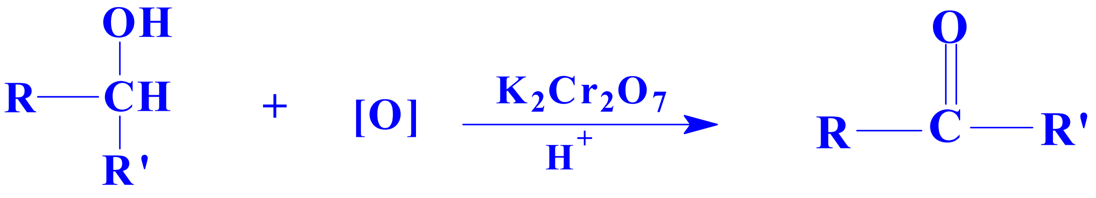
The aldehydes formed in the above reaction are very easily oxidised to carboxylc acids if allowed to remain in the reaction mixture.



$$R-\overset{\overset{O}{\|}}{C}-H + [O] \xrightarrow[H^+]{K_2Cr_2O_7} R-\overset{\overset{O}{\|}}{C}-OH$$

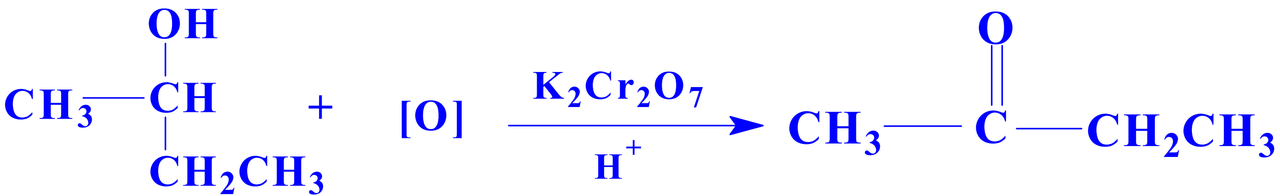
Carboxylic acid

Ketones are prepared by the oxidation of secondary alcohols.



$$R-\underset{R'}{\overset{OH}{CH}} + [O] \xrightarrow[H^{+}]{K_2Cr_2O_7} R-\overset{O}{\overset{\|}{C}}-R'$$

Ketone



$$CH_3-\underset{CH_2CH_3}{\overset{OH}{CH}} + [O] \xrightarrow[H^{+}]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

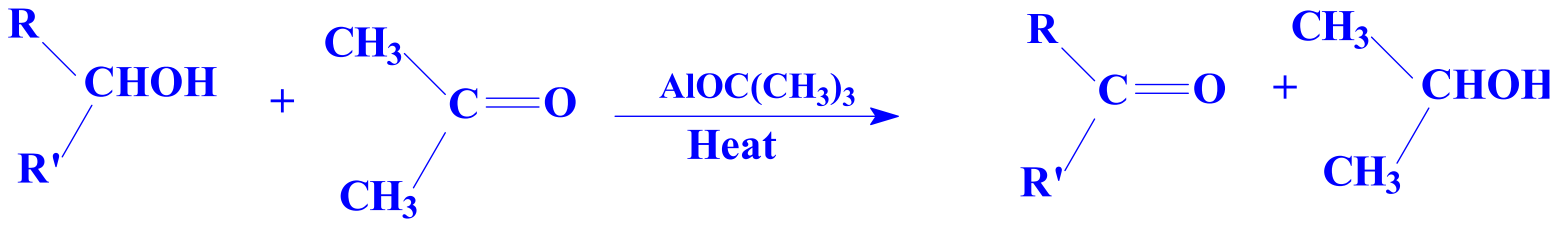
2-propanol

Ethyl MethylKetone

Ketones are not easily oxidised further and can be obtained in high yield by this methods.

Ketones can also be obtained from secondary alcohols by **Oppenauer Oxidation**. In this process, the appropriate secondary alcohol is refluxed with excess of acetone in the presence of aluminium tertiary-butoxide, $AlOC(CH_3)_3$.

Note: The mechanism of following reaction has already been discussed in Alcohols.



2^0 Alcohol   Acetone   Ketone   2-Propanol

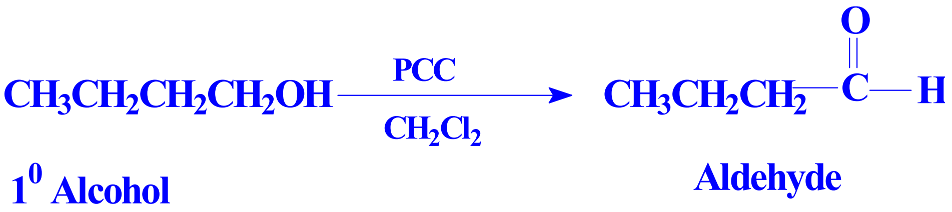
Other reagents used for the oxidation of alcohols to aldehydes and ketones are:

A. Alkaline potassium permanganate: $KMnO_4/OH^-$

B. Chromic acid: $H_2Cr_2O_7$ (CrO_3 or $Na_2Cr_2O_7$ With dil. H_2SO_4.

C. Pyridine chlorochromate (PCC) $C_5H_6NCrO_3Cl$, in dichloromethane

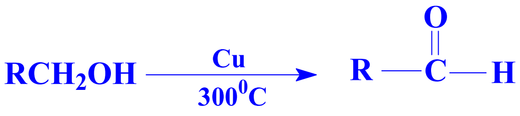
Pyridine chlorochromate (PCC) $C_5H_6NCrO_3Cl$, in dichloromethane is a special oxidizing agent. It is used to convert primary alcohols to aldehydes. This reagent does not oxidize aldehydes to carboxylic acids.



$$CH_3CH_2CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

b. Catalytic Dehydrogenation of Alcohols:

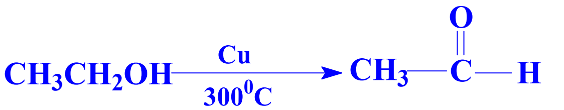
Aldehydes May be Prepared by passing the vapours of primary alcohols over a copper catalyst heated of about 300^0C.



$$RCH_2OH \xrightarrow[300^0C]{Cu} R-\overset{\overset{O}{\|}}{C}-H$$

1^0 Alcohol

Aldehyde

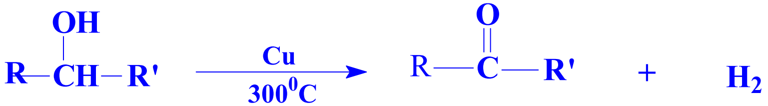


$$CH_3CH_2OH \xrightarrow[300^0C]{Cu} CH_3-\overset{\overset{O}{\|}}{C}-H$$

Ethyl Alcohol

Acetaldehyde

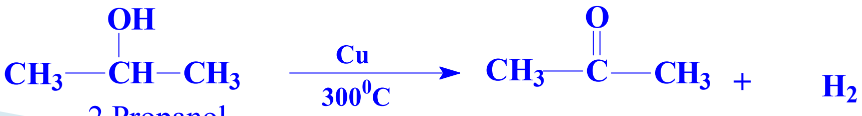
Similarly Ketones are produced from secondary alcohols.



$$R-\overset{\overset{OH}{|}}{CH}-R' \xrightarrow[300^0C]{Cu} R-\overset{\overset{O}{\|}}{C}-R' + H_2$$

2^0 Alcohol

Ketone



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[300^0C]{Cu} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_2$$

2 Propanol

Acetone

2. From Acyl halides:

A.Rosenmund Reduction

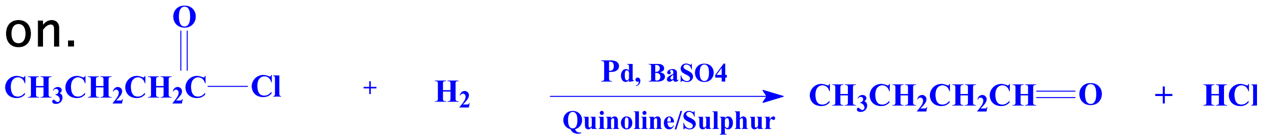
B. By Grignard reagents

C. By organocadmium compounds

D. By Lithium oragano cuprates

2. From Acyl halides:

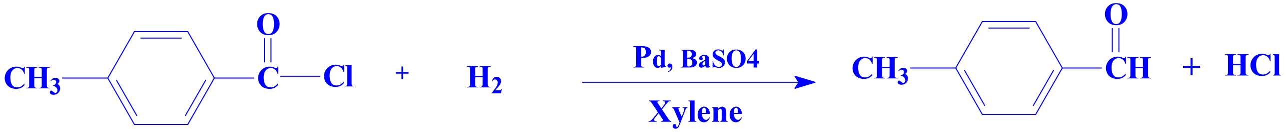
Rosenmund Reduction: Acid Chlorides can be reduced to Aldehydes when they are hydrogenated in the presence of a catalyst such as palladium deposited on $BaSO_4$. A catalyst poison like Quinoline or Pyridine and sulphur is frequently added to moderate the activity of the catalyst and thus inhibit the further reduction of aldehyde into alcohol. This conversion of COCl into -CHO is known as Rosenmund reduction.



$$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{Quinoline/Sulphur}]{\text{Pd, BaSO4}} CH_3CH_2CH_2CH=O + HCl$$

Butanoyl chloride

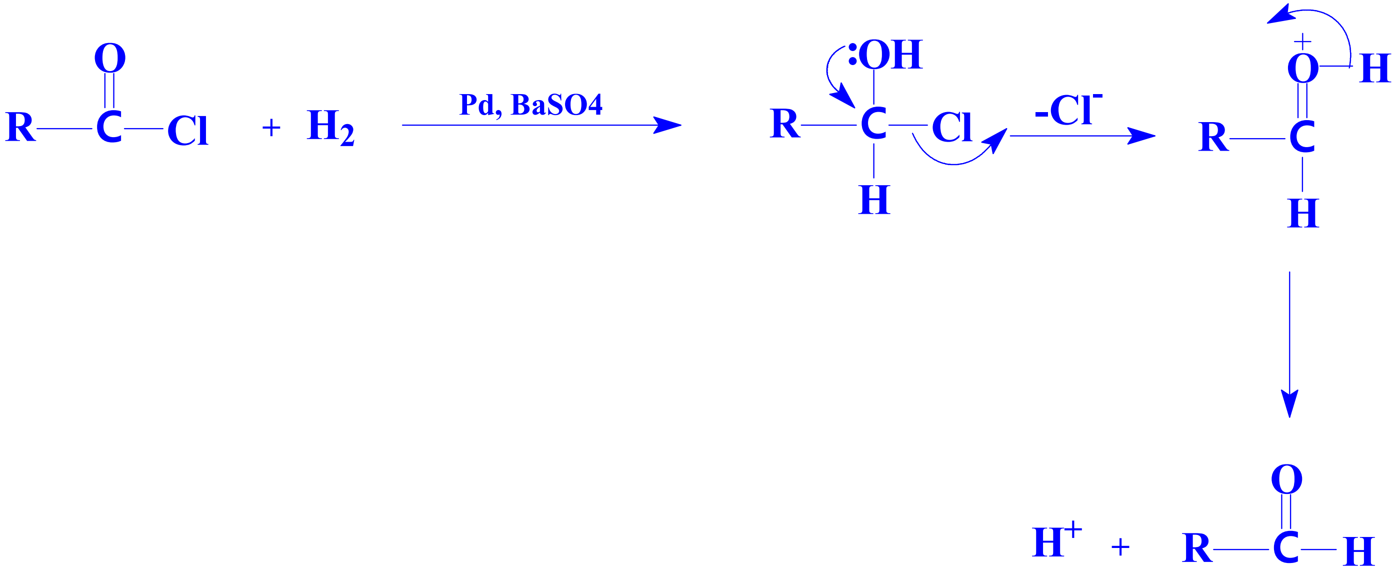
Butanal



4-methyl benzoyl chloride

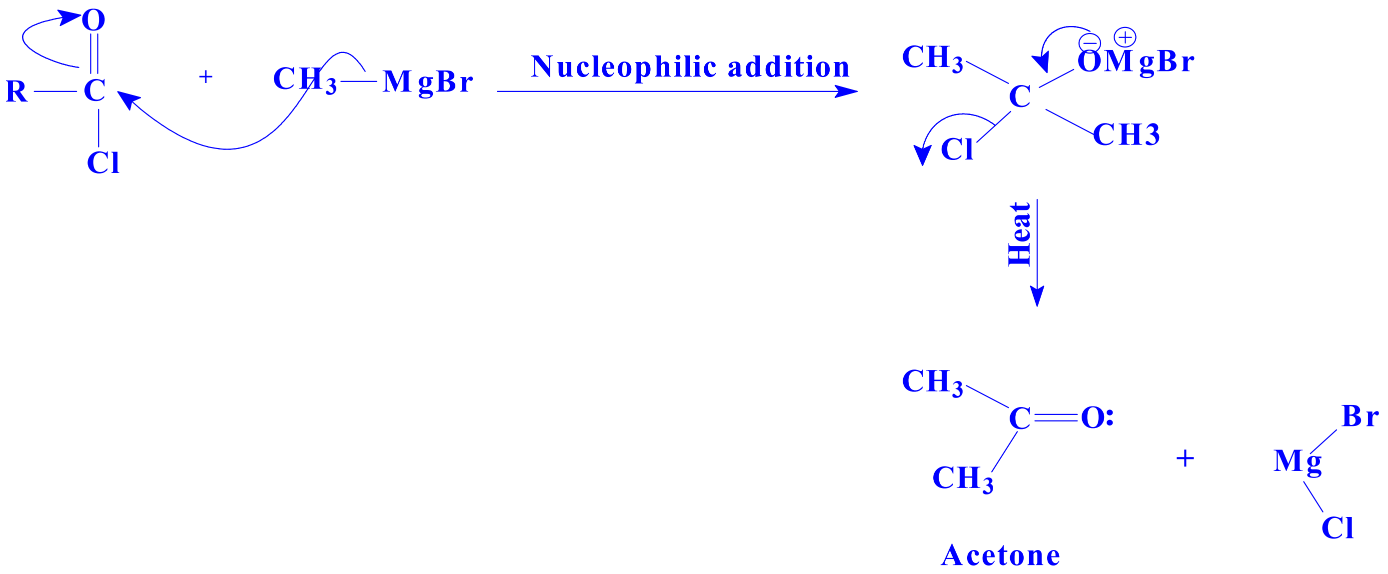
4-methyl benzaldehyde

- Mechanism of Rosenmund reduction:



b. By Grignard reagents: Grignard reagent reacts with acyl halides under controlled conditions to form ketones. The resulting ketone can otherwise react further with excess grignard reagent to form tertiary alcohol.

Mechanism:

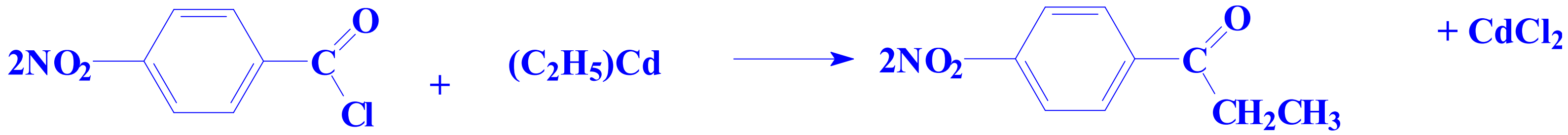


c. By organocadmium compounds.

Ketones can be prepared from acid chlorides by the reaction of suitable organocadmium compounds.

$$R_2Cd + 2R'COCl \longrightarrow 2R'COR + CdCl_2$$

(R is preferablly a primary alkyl group bur R' cab be alkyl or Aryl group)



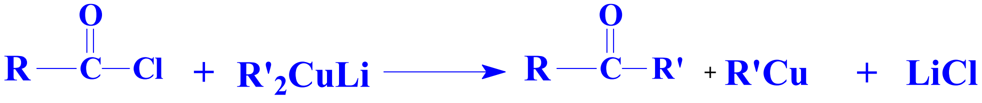
p-nitrobenzoyl chloride

Diethyl cadmium

Ethyl-p-nitrophenylketone

D. By Lithium organocuprates (for ketones only).

Lithium dialkylcuprates react readily with acid chlorides to form ketones in good yields.



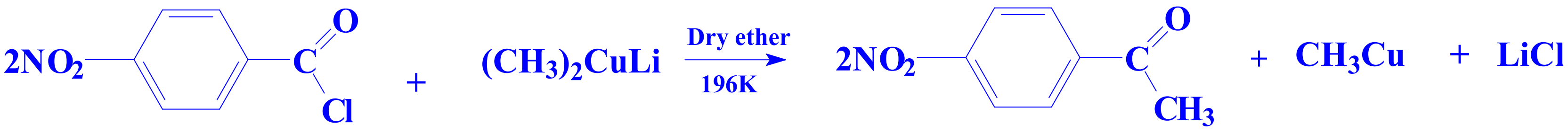
$$\mathrm{R}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{Cl} + \mathrm{R'_2CuLi} \longrightarrow \mathrm{R}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{R'} + \mathrm{R'Cu} + \mathrm{LiCl}$$

(R and R' can be alkyl or aryl groups)

Lithium dialkylcuprates needed for this purpose are themselves prepared as below:

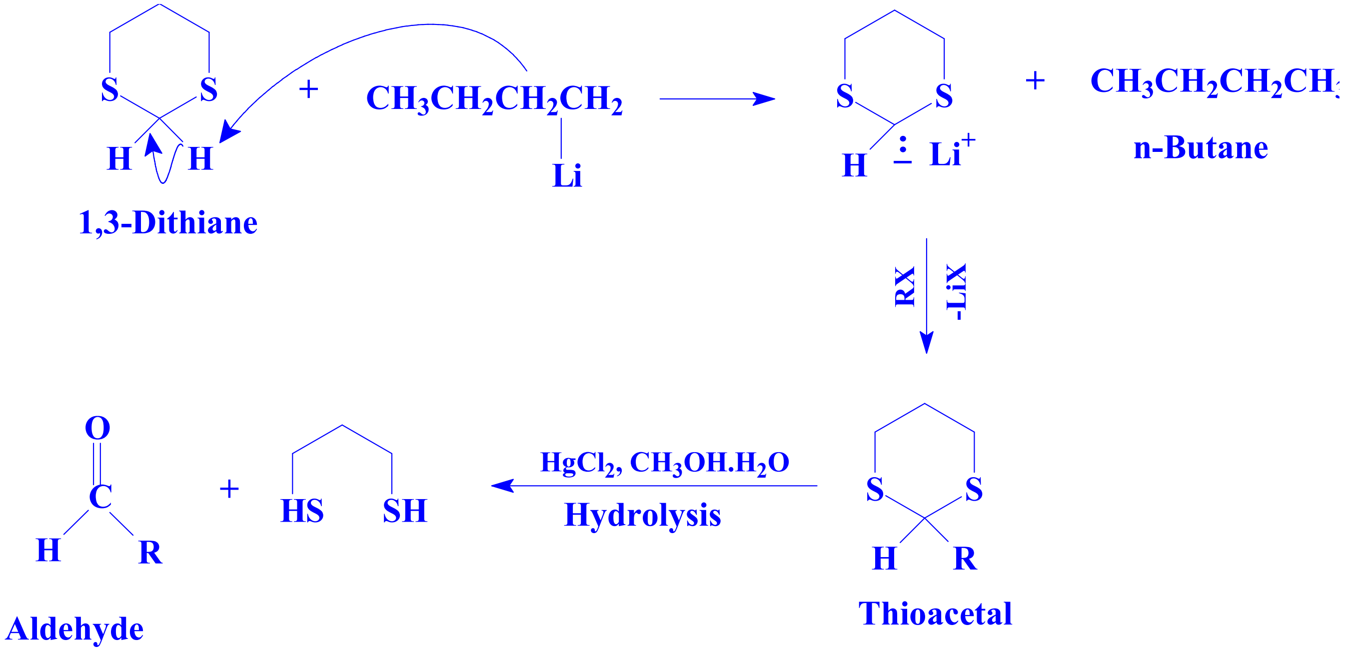
$$\mathrm{2R'X} \xrightarrow[\mathrm{-2LiX}]{\mathrm{4Li}} \mathrm{2R'Li} \xrightarrow{\mathrm{CuX}} \mathrm{R'_2CuLi} + \mathrm{LiX}$$

The advantage of this method is that Lithium dialkylcuprates do not ract with many of the functional group like NO_2, CN, COOR etc with which grignard reagents and organolithiums do react.



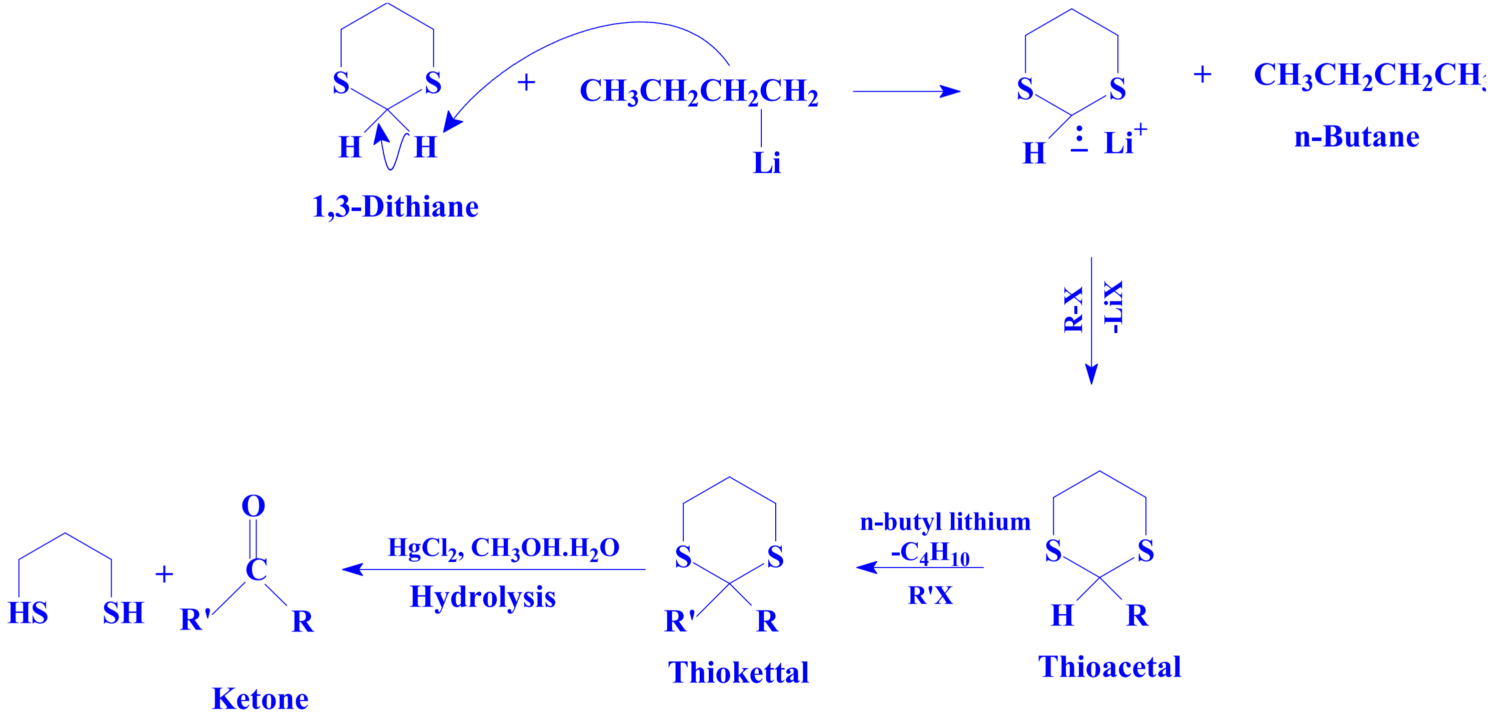
p-nitrobenzoyl chloride **Lithium dimethyl cuprate** **p-nitroacetophenone**

- **3. From 1,3 Dithiane**:
- 1, 3-Dithiane is a weak protonic acid and can be converted into its anion by treatment with strong base like n-butyl lithium. The 1,3-Dithane anion being a strong nucleophile reactions with alkyl halide by S_N2 mechanism to form alkyl derivatives of 1,3 dithiane which upon subsequent hydrolysis with $HgCl_2$ in methanol or aq. CH_3CN gives aldehydes.

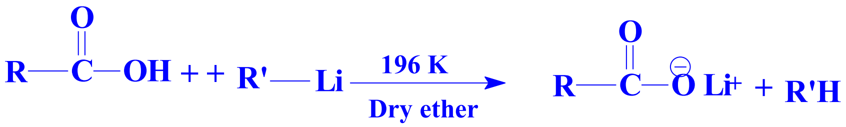


From 1,3....

- Similary ketones can be eaisly prepared from 1,3-dithiane by first converting it into its disubstitued derivatives, thioketal in two stages followed by hyrdolysis under the similar above conditions.

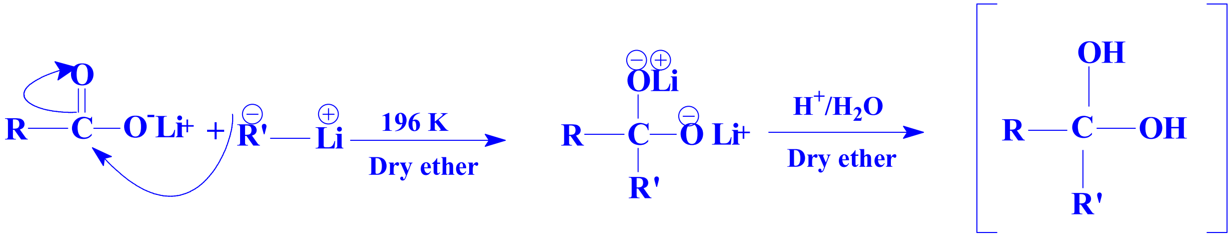


- **4. From Carboxylic acids:**
- Reaction of lithium alkyls with carboxylic acids provides a useful route for the synthesis of ketones. *For e.g.*



$$R-\overset{O}{\overset{\|}{C}}-OH + + R'-Li \xrightarrow[\text{Dry ether}]{196\ K} R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\,Li^{+} + R'H$$

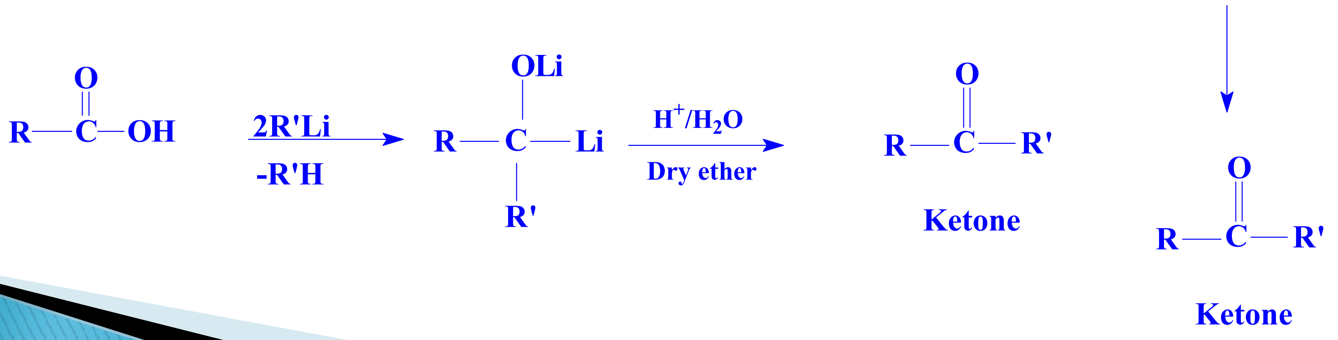
R' = 1^0, 2^0, 3^0 alkyl or aryl group



$$R-\overset{O}{\overset{\|}{C}}-O^{-}Li^{+} + \overset{\ominus}{R'}-\overset{\oplus}{Li} \xrightarrow[\text{Dry ether}]{196\ K} R-\overset{\overset{\ominus\oplus}{OLi}}{\underset{R'}{C}}-\overset{\ominus}{O}\,Li^{+} \xrightarrow[\text{Dry ether}]{H^+/H_2O} \left[R-\overset{OH}{\underset{R'}{C}}-OH\right]$$

Unstable

The overall reaction may be represented as

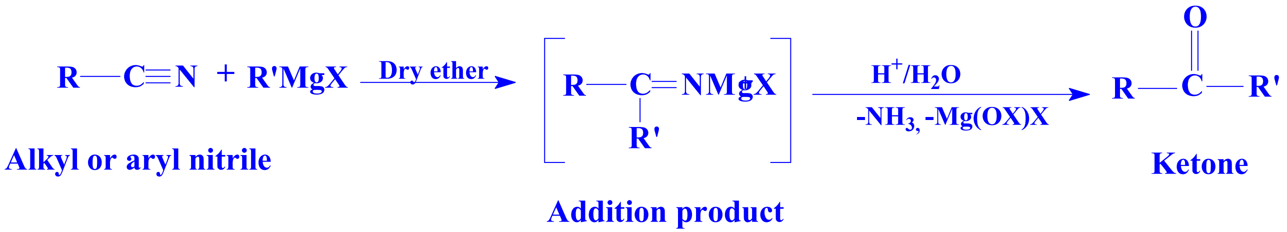


$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-R'H]{2R'Li} R-\overset{OLi}{\underset{R'}{C}}-Li \xrightarrow[\text{Dry ether}]{H^+/H_2O} R-\overset{O}{\overset{\|}{C}}-R'$$

$$R-\overset{O}{\overset{\|}{C}}-R'$$

5. From Nitriles:

By Reaction with Grignard Reagents or organolithium compounds: Grignard reagents or organolithium compounds add to alkyl or aryl nitriles to form addition products which upon subseqent hydrolysis gives ketones.

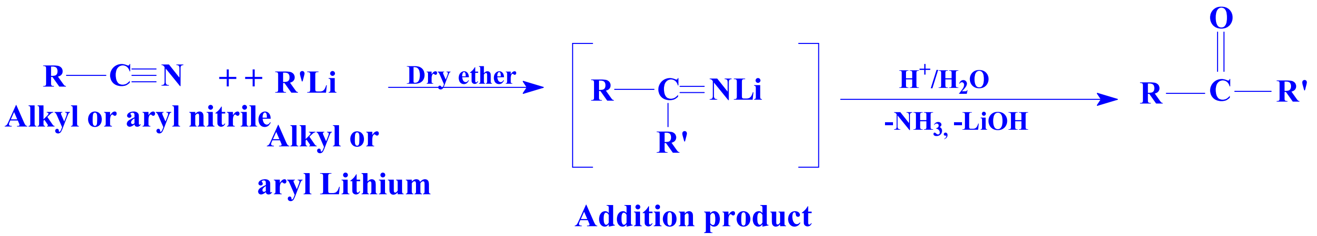


$$R-C\equiv N + R'MgX \xrightarrow{\text{Dry ether}} \left[R-\underset{R'}{\underset{|}{C}}=NMgX \right] \xrightarrow[\text{-NH}_3,\ \text{-Mg(OX)X}]{H^+/H_2O} R-\overset{\overset{O}{\|}}{C}-R'$$

Alkyl or aryl nitrile

Addition product

Ketone

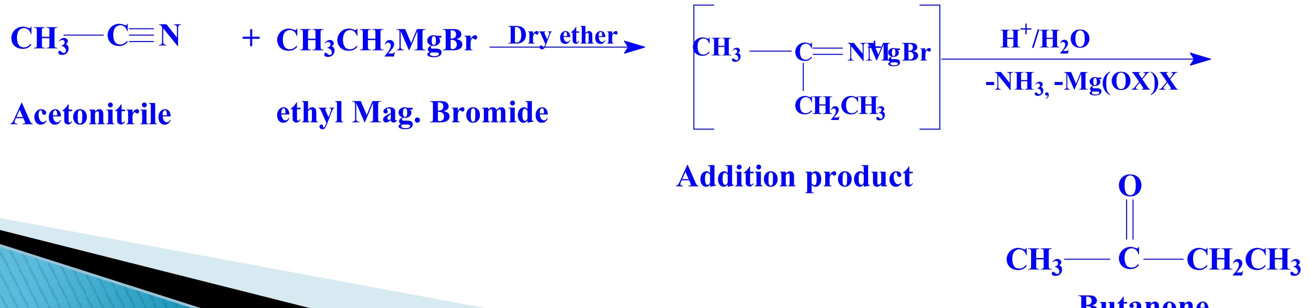


$$R-C\equiv N\ ++\ R'Li \xrightarrow{\text{Dry ether}} \left[R-\underset{R'}{\underset{|}{C}}=NLi \right] \xrightarrow[\text{-NH}_3,\ \text{-LiOH}]{H^+/H_2O} R-\overset{\overset{O}{\|}}{C}-R'$$

Alkyl or aryl nitrile

Alkyl or aryl Lithium

Addition product



$$CH_3-C\equiv N + CH_3CH_2MgBr \xrightarrow{\text{Dry ether}} \left[CH_3-\underset{CH_2CH_3}{\underset{|}{C}}=NMgBr \right] \xrightarrow[\text{-NH}_3,\ \text{-Mg(OX)X}]{H^+/H_2O} CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

Acetonitrile

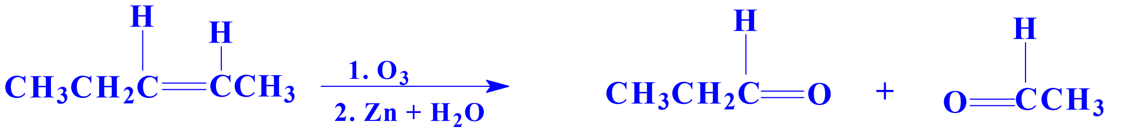
ethyl Mag. Bromide

Addition product

Butanone

6. Oxidation of Alkenes (Ozonolysis):

Aldehydes and ketones can be obtained by ozonolysis of alkenes. This involves the treatment of the alkenes with ozone to give ozonides. The ozonides are not isolated because they are explosive often in dry state. They are decomposed with Zn + H2O to form aldehydes and ketones.



$$CH_3CH_2\overset{H}{C}=\overset{H}{C}CH_3 \xrightarrow[2.\ Zn\ +\ H_2O]{1.\ O_3} CH_3CH_2\overset{H}{C}=O + O=\overset{H}{C}CH_3$$

2-Pentene **Propanal** **Acetaldehyde**

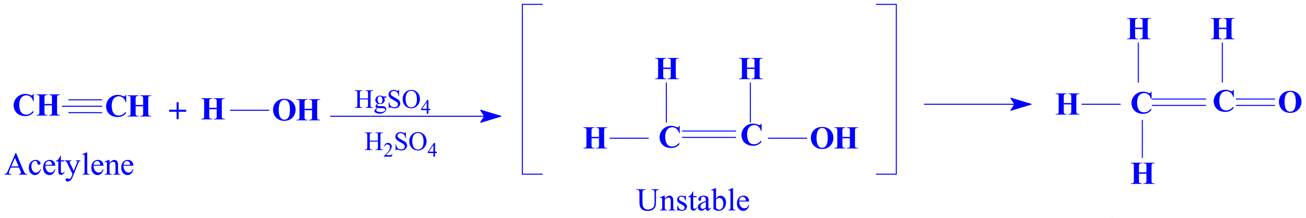
This is not a good method because a mixture of carbonyl compounds is often produced. However, if the starting alkene is symmetrical, only one carbonyl compound will be obtained. For e.g.

$$CH_3-\overset{H}{C}=\overset{H}{C}CH_3 \xrightarrow[2.\ Zn + H_2O]{1.\ O_3} CH_3-\overset{H}{C}=O + O=\overset{H}{C}CH_3$$

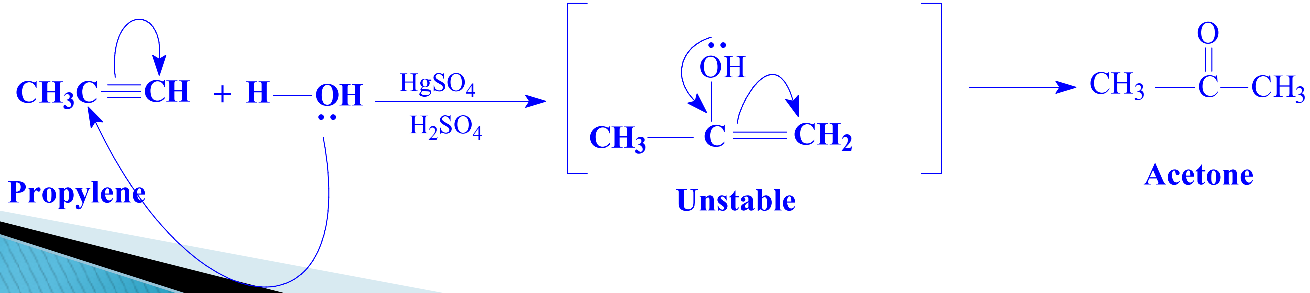
2-Butene **Acetaldehyde** **Acetaldehyde**

7. Hydration of alkynes:

Hydration of Acetylene yields acetaldehyde. Water adds to acetylene in the presence of mercuric sulpahte and sulphuric acid to form the unstable enol-intermediate which tautomerise to give acetaldehyde.

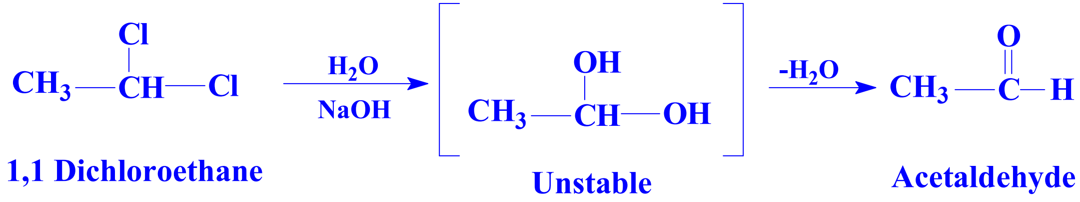

$$CH{\equiv}CH + H{-}OH \xrightarrow[H_2SO_4]{HgSO_4} \left[H{-}\overset{H}{C}{=}\overset{H}{C}{-}OH \right] \longrightarrow H{-}\underset{H}{\overset{H}{C}}{-}\overset{H}{C}{=}O$$

Hydration of alkynes other than acetylenes gives ketones. Water adds according to *Markonikov rule* to give an unstable enol-intermediate which rearranges to form ketones.


$$CH_3C{\equiv}CH + H{-}\ddot{O}H \xrightarrow[H_2SO_4]{HgSO_4} \left[CH_3{-}\overset{\ddot{O}H}{C}{=}CH_2 \right] \longrightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

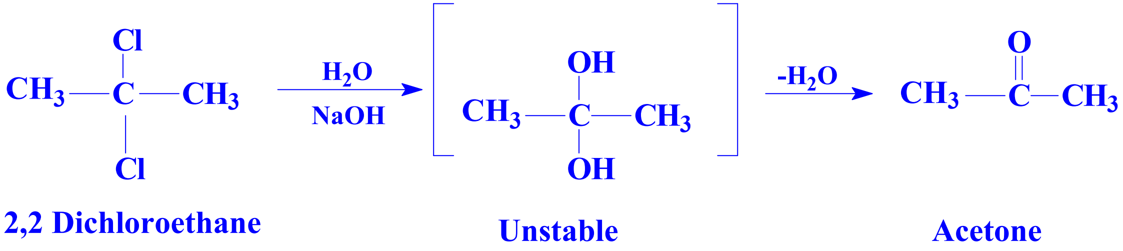
8. Hydrolysis of *gem*-Dihalides:

Aldehydes are prepared by alkaline hydrolysis of those *gem*-dihalides in which two halogen atoms are attached to the terminal carbon atom. For e.g.



$$CH_3-\overset{Cl}{CH}-Cl \xrightarrow[NaOH]{H_2O} \left[CH_3-\overset{OH}{CH}-OH \right] \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-H$$

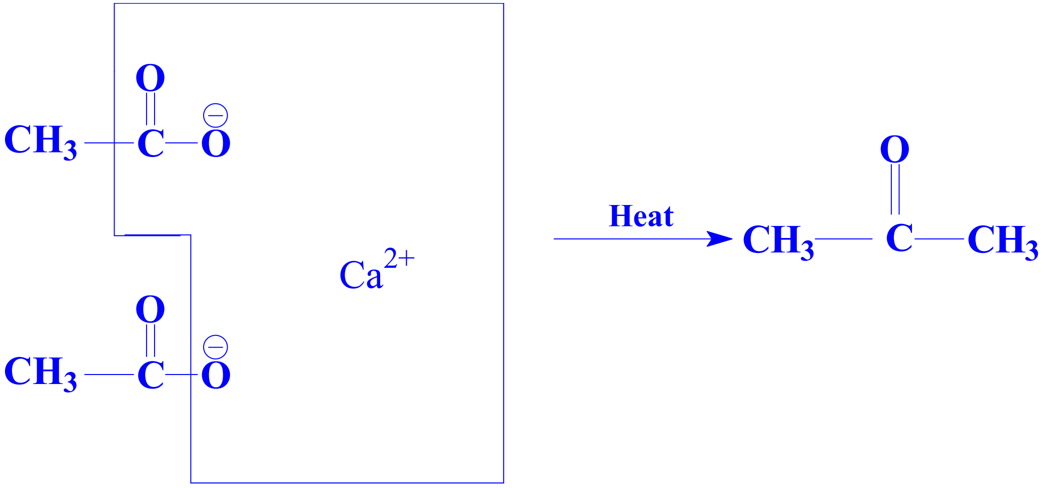
Ketones are produced by alkaline hydrolysis of those *gem*-dihalides in which the two halogen atoms are attached to a non-terminal carbon atom. For e.g.



$$CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_3 \xrightarrow[NaOH]{H_2O} \left[CH_3-\underset{OH}{\overset{OH}{C}}-CH_3 \right] \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

9. Pyrolysis of Calcium Salts of Acids:

Symmetrical ketones may be prepared by heating calcium Salts of acids at 400^0C.



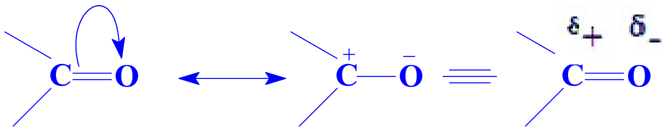
$$\left(CH_3-\overset{\overset{O}{\|}}{C}-O^{\ominus}\right)_2 Ca^{2+} \xrightarrow{Heat} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Calcium acetate

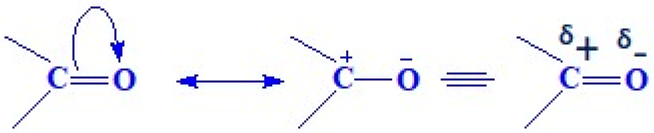
Acetone

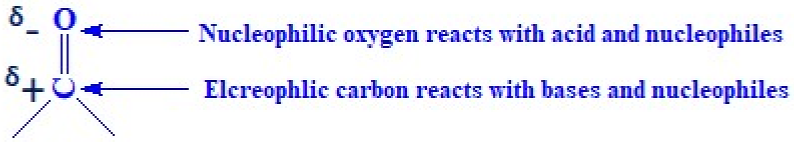
Nucleophilic Addition Reactions:

The carbonyl group of aldehydes and ketones is highly polar group.



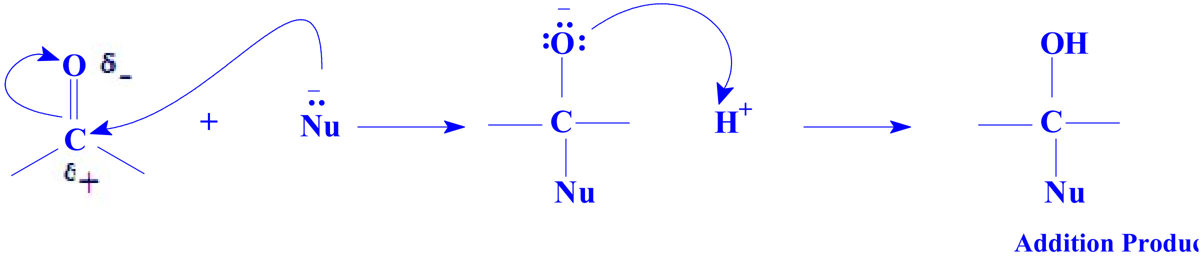
The positive charged carbon is readily attacked by electron-rich nucleophiles. The negatively charged oxygen is attacked by electron-deficient electrophiles.




Nucleophilic oxygen reacts with acid and nucleophiles

Elcreophlic carbon reacts with bases and nucleophiles

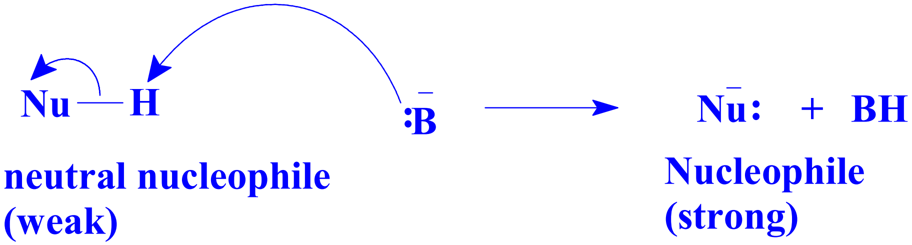
Mechanism of Nucleophilic Addition Reactions:



The nucleophilic addition reactions of carbonyl compounds may be catalyzed by acids or bases.

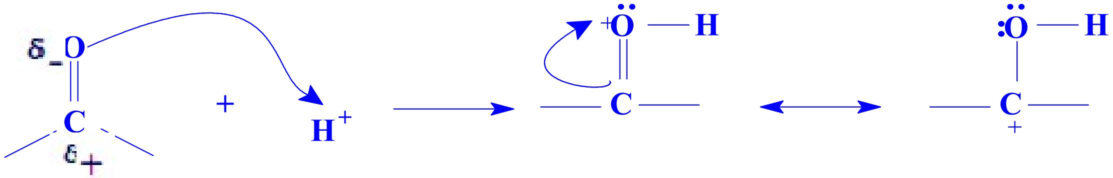
Base catalysed addition:

Base convert a weak neutral electrophile to a strong one by removing a proton. The strong nuclophile then adds to the carbonyl group as shown below.



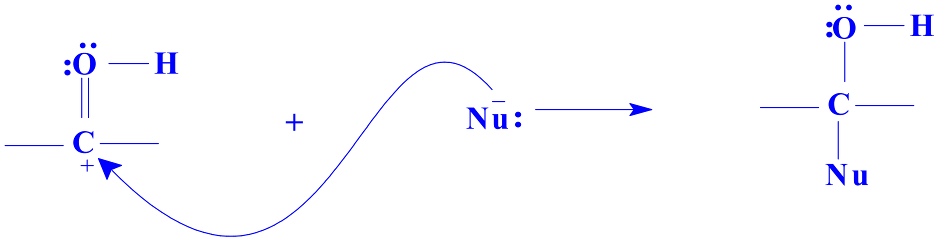
Acid catalysed addition:

Step 1: The hydrogen ion from the acid attacks the negatively charged carbonyl oxygen to give protonated carbonyl group.



Protonated carbonyl group

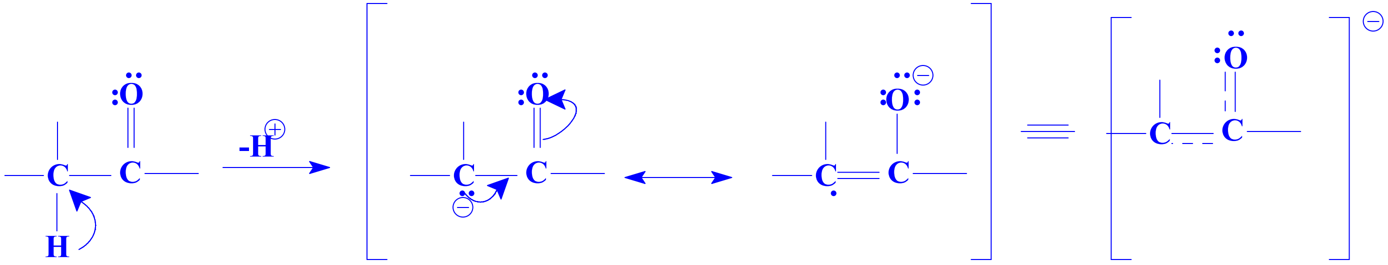
Step 2: The nucleophile attacks the protonated carbonyl group to form the addition product.



Addition produc

Acidity of **α**-hydrogens:

The hydrogen on carbon alpha to carbonyl group is acidic because the carbanion resulting after removal is resonance stablized as shown below:



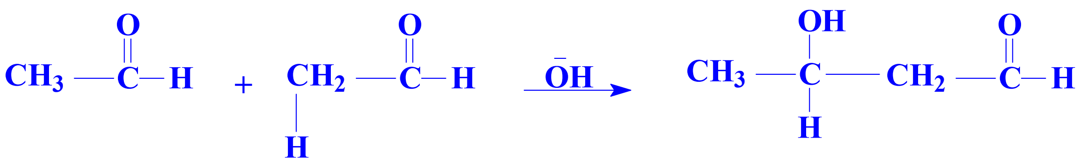
carbanion:resonance stabilized

Resonance hybrid

These carbanion acts as a nucleophile and undergoes nucleophilic addition with its own counterpart or with other aldehyde or ketone to form condensation products.

Aldol Condensation

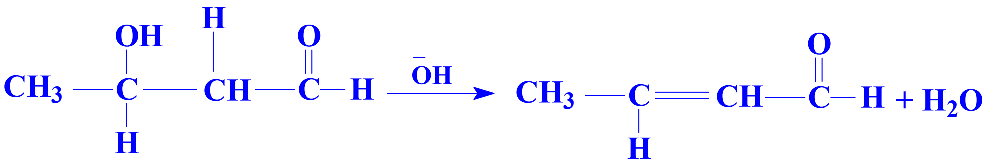
Aldehydes containing α-hydrogens undergo self-addition in the presence of a base to form products called **Aldols**. The reaction is called *Aldol Condensation. For e.g.*



$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-H + \underset{H}{\underset{|}{CH_2}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\bar{O}H} CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-H}$$

Acetaldehyde **Acetaldehyde** **3-hydroxy butanol (aldol)**

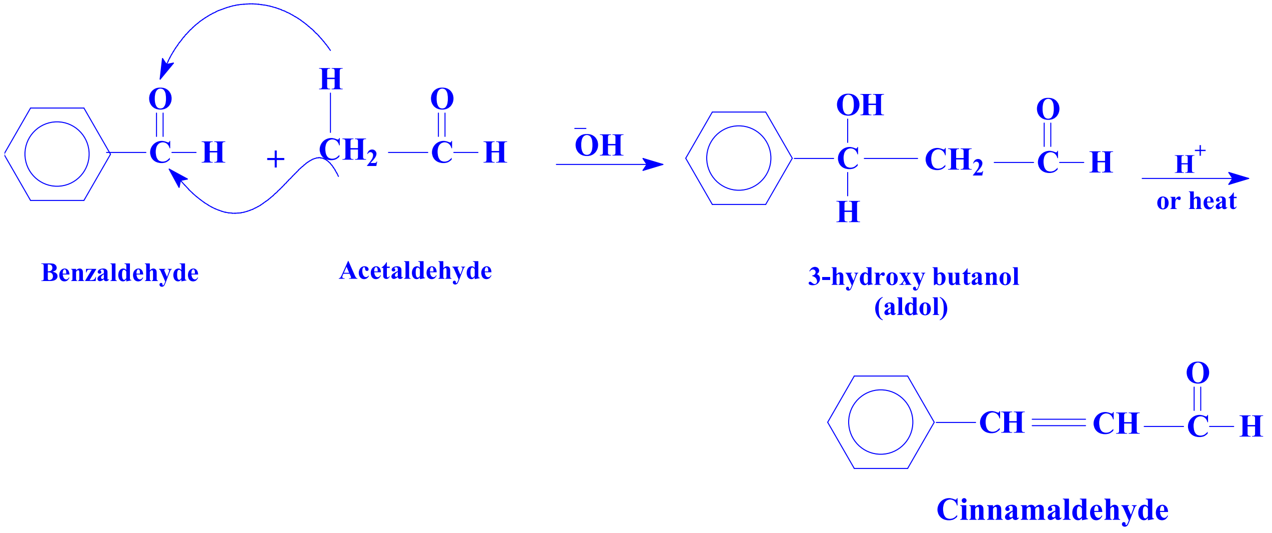
Aldols are easily dehydrated either by heating or by treatment with dilute acid to form unsaturated α, β-aldehydes. For e.g.



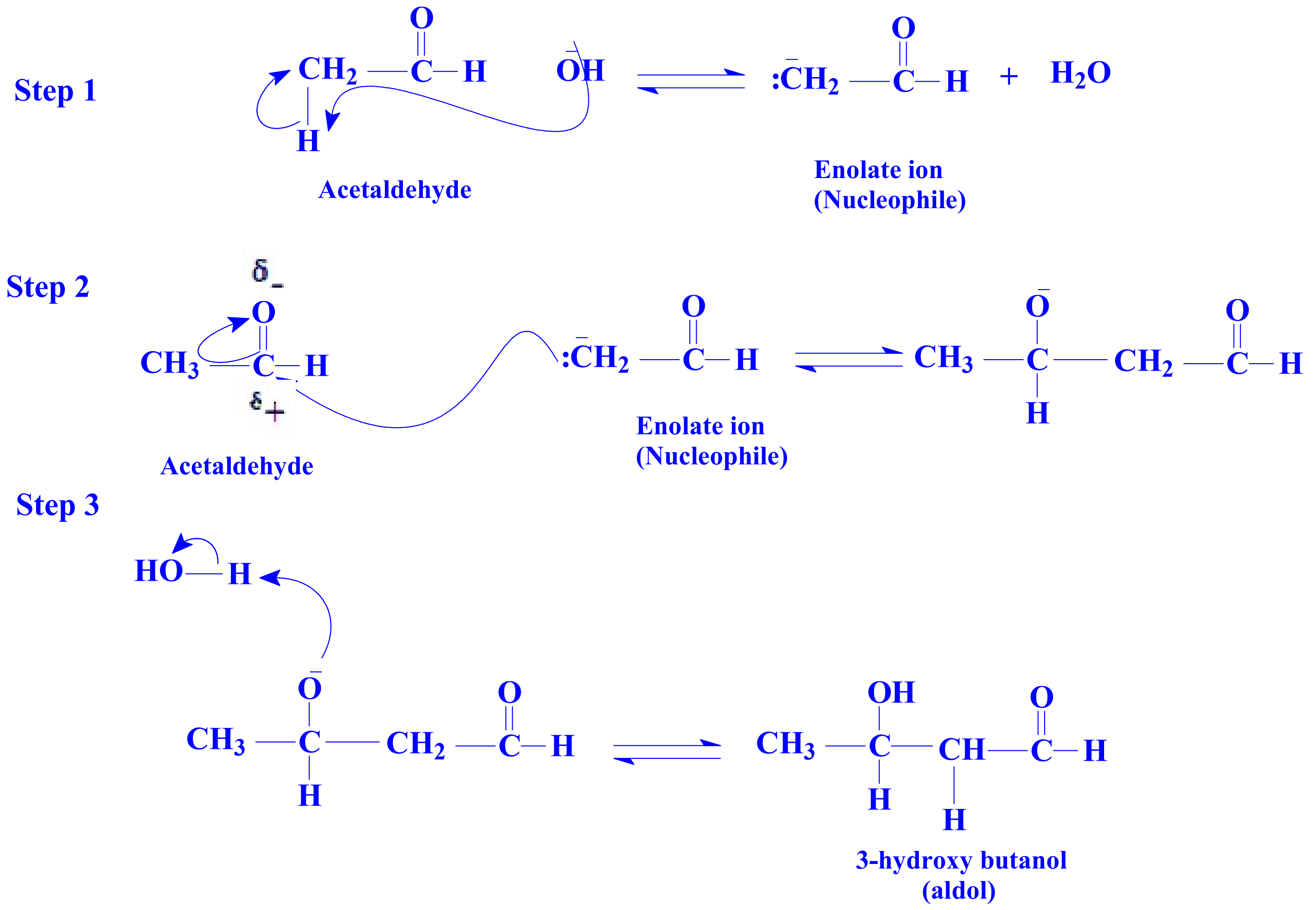
$$\mathrm{CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\overset{H}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\bar{O}H} CH_3-\underset{H}{\underset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-H + H_2O}$$

3-hydroxy butanal (aldol) **2-butenal or crotonaldehye**

Mixed/Crossed Aldol Condensation: The reaction between **a.** two aldehydes or two ketones which are different **b.** between an aldehyde and a ketone containing α-hydrogen atoms. Such type of aldol condensation is known as Mixed/Crossed Aldol Condensation.

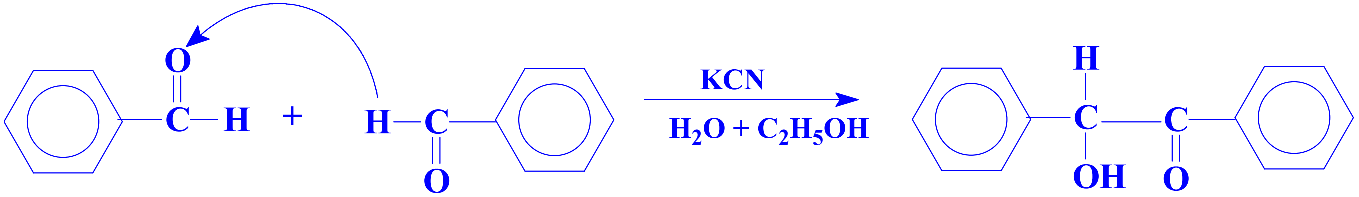


Mechanism of Aldol Condenstion



Benzoin Condensation

Aromatic aldehydes undergo self condensation of two molecules in the presence of cyanide ion to form benzoin. This reaction is known as **Benzoin condensation**.

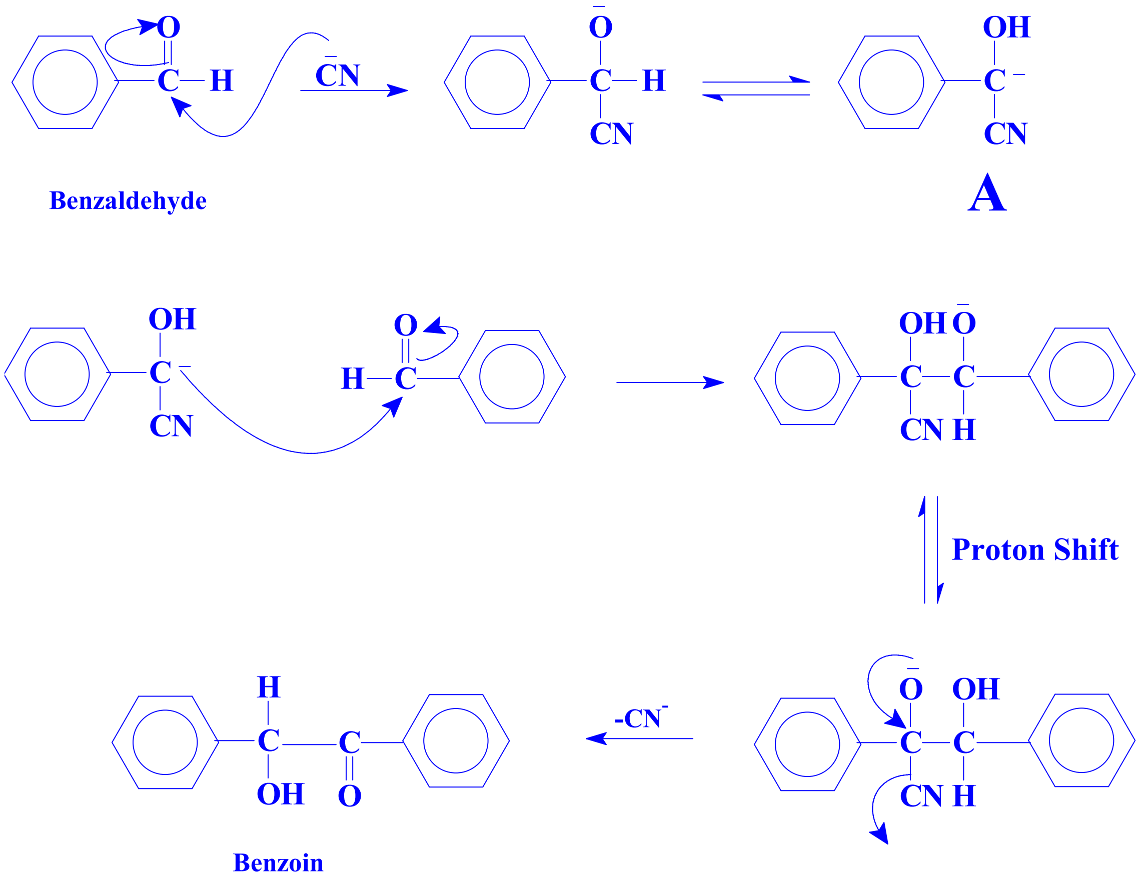


Benzaldehyde

Benzaldehyde

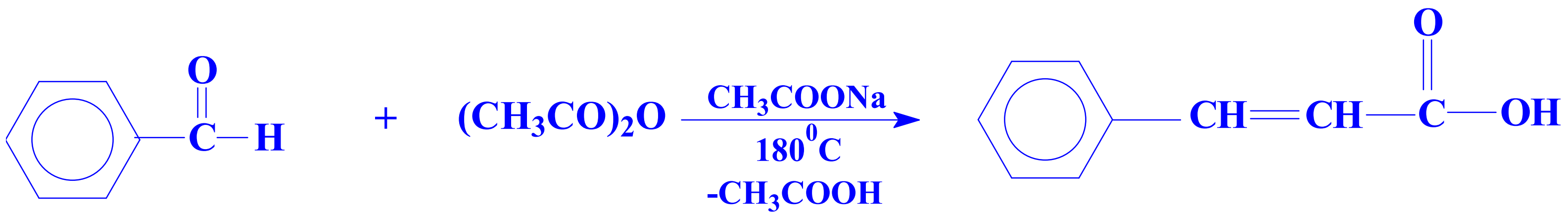
Benzoin

Mechanism of Benzoin Condenstion



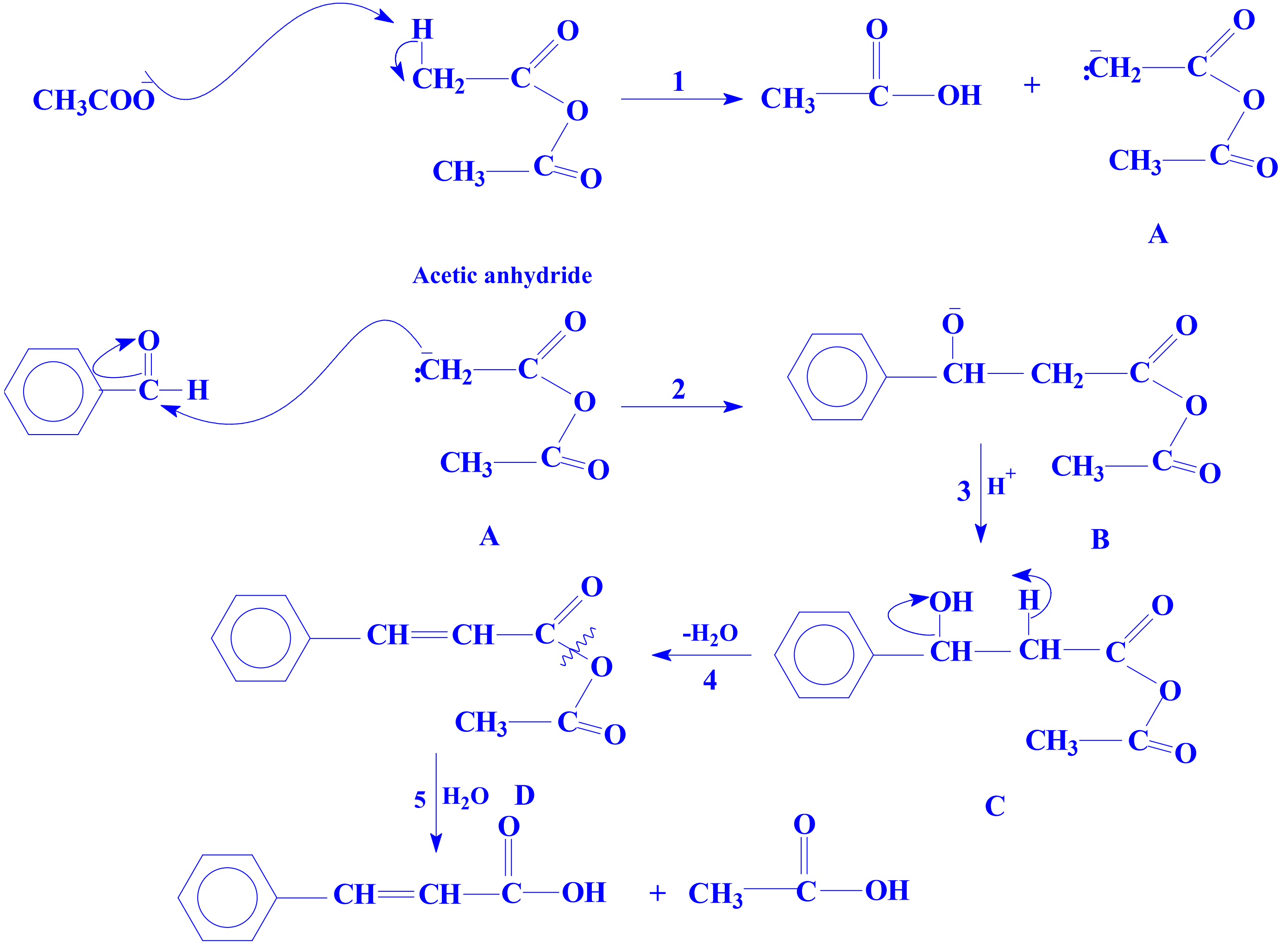
Perkin Reaction:

The addition of acid anhydrides (containing α-hydrogen atoms) to aromatic aldehydes in the presence of bases like sodium salts of the acids (from which the anhydride is derived) to form α, β-unsaturated acids is known as Perkin reaction.



Cinnamic acid

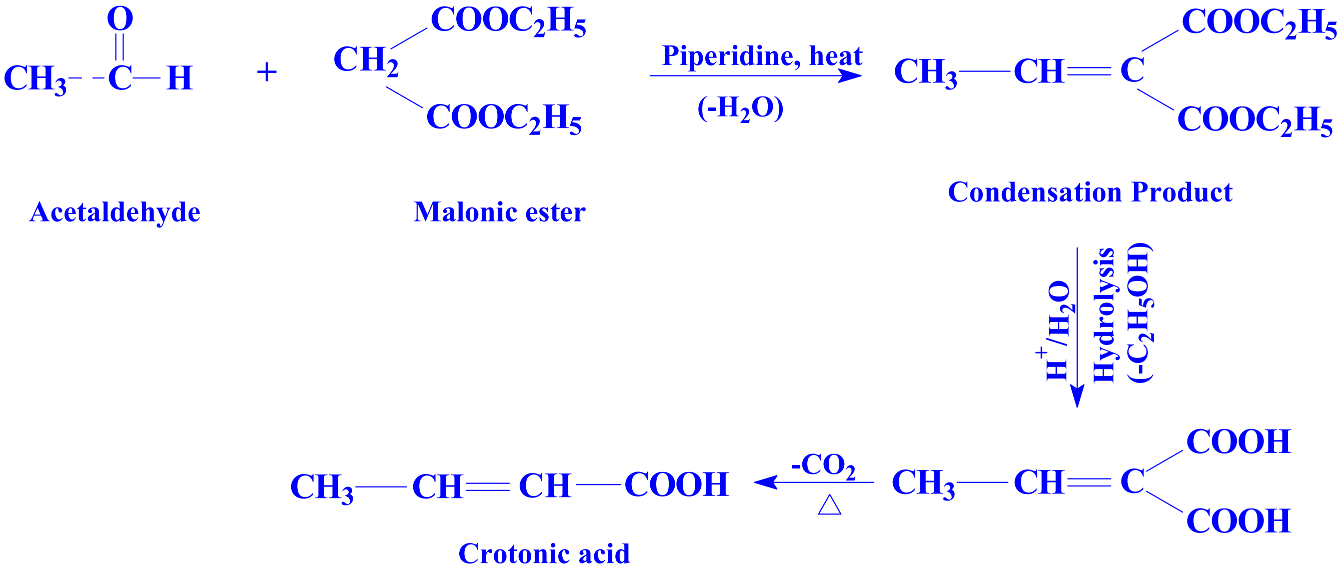
Mechanism of Perkin Reaction



Cinnamic acid

Knoevenagel Reaction:

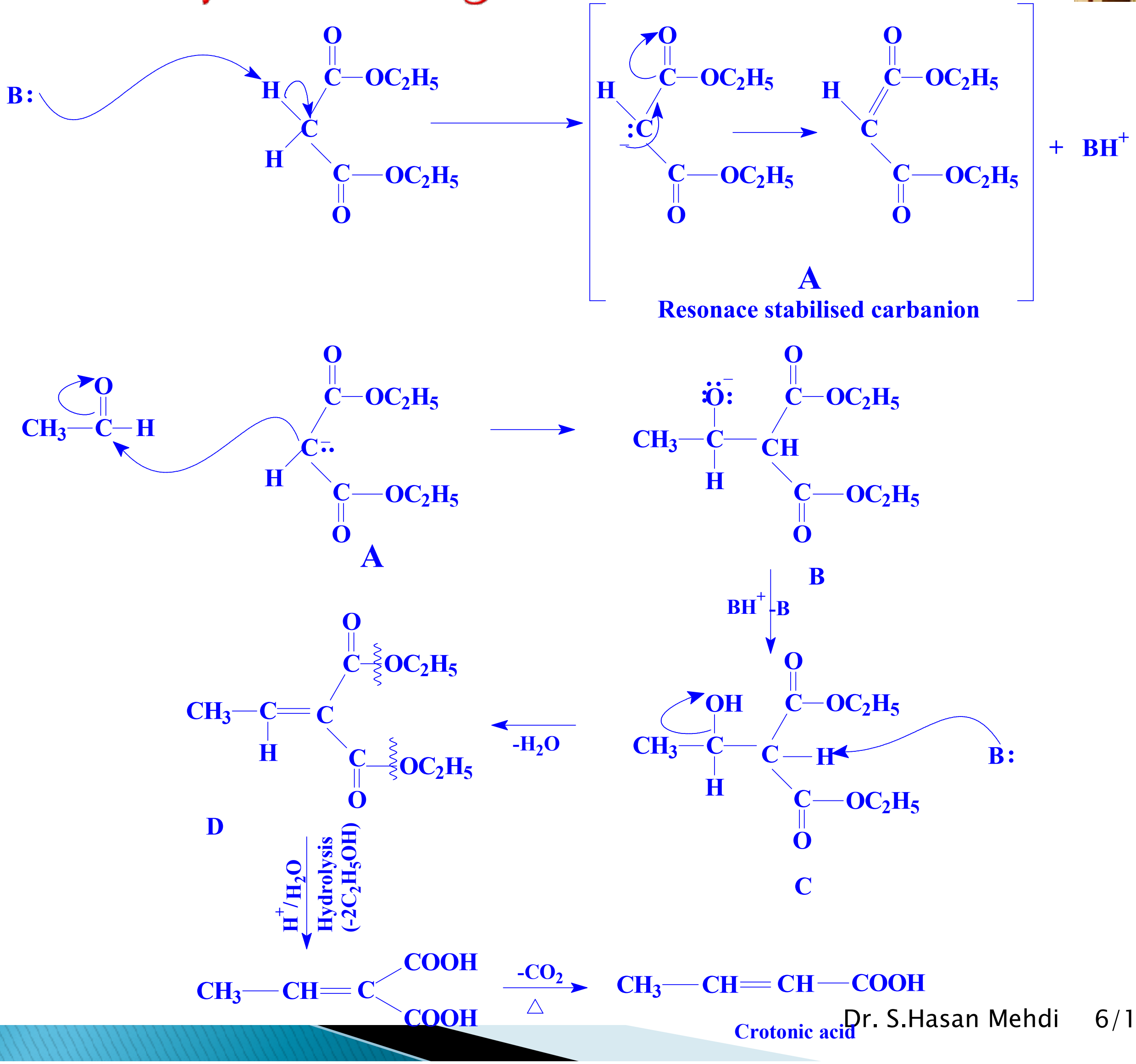
When malonic ester or acetoacetic ester is treated with aldehydes or ketones, in the presence of bases like pyridine or piperidine, α, β-unsaturated esters are formed. These esters on hydrolysis and decarboxylation, yield α, β-unsaturated acids. For e.g.



$$CH_3CHO + CH_2(COOC_2H_5)_2 \xrightarrow[(-H_2O)]{\text{Piperidine, heat}} CH_3{-}CH{=}C(COOC_2H_5)_2$$

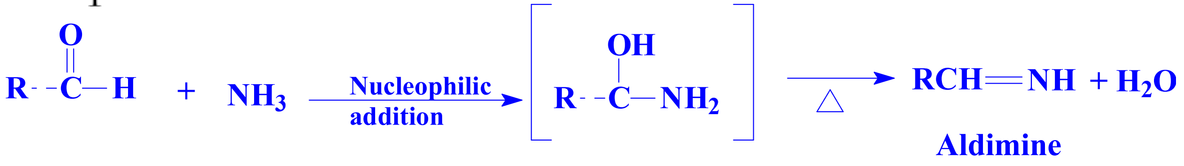
$$CH_3{-}CH{=}C(COOC_2H_5)_2 \xrightarrow[(-C_2H_5OH)]{H^+/H_2O,\ \text{Hydrolysis}} CH_3{-}CH{=}C(COOH)_2 \xrightarrow[\triangle]{-CO_2} CH_3{-}CH{=}CH{-}COOH$$

Mechanism of Knoevenagel Reaction:



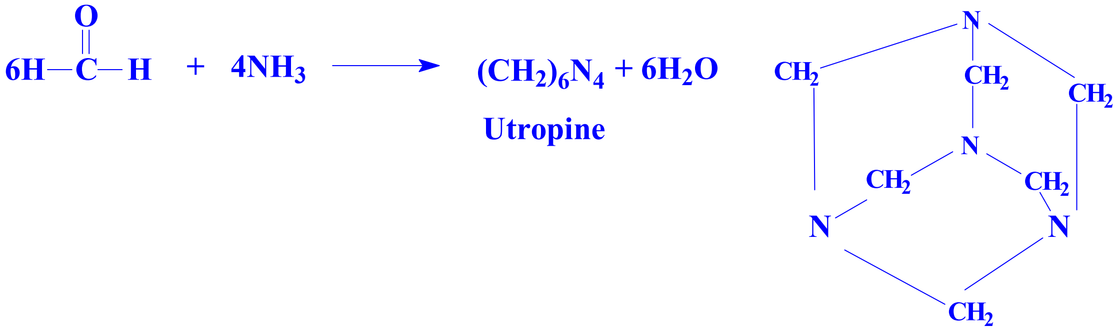
Reaction with ammonia :

Aldehydes (except formaldehyde) react with ammonia to form aldehyde ammonia that readily dehydarte to aldimine. Whereas formaldehyde gives a complex compound called hexamethylene tetramine or urotropine (a drug used in urianry infection). On the other hand ketones give complex ketonic amines.



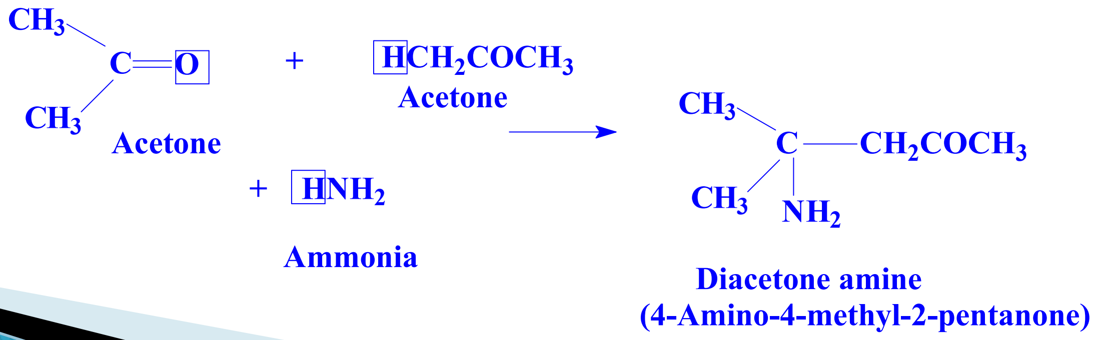
$$R-\overset{\overset{O}{\|}}{C}-H + NH_3 \xrightarrow[\text{addition}]{\text{Nucleophilic}} \left[R-\overset{\overset{OH}{|}}{C}-NH_2 \right] \xrightarrow{\triangle} RCH{=}NH + H_2O$$

Aldimine



$$6H-\overset{\overset{O}{\|}}{C}-H + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$

Utropine



$$(CH_3)_2C{=}\boxed{O} + \boxed{H}CH_2COCH_3 + \boxed{H}NH_2 \longrightarrow (CH_3)_2\underset{\underset{NH_2}{|}}{C}-CH_2COCH_3$$

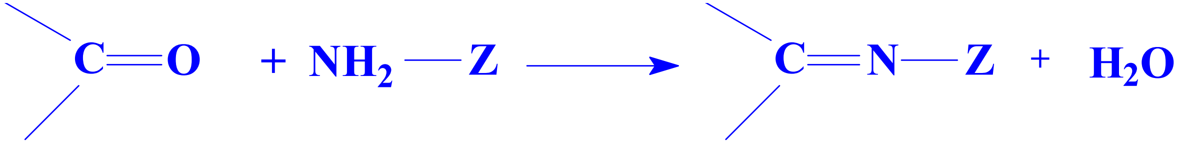
Acetone **Acetone** **Ammonia**

Diacetone amine
(4-Amino-4-methyl-2-pentanone)

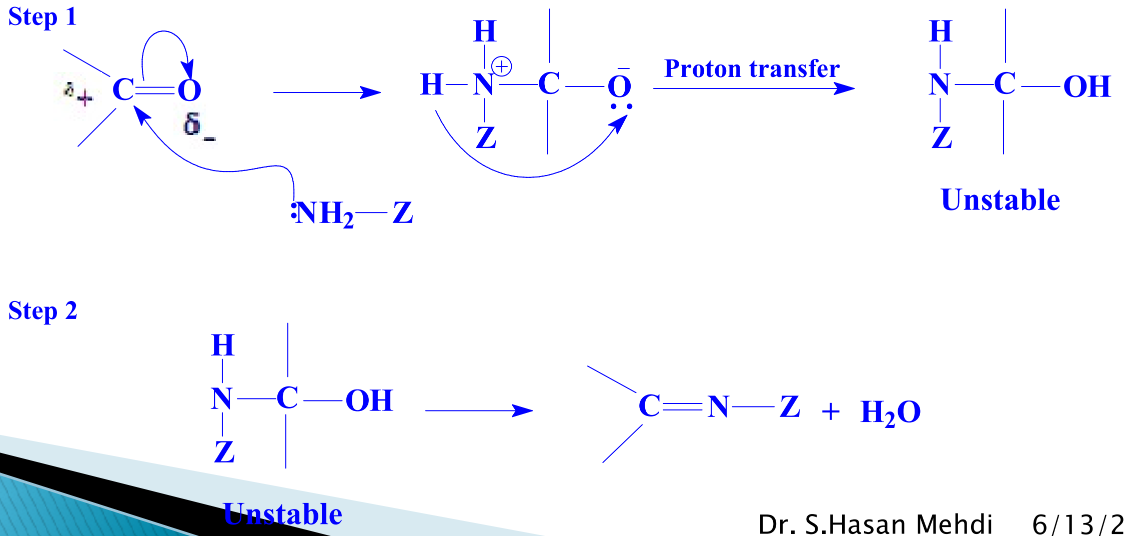
Reaction with ammonia derivatives

Some ammonia derivatives (NH_2-Z) react with aldehydes and ketones to form compounds containing carbon-nitrogen double bonds, together with the elimination of water molecule.

The reaction products are usually crystalline solids whose melting points can be used to identify aldehydes and ketones, most of which are liquids.

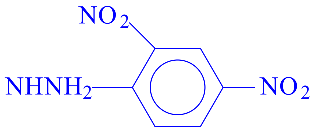
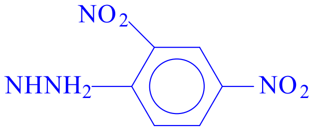


The mechanism of the above reaction involves the following steps:



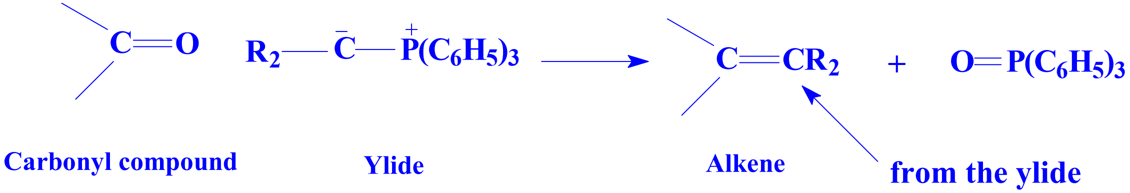
Reaction with ammonia............

Hydroxyl amine, hydrazine, phenylhyrazine, 2,4-dinitrophenylhydrazine, 2,4-dinitrophenyl hydrazine and semicarbazide react in this way.

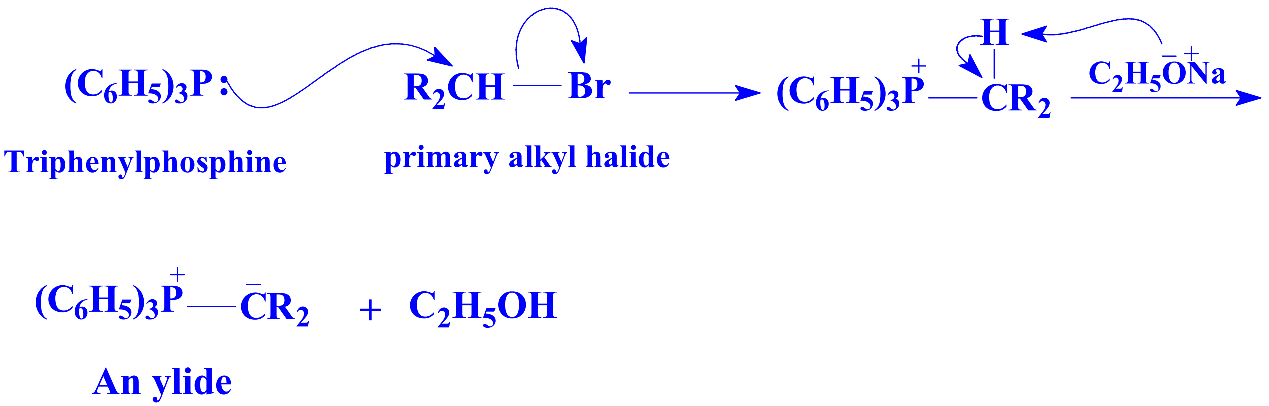
Reactant	**Z**	**Reagent**	**Product**
Aldehyde	OH	Hydroxyl amine	Aldehyde oxime
Acetone	OH	Hydroxyl amine	Ketone oxime
Aldehyde	NH_2	Hydrazine	Aldehyde hydrazone
Ketone	NH_2	Hydrazine	Ketone hydrazone
Aldehyde	C_6H_5—NH	Phenylhydrazine	Aldehyde phenylhydrazone
Ketone	C_6H_5—NH	Phenylhydrazine	Ketone phenylhydrazone
Aldehyde		2,4 dinitroPhenylhydrazine	Aldehyde 2,4 dinitrophenylhydraz
Ketone		2,4 dinitroPhenylhydrazine	Ketone 2,4 dinitrophenylhydrazon

Wittig Reaction:

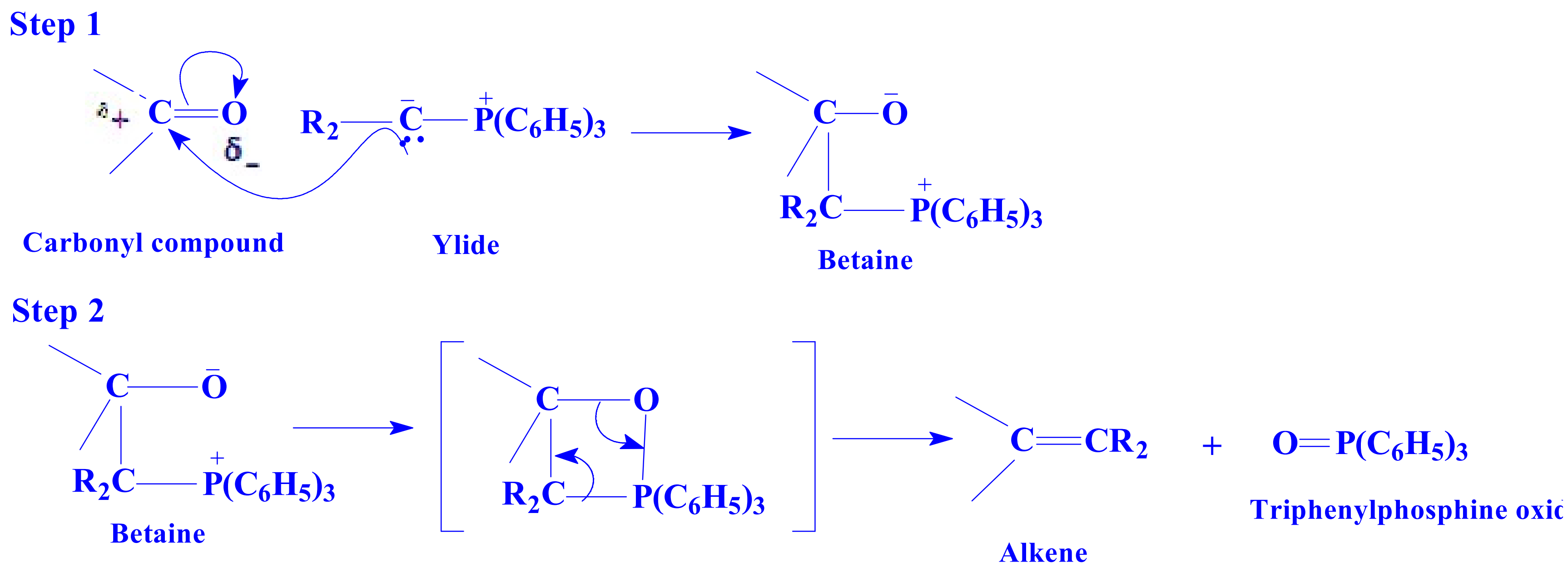
The reaction of aldehydes and ketones with substituted **triphenyl phosphoranes (ylides)** to form alkenes is called Wittig Reaction.



Phosphorous ylides are prepared from primary alkyl halides and triphenylphosphone.



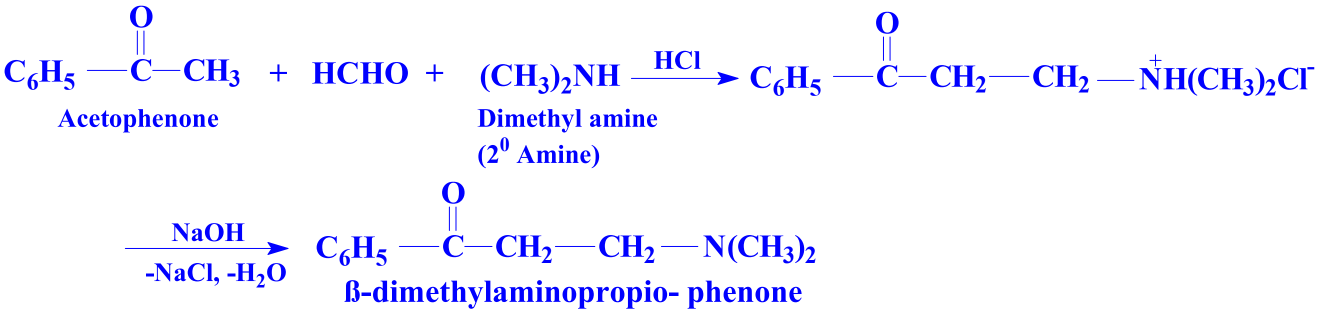
Mechanism of Wittig Reaction:



Mannich Reaction:

It involves the reaction between an active methylene compounds* (usually an enolizable ketone), formaldehyde and an amine (usually a secondary amine) in presence of of an acid (neutral or basic media can also be used) to give a prodct which upon treating with a base yields β-amino carbonyl compound commonly known as Mannich base. For. e.g.

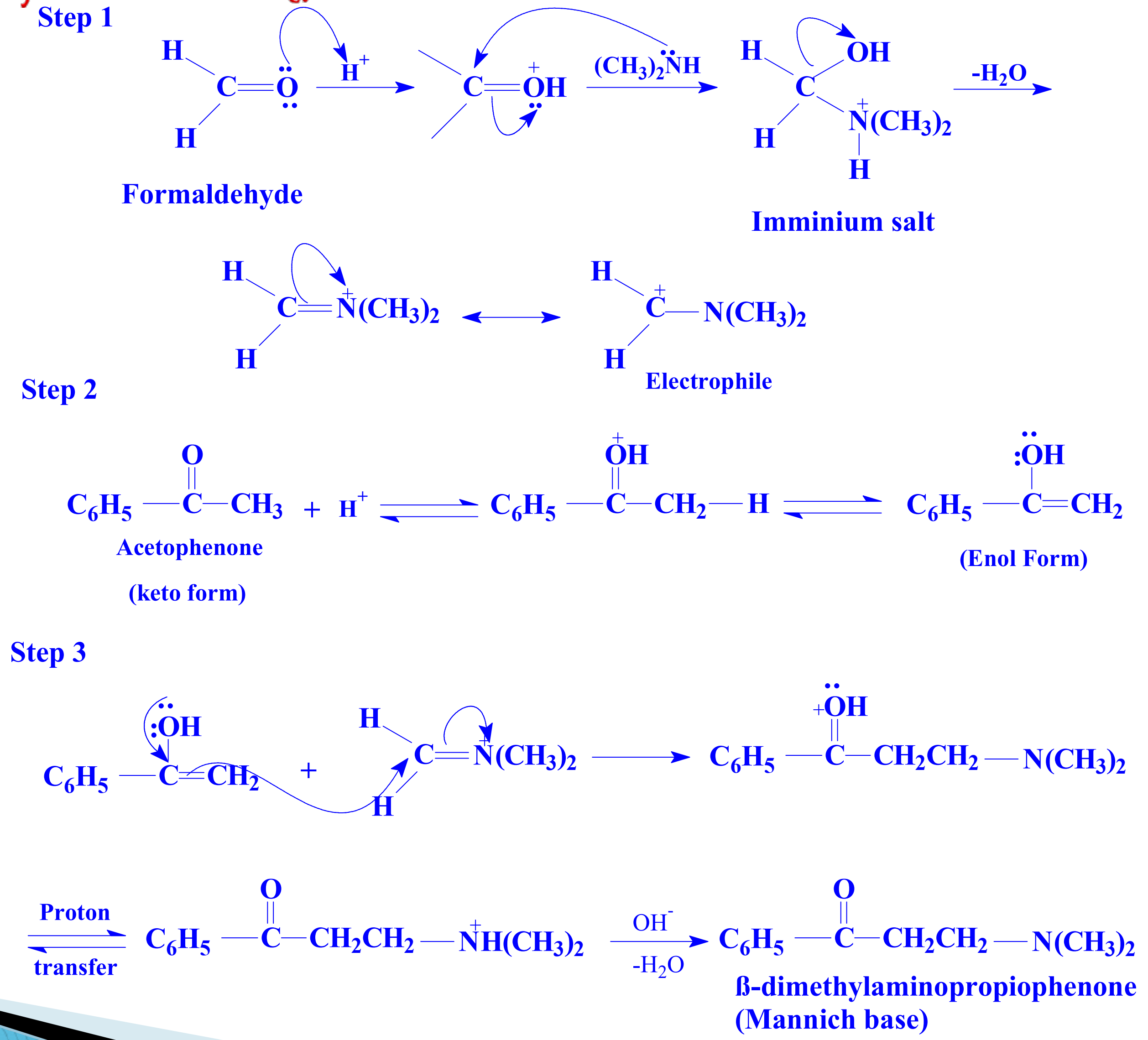
* Besides ketones β-keto esters, β-cyano esters, nitroalkanes and terminal alkynes have also been used.



$$\underset{\text{Acetophenone}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + HCHO + \underset{\substack{\text{Dimethyl amine}\\(2^0\ \text{Amine})}}{(CH_3)_2NH} \xrightarrow{HCl} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-\overset{+}{N}H(CH_3)_2Cl^-$$

$$\xrightarrow[-NaCl,\ -H_2O]{NaOH} \underset{\text{ß-dimethylaminopropio- phenone}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-N(CH_3)_2}$$

Mechanism of Mannich Reaction.



Step 1

$$H_2C{=}\ddot{O} \xrightarrow{H^+} H_2C{=}\overset{+}{O}H \xrightarrow{(CH_3)_2\ddot{N}H} H_2C(OH)\overset{+}{N}H(CH_3)_2 \xrightarrow{-H_2O}$$

Formaldehyde

Imminium salt

$$H_2C{=}\overset{+}{N}(CH_3)_2 \longleftrightarrow H_2\overset{+}{C}{-}N(CH_3)_2$$

Electrophile

Step 2

$$C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + H^+ \rightleftharpoons C_6H_5{-}\overset{\overset{+}{O}H}{\overset{\|}{C}}{-}CH_2{-}H \rightleftharpoons C_6H_5{-}\overset{:\ddot{O}H}{\overset{|}{C}}{=}CH_2$$

Acetophenone

(keto form)

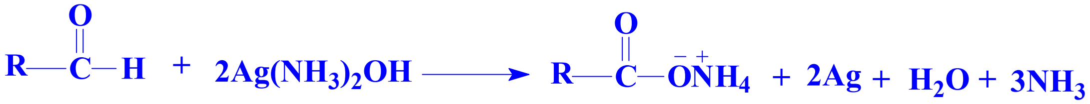
(Enol Form)

Step 3

$$C_6H_5{-}\overset{:\ddot{O}H}{\overset{|}{C}}{=}CH_2 + H_2C{=}\overset{+}{N}(CH_3)_2 \longrightarrow C_6H_5{-}\overset{+\ddot{O}H}{\overset{\|}{C}}{-}CH_2CH_2{-}N(CH_3)_2$$

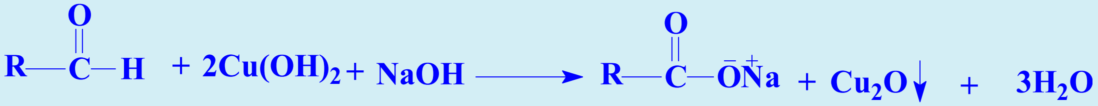
$$\xrightleftharpoons[\text{transfer}]{\text{Proton}} C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2{-}\overset{+}{N}H(CH_3)_2 \xrightarrow[-H_2O]{OH^-} C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2{-}N(CH_3)_2$$

ß-dimethylaminopropiophenone
(Mannich base)



$$R-\overset{\overset{O}{\|}}{C}-H + 2Ag(NH_3)_2OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{N}H_4 + \underset{\text{Silver mirror}}{2Ag} + H_2O + 3NH_3$$

Fehling’s solution: It is an alkaline solution of cupric ion complexed with sodium potassium tartrate ions. On treating with an aldehyde, the complex cupric ion (deep blue) is reduced to cuprous oxide (red). The presence of red precipitate of cuprous oxide indicates the presence of aldehyde group in a molecule.

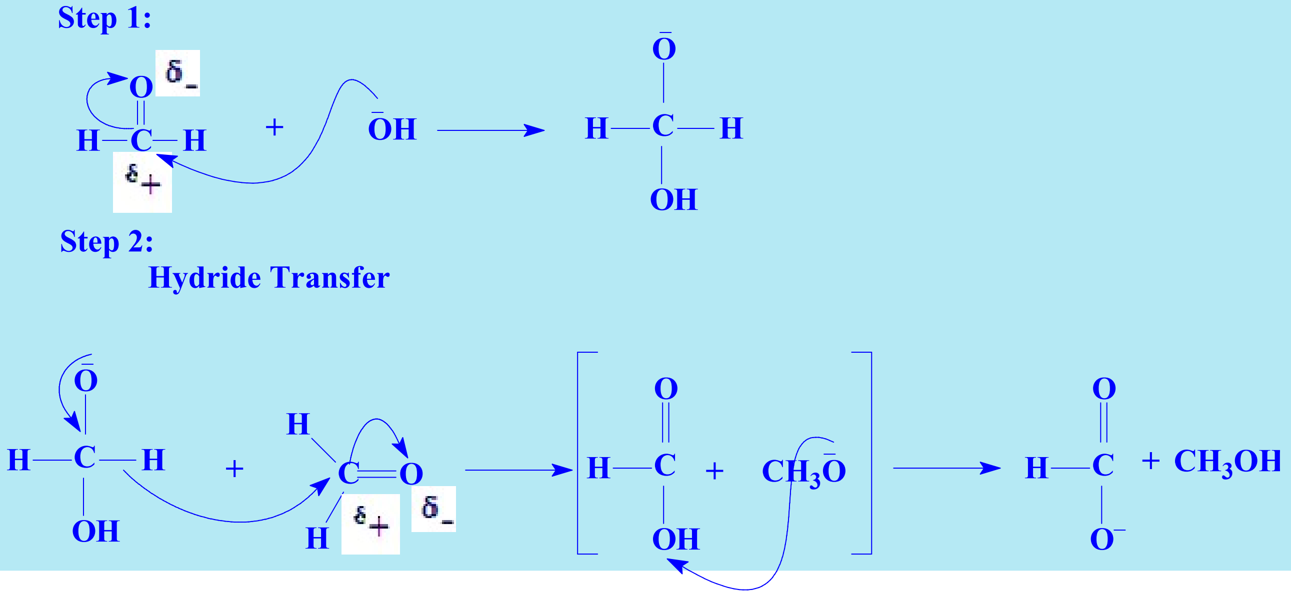


$$R-\overset{\overset{O}{\|}}{C}-H + 2Cu(OH)_2 + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{N}a + \underset{\text{(red)}}{Cu_2O\downarrow} + 3H_2O$$

Bendict’s solution: It is an alkaline solution of cupric ion complexed with citrate ions. It reacts in the same way as Fehling’s solution.

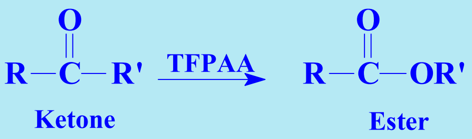
Cannizaro reaction:

Aldehydes which lack an α-hydrogen, when heated with conc. NaOH, undergo disproportionation reaction. One half of the aldehyde molecules are oxidised to a carboxylic acid and on half are reduced to alcohol. This reaction is known as *Cannizaro reaction*. Aldehyde with α-hydrogen undergo an aldol condensation under these conditions.

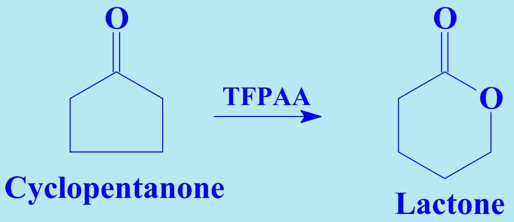


Baeyer-Villiger Oxidation:

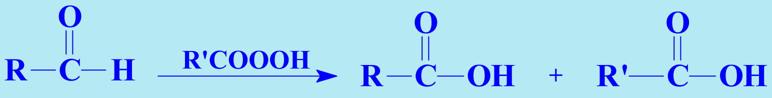
Oxiation of ketones (acyclic/cyclic) into esters/lactones by means of peracids such as perbenzoic acid (PAA), trifluroperacetic acid (TFPAA) etc is known as **Baeyer-Villiger Oxidation.** *for e.g.*



$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{TFPAA} R-\overset{O}{\overset{\|}{C}}-OR'$$



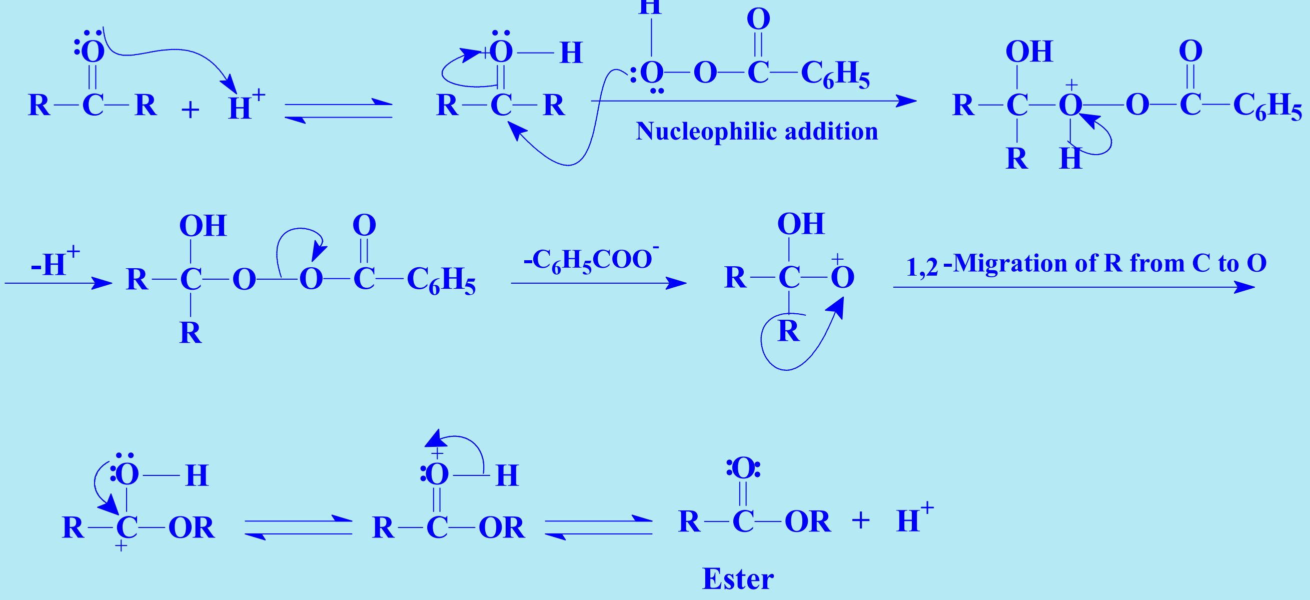
Aliphatic aldehydes are oxidised to acids by the migration of hydrogen.



$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{R'COOOH} R-\overset{O}{\overset{\|}{C}}-OH + R'-\overset{O}{\overset{\|}{C}}-OH$$

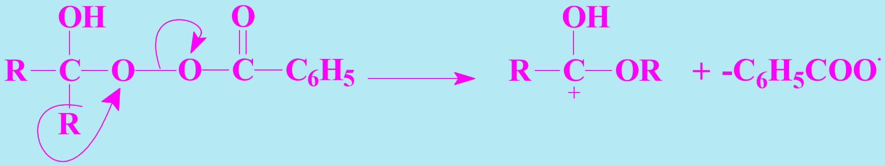
Mechanism:

It involves 1. ***protonation*** of carbonyl oxygen, 2. ***nucleophilic attack of per benzoic acid*** on carbonylic carbon, 3. ***migration of R to electron deficient oxygen*** with release of carboxylate anion and 4. ***deprotonation*** *of* ***protonated ester*** to ester.



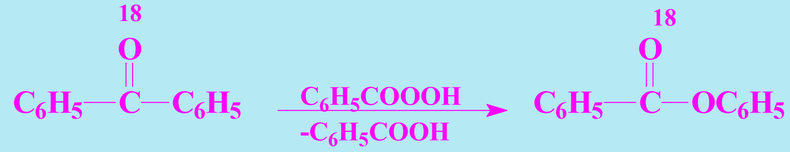
Most probably the two steps involving the 1,2-migration of group R and loss of carboxylate ion are concerted i.e. occurs simultaneously.

Mechanism continued........



$$R-\overset{OH}{\underset{R}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow R-\overset{OH}{\underset{+}{C}}-OR \;+\; -C_6H_5COO^{\cdot}$$

This shows that the carbonyl oxygen of the ester group is one that is on the original ketone.



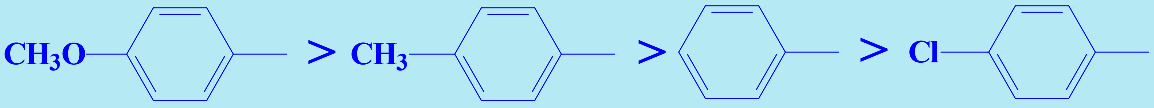
$$C_6H_5-\overset{\overset{18}{O}}{\overset{\|}{C}}-C_6H_5 \xrightarrow[-C_6H_5COOH]{C_6H_5COOOH} C_6H_5-\overset{\overset{18}{O}}{\overset{\|}{C}}-OC_6H_5$$

(O^{18} = isotopic oxygen)

Phenyl benzoate

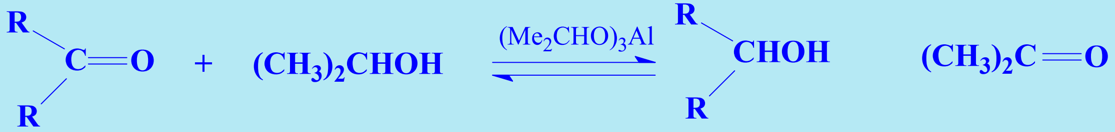
In unsymmetrical ketones, that group migrates which is more electron-releasing. Among alkyl group, the order of migration is $3^0 > 2^0 > 1^0 > CH_3$.

Among aryl group the migratory order is:

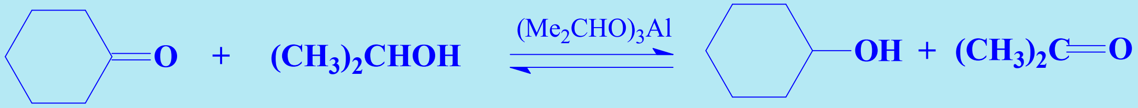


Meerwin-Pondorrf-Verley reduction:

This reaction converts **carbonyl** group into **alcoholic group** on reduction. It consists in treating **aldehyde** or **ketone** with **aluminium isopropoxide** in **isopropyl alcohol**. *for e.g.*



Ketone Isopropyl alcohol Sec. Alcohol Acetone



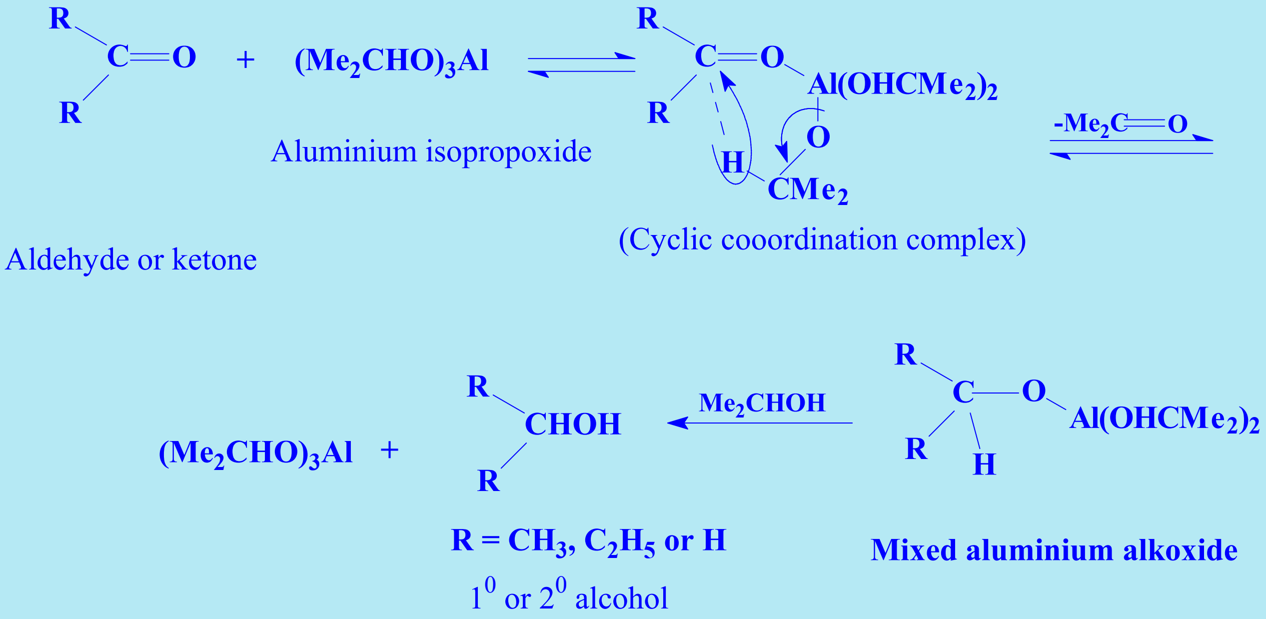
Cyclohexanone Isopropyl alcohol Cyclohexanol Acetone

This method is also useful for the **selective reduction** of carbonyl group **without** affecting the alkene double bond, when present in conjugation with aldehyde group.

$$CH_3CH{=}CH{-}CH{=}O + (CH_3)_2CHOH \xrightleftharpoons{(Me_2CHO)_3Al} CH_3CH{=}CH{-}CH_2OH + (CH_3)_2C{=}O$$

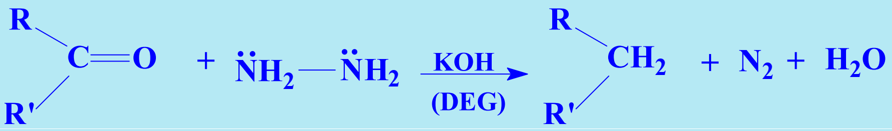
Crotonaldehyde Isopropyl alcohol Crotyl Alcohol Acetone

Mechanism of MPV reduction:



Wolff-Kishner reduction:

It involves the treatment of carbonyl compounds with **hydrazine** followed by strong base like KOH or potassium tert-butoxide in solvents like diethylene glycol or dimethyl sulphoxide (DMSO). This rection reduces C=O into CH_2 Group.



[R, R' are Alkyl or aryl group

Ketone Hydrazine Hydrocarbon

Clemmensen reduction:

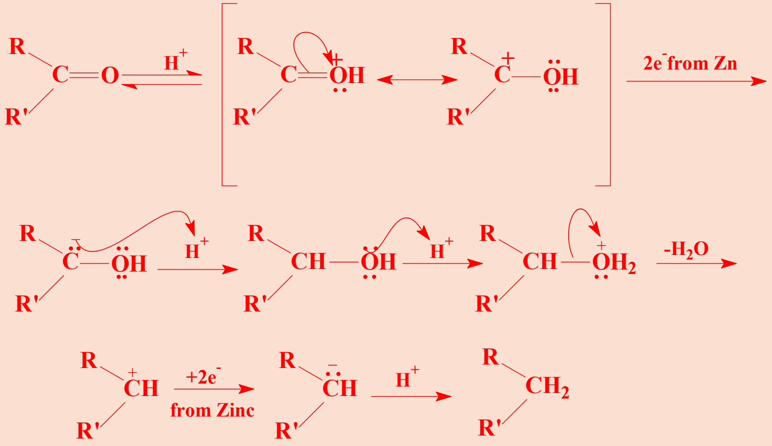
It reduces aldehyde or ketone by heating with amalgamated zinc (Hg-Zn) and conc. HCl to form corresponding hydrocarbon (-C=O into CH_2 Group). This reduction works well for ketones but not for aldehydes. The ketones which are sensitive to alaklies are well reduced by this reduction.

[R, R' are Alkyl or aryl group

Ketone

Hydrocarbon

Mechanism:



Hydrocarbon

Reduction with Lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$)

Lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) converts **aldehydes** and **ketones** to **primary** and **secondary alcohols** respectively. In these reduction hydride ion (H^- ion) acts as a nucleophile. For e.g.

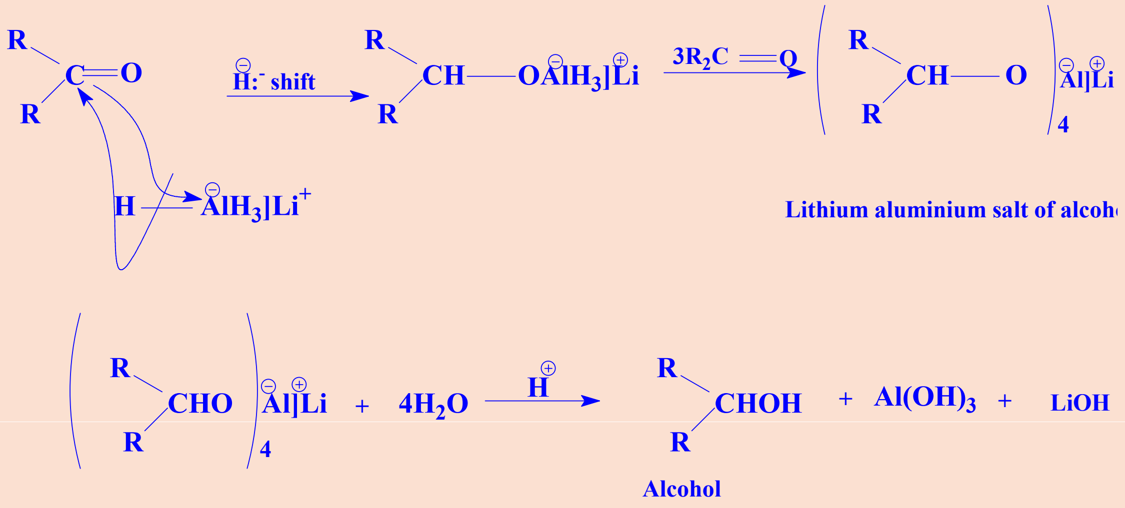
$$RCH{=}O \quad + LiAlH_4 \xrightarrow{\text{or } NaBH_4} RCH_2OH$$

Aldehyde **Primary Alcohol**

$$C_6H_5COCH_3 \xrightarrow[\text{or } NaBH_4]{LiAlH_4} C_6H_5CH(OH)CH_3$$

Acetophenone **1-phenyl ethanol (sec. alcoho**

Mechanism:



Sodium borohydride also reacts in the same way. It has an additional advantage that the carbon-carbon double bond, if present in conjugation to –CH=O), **remain unaffected**. *For. e.g.*

$$C_6H_5CH{=}CH\text{-}CH_2OH \xleftarrow[\text{Selective reduction}]{NaBH_4} C_6H_5CH{=}CH\text{-}CH{=}O \xrightarrow{LiAlH_4} C_6H_5CH_2CH_2CH_2OH$$

Cinnamyl alcohol — cinnamaldehyde — Dihydrocinnamyl alcoh

References:

- A TEXTBOOK OF ORGANIC CHEMISTRY by **Arun Bahl & B.S. Bahl**, S. Chand & Company Ltd. Publication.
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- Pradeep's Organic Chemistry **Vol II** by **R. N. Dhawan,** Pradeep Publication, Jalandhar.